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Introduction

The area currently known as Walker Riverside Park is affected by what could be defined as industrial activity legacy. The site used to host the St Anthony's Lead Works (Figure:1) that operated from 1840 to mid-1930s. The factory performed the smelting of lead using the "Pattison Process". Production included white and red lead, sheet metal and lead pipe. The surrounding sites hosted additional industrial activities including copper/arsenic works, tars works. A previous report by the City Council of Newcastle (Environment and Regeneration Directorate, 2010) estimated that the activity produced the following source of pollution: made ground, mining and quarry activities, manufacturing processes for red lead, silver/lead smelting, production of bone ash.With the general intent of a change of function for public use, the site was transformed into a park in the mid-60s. The landscaping did not include any major remediation work beside the application of a top soil layer and the addition of plantation. These interventions did not prevent the site from contamination. Currently the site is included in the Walker Riverside Area (Emms, 2007). In recent years this site has caused major health and environmental concerns about its use (Chronicle, 2011). Clear remediation strategies are not planned soon and the site may still be a hazard for health and the environment.

Aims

This study aims at addressing the following issues:

- 1. Assess the current quality of groundwater.
- 2. Assess possible effects of ground water on river water quality.
- 3. Presence of contaminants in the water and mode of transport.
- 4. Relation between water systems tapped by the 3 boreholes analysed.
- 5. Search of evidence for tidal influence on the groundwater and possible implications.



Figure 1: current satellite image of Walker Riverside Park with with the historic positioning of the St. Anthony Lead Works building. Adapted from (Okorie et al., 2010)

Samples

For the purpose of this study groundwater samples were taken at 3 of the existing boreholes and in two locations on the river edge (Figure: 2).

Analytes

For each sample the following analyses were performed: pH, conductivity, temperature, alkalinity and dissolved oxygen (in situ). Laboratory analyses included Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major cations (Na+, K+, Ca2+, Mg2+) and Ion Chromatography (IC) for major anions (Cl-, SO42-) and minor anions (NO3-, PO43-). Trace metal analysis using Inductively coupled plasma mass spectrometry (ICP- MS) was carried for metals AI, Sr, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb.

Sampling strategy

The sampling was done relying on the presence of different boreholes. The original sampling strategy included the collection from 4 boreholes along two transects (BHE04-BHE03 and BH06-BHE01). Due to inaccessibility of BH06, it was revised and BH05 was used instead. A sample set with one replicate was gathered at each borehole. To assess river quality water sample were taken in two locations that were chosen based on proximity to the boreholes used for sampling. Water was taken from the surface of the river, next to the riverbank.



Figure 2: sample locations. BHE01, BHE03, BHE05 indicate the three existing boreholes used for groundwater sampling. Boreholes BH06 and BHE04 were initially considered in the study but not used for sampling due to inaccessibility of BHE06. TW1 and TW2 indicate river water sampling locations.

Method

Sampling was done at the site on March 12 2019 in the afternoon. Replicated samples were collected from 3 boreholes (BHE1,BHE3, BHE5) and two locations on the River Tyne (TW1, TW2). Sampling procedures were carried in accordance with BS ISO 5667-11:2009. Samples were collected at 3 boreholes (BHE1, BHE3, BHE5) around 2pm, 3.30pm and 4.30pm. Using a peristaltic pump, twice the volume of the water present in the borehole was extracted prior to sample taking. For each site the following analysis were performed in situ: dissolve oxygen, pH and conductivity.Alkalinity was calculated by titration. After these analyses 100 ml samples in polypropylene containers were collected. For each site 8 samples were gathered: 2 unfiltered and 2 filtered samples for anion analysis, 2 unfiltered and 2 filtered samples for cation analysis. Samples were filled till the edge of the container to avoid volatilisation. Cation samples bottles contained nitric acid for stabilisation.

River water sampling - River water was collected at two locations according to BS EN ISO 5667-6-2016. The two sampling points chosen were located next to the river bank in order to evaluate possible effect of ground water discharge from the site. Alkalinity, dissolved oxygen and conductivity were measured using the same method as for the borehole. At each site, two replicates of 100 ml sample were taken and stored in a polypropylene container.

Laboratory analysis – Transportation and storage was carried in accordance to BS ISO 5667-3-2012. After two days, within the accepted holding time, the samples were analysed in the laboratory at Newcastle University. Anions were analysed using ion chromatography (IC). For cations analysis the used method was inductively coupled plasma optical emission spectrometry (ICP-OES). For trace metals, Inductively coupled plasma mass spectrometry (ICP-MS) was the method of choice due to the ability to detect multiple elements and the low detection limit.

