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ABSTRACT

Red mud is a by-product of alumina production. Little is known about the long-term fate of red mud constituents in fresh waters or of the processes regulating recovery of fresh waters following pollution control. In 1983, red mud leachate was diverted away from Kinghorn Loch, UK, after many years of polluting this shallow and monomictic lake. We hypothesised that the redox-sensitive constituents of red mud leachate, phosphorus (P), arsenic (As) and vanadium (V), would persist in the Kinghorn Loch for many years following pollution control as a result of cycling between the lake bed sediment and the overlying water column. To test this hypothesis, we conducted a 12-month field campaign in Kinghorn Loch between May 2012 and April 2013 to quantify the seasonal cycling of P, As, and V in relation to environmental conditions (e.g., dissolved oxygen (DO) concentration, pH, redox chemistry and temperature) in the lake surface and bottom waters. To confirm the mechanisms for P, As and V release, a sediment core incubation experiment was conducted using lake sediment sampled in July 2012, in which DO concentrations were manipulated to create either oxic or anoxic conditions similar to the bed conditions found in the lake. The effects on P, As, and V concentrations and species in the water column were measured daily over an eight-day incubation period.

Phosphate (PO_4-P) and dissolved As concentrations were significantly higher in the bottom waters ($75.9 \pm 30.2\ \mu g\ L^{-1}$ and $23.5 \pm 1.83\ \mu g\ L^{-1}$, respectively) than in the surface waters ($12.9 \pm 1.50\ \mu g\ L^{-1}$ and $14.1 \pm 2.20\ \mu g\ L^{-1}$, respectively) in Kinghorn Loch. Sediment release of As and P under anoxic conditions was confirmed by the incubation experiment and by the significant negative correlations between DO and P and As concentrations in the bottom waters of the lake. In contrast, the highest dissolved V concentrations occurred in the bottom waters of Kinghorn Loch under oxic conditions ($15.0 \pm 3.35\ \mu g\ L^{-1}$), with the release from the bed sediment apparently being controlled by a combination of competitive ion concentrations, pH and redox conditions.

1. Introduction

Inappropriate storage of red mud, a by-product of alumina production, is of increasing concern, as illustrated by a major pollution incident in Ajka, Hungary, in October 2010, that resulted in the release of ~1 million m^3 of red mud waste (Burke et al., 2012), contaminating the Marcal river (catchment area 3078 km^2) and entering the Danube River (Klebercz et al., 2012). Nevertheless, the chemical and ecological impact-response trajectories following red mud pollution in fresh waters are largely unknown. This is confounded by a lack of knowledge of the changes in composition of red mud that occur as a result of interactions with sediments and freshwater organisms during transport through aquatic ecosystems (Klebercz et al., 2012). Research after the Ajka accident focused on the short-term impact of red mud waste on fresh waters (Mayes et al