Anion analysis preparation - Prior to analysis a standard solution was prepared containing chloride (50 mg/L), nitrate (25 mg/L), sulphate (50mg/L), phosphate (25 mg/L). For calibration purposed, the solution was used in four different dilutions factor 1,2,4,8. For the ion chromatography analysis 50 ml water samples were prepared with a dilution factor of 5 (10 ml of sample water and 40 ml deionized water). They were analysed using a Dionex chromatography system. For the ICP-MS analysis 10 μ L samples were placed in the centrifuge tubes.

Cation analysis preparation – The standard solution was prepared using potassium (25 mg/L), sodium (50 mg/L), calcium (250 mg/L), magnesium (100 mg/L), iron (10 mg/L), manganese (10 mg/L). For calibration the solution was used in different dilutions (1,5,20,20,50). Water samples of 50 ml were prepared with a dilution factor of 10 (5ml of sample water and 45 ml of deionized water). For the ICP-MS analysis 10 μ L samples were placed in the centrifuge tubes. Laboratory analyses were (ICP-MS and ICP-EOS) carried 5 days later at Newcastle University. This time span complies with accepted holding times (Zhang, 2007).

Results

In situ analysis.A first set of analysis was done at site during the collection of samples. Alkalinity was calculated via titration, pH, dissolved oxygen and conductivity. The results, shown in (Table:1) were within standard ranges with the exception of borehole 1 (BHE1) were the conductivity was found above the detection limit of 20 μ S/cm. The three boreholes, despite being within a radius of 65meters, present distinct characteristics.

Test	TW1	TW2	BHE1	BHE3	BHE5
Alkalinity (mg/l as CaCO3)	52	50	560	104	311
рН	8.05	8.47	6.83	7.3	6.83
DO (mg/l)	12.13	12.17	1.14	4.77	1.62
Conductivity (µS/cm)	9.48	8.75	6.87	>20	2.74
Borehole upper water level (m)			3.75		0.65
Borehole lower water level (m)			10.54		2.96
Temperature C			6.6		6.6

Table 1: boreholes and water river in situ analyses.

ICP-MS data. - Values recorded with the ICP-MS are shown in Figure:3. In most cases above the lower limit of detectability (LLD) and the limit of quantification (LoQ). The only exceptions were for the analysis of arsenic (As), antimony (Sb) and Nickel (Ni). Some measurements could not be quantified: 36% of samples for Ni, 64% for As, 57% for Sb. In some cases were not even detected: 29% of As measurements and 57% of Sb. Considering all the samples, 93% of measurements were within detection limits and 88% within quantification limits.

ICP-OES analysis. Results are shown in Table:3. Values are within detectable range except for conductivity in BHE3. A charge balance check was performed. Result were satisfactory for the river water samples (TW1, TW2) and from borehole 1 (BHE1). Samples from borehole 3 (BHE3) had an average difference around 11% which was considered acceptable but samples from borehole 5 (BHE5) presented significant differences with an average of 17% more cations. The difference between anions and conductivity values is shown in the last column of Table:3. Ions concentrations and conductivity seem to agree with the exceptions of BHE5 where a difference around 20% was found. For BHE3, due to the conductivity values above the maximum detectable limit, a comparison was not possible. Using the total anions meq/L a conductivity around 33,000-40,000 μ S/cm could be estimated.

Sample and analysis error. Standard deviations were calculated assuming the river quality of equivalent characteristics in the 4 samples taken. A cumulative relative standard deviation for the sampling and analysis was calculated at 2.57%. Analysis error was calculated comparing results for 3 standard solutions. This produced a relative standard deviation of 1.32%. Sampling error was then estimated at 1.25%. These results are within acceptable error ranges.

	Max value	Min value	LLD	LoQ	>LLD	>LoQ
	$\mu g/1000L$	$\mu g/1000L$	$\mu g/1000L$	$\mu g/1000L$		
Al	26.041	15.456	0.041	0.077	100%	100%
Cr	0.053	0.031	0.001	0.011	100%	100%
Mn	7.173	0.067	0.011	0.027	100%	100%
Fe	10.281	1.415	0.343	0.646	100%	100%
Ni	0.047	0.007	-0.001	0.018	100%	64%
Cu	1.286	0.415	0.055	0.143	100%	100%
Zn	2.327	1.428	-0.003	0.109	100%	100%
As	0.09891	-0.00045	0.00312	0.00835	71%	36%
Sr	5.922	0.996	0.031	0.043	100%	100%
Cd	0.035	0.022	0.002	0.006	100%	100%
Sb	0.131	0.003	0.015	0.041	43%	43%
Ba	2.353	0.893	0.013	0.038	100%	100%
Pb	0.699	0.441	0.035	0.097	100%	100%

Table 2: lower limit of detectability and limit of quantification for trace metal analysis. Note: values include all the borehole and river water samples.



Figure 3: trace metal concentrations found in the water samples compared to different standards. Note: low concentration for Arsenic and Antimony fell outside detectable range. Legend: within standards (gray), outside WHO (3) drinking water standards (orange), outside DEFRA (1) or EU(2) standards (red).

Sample	Na	Κ	Ca	Mg	CI	NO3	SO4	HCO3	balance	k	[An]/k
TW1 A	65	2.01	3.82	15.5	82.3	0.063	10.8	0.52	-4%	9480	-1%
TW1 B	64.9	1.99	3.85	15.5	88.9	0.059	10.4	0.52	-7%	9480	5%
TW2 A	68.6	2.08	3.96	16.3	87.6	0.051	10.2	0.5	-4%	8750	12%
TW2 B	68.1	2.08	3.99	16.3	86.3	0.052	10	0.5	-3%	8750	11%
BHE1 A	23.1	0.41	26.7	20.2	28.4	0	23.9	5.59	10%	6870	-16%
BHE1 B	22.8	0.4	26.1	19.9	27.1	0.025	32.6	5.6	3%	6870	-5%
BHE1 C	23.4	0.42	27.2	20.5	28.3	0.025	34.8	5.6	2%	6870	0%
BHE1 D	24.1	0.45	26.7	20.5	27.8	0.036	33.3	5.6	4%	6870	-3%
BHE3 A	251.5	8.63	13.1	63.5	382.5	0.048	42.4	1.04	-12%	>20000	
BHE3 B	249.1	8.64	13.2	63.8	377.2	0.056	42.5	1.04	-11%	>20000	
BHE3 C	250.7	8.72	13.3	64.1	380.8	0.047	41.1	1.04	-11%	>20000	
BHE3 D	250.4	8.73	13.3	64.2	412.7	0.053	46.3	1.04	-15%	>20000	
BHE5 A	1.69	0.32	16.26	4.47	1.26	0.59	12.02	3.11	15%	2740	-17%
BHE5 B	1.34	0.29	15.07	4.08	0.89	0.6	9.93	3.11	18%	2740	-24%

Table 3: summary of ions analysis for water samples

Discussion

Water characterisation.- Ions concentration were displayed on a Piper diagram for a better understanding of the chemical characteristics of each sample (Figure:4). BHE1 could be defined as a calcium-chloride type with no dominating cations and sulphate anions. BHE3 as sodium-chloride type and BHE5 as calcium chloride type with calcium as dominating anions and sulphate as dominating anion. Tyne water showed same characteristics as BHE3. These observations seem to suggest that BHE3 and the Tyne river are connected with a tidal effect on the groundwater at BHE3. BHE1 showed distinct characteristics suggesting that the water quality at the borehole is not influenced by the river. The small variation in the metal concentration between the boreholes (BHE1, BHE3) and river water suggests a discharge of metals over the quay wall. This was already observed in a previous report (Environment and Regeneration Directorate, 2010). The same report concluded that the river water was not affected by the discharge because of its dilution.

River water samples differences. – TW1 and TW2 were collected at locations 100m apart from each other and with 1.5h interval difference. Ions concentration were very similar with the exception of sodium that is slightly higher in the second sample. This could be due to tidal cycle. Regarding trace metals, the samples showed similar concentrations with only few exceptions. Copper, barium and nickel have significantly different values. Chromium and cadmium show a difference but of a minor magnitude.

Charge balance discrepancy. – As previously mentioned, charge balance produced acceptable results for samples at river and at boreholes BHE1,BHE3 while at BHE5 there was a significant amount of excessive cations (+17%). Considering the shallow depth of the borehole BHE5 (2.96-6.6 m), other anions, as NO2, may be present but were not calculated in this study. Further tests to identify these additional ions would be needed to have a clearer characterisation of the water.



Figure 4: Piper Diagram for the water sampled at the site.

Salinity levels. – Total suspended solids were calculated multiplying conductivity by a converting factor of 0.65 (Younger, 2007, p92). The results showed that all the water sampled were brackish (BHE1 4,4 g/L, BHE5 1,7 g/L, TW1 6,1 g/L and TW2 5,7 g/L) with the exception of BHE3 (>13 g/L) that reached saline water levels.

Regulatory limits for trace metals. - Metal in river water is an increasingly important issue acknowledged by different stakeholders (Tyne Catchment Partnership, 2017). ICP-MS results showed concentration levels significantly above standards in all water samples for almost all the trace metals analysed (Figure:3). This trend seems to agree with the data published by a previous report (Environment and Regeneration Directorate, 2010) that found soil mean concentrations as: lead (Pb) - 16,500ppm, zinc (Zn) - 241ppm, copper (Cu) - 2475ppm and Cadmium (Cd) - 14ppm. It is reasonable to consider the high levels of the trace metal due to the previous industrial activities that included smelting, manufacture of red lead, lead/silver separation, extraction of lead from litharge. To better understand the variation between sampling points of some metals (Sb, As, Sr, Ni,Mn) further studies would be needed and a comparison with other studies done on soil could be carried (Hartley et al., 2006; Gbefa et al., 2011; Rothwell, Cooke, 2015) Some of the factor that may be considered are the different depth of BHE5, the original position of the buildings, ground composition.

Mode of transport. – In order to understand the possible mode of transport of the metal contaminants a comparison between filtered and unfiltered samples was conducted. Figure 5 shows the amount of trace metals found in filtered samples versus the amount found in unfiltered samples. Results for BHE1 (pH 6.8) and BHE3 (pH 7.3) tend to be



Figure 5: percentage of trace metal found in filtered samples versus amount found in unfiltered samples.

quite similar. A first group of metals are those found almost only in particulate state (measurements from filtered samples above 90%). These are As, Ba, Al, Cu, Mn,Pb, Ni (BHE1 only), Sr (BHE1 only), Zn. With the exception of Al, they are divalent metals. The second group consist of metal with a significant part found in dissolved state: Cd, Cr, Ni (BHE3 only), Fe(only BHE3), Sb, Sr(BHE3 only). Fe at BHE1 was found mostly in dissolved state (60%). Analysis done with samples from BHE5 (pH 6.8) showed quite significant differences. Overall, a larger portion of the metals are found in dissolved state. Metals found almost entirely as particulate (>80%) were: Cr, Cd, Cu, Pb, Zn. Another group of metals with a third of the overall quantity in dissolved state were: As, Ba, Al, Ni, Sb, Sr. Iron and manganese were found mostly in dissolved state: Fe 60% and Mn 70%. A comparison of concentrations found in this study versus solubility from published resources is shown in figure:6



Figure 6: Comparison of dissolved concentrations of trivalent (a) and divalent (b) trace metals versus published values (Oliva et al., 2011). The dots indicates values found in this study.

Errors. – Sampling was conducted aligned with BS EN ISO 5667-14:2016. Sampling error was previously estimated with a relative standard deviation of 1.25% which indicates that the procedure was conducted properly and therefore no major improvement could be implemented. Regarding the sampling strategy, few improvements could be done. Including additional sample of river water just before and after the site could help

describing the effect the discharges have on the river. One improvement would consist in collecting river water samples at the same time in order to minimise tidal influence. Sampling time at the site could be extended.Due to time constraint and accessibility only 3 boreholes were sampled. BHE5 has significant different characteristics in term of location and depth, this create difficulties in making any comparison with the other samples. A larger set of boreholes should be used.In this study As, Sb, Ni had a significant amount of sample out of detection range. During analysis preparation, estimating the lower limit of detection before preparing diluted solutions could avoid outliers. Finally, charge balance analysis showed a lack of measurements for anions in BHE5 and suggests for additional ions to be tested.

Conclusion

A pilot study was conducted in the former St. Anthony Lead Works. Samples were collected from 3 boreholes and in two points on the river. The following conclusion can be made:

1 - The current quality of the ground water did not meet neither DEFRA proposed standards nor EU Directive on Hazardous Substances. Concentration of most trace metals (Al, Cd, Ba, Cr, Cu, Fe, Pb, Zn) were significantly above limits both in the boreholes and in the river. Some metals were beyond limits only at specific locations: Mn at BHE1, Ni at BHE5, As at BHE3, Sb at BHE3 and BHE5.

2 - Similarities between groundwater and river water suggests that there is a discharge of pollutants from the site to the river. A quantification of this impact was not done and could be the focus of further investigations.

3 - All the samples showed a significant concentration of pollutants. With the exception of Fe the trace metals were in particulate form.

4 - A clear understanding of the water system at the site was not reached. Additional sampling at the other boreholes would be needed. The data collected showed diverse chemical characteristics of the water at the three boreholes. This may suggest different local geological characteristics. Trace metal concentration, with the exception of Mn, Sb, As, are very similar at each borehole. This may indicate that the site has a single connected water system.

5 - Similarity in terms of water characterisation and concentration of trace metals was observed between BHE3 and TW1. This suggests the presence of tidal influence on BHE3. On the contrary, BHE1 sample showed different characteristics to the river water TW2, suggesting no tidal effect on this portion of ground water.

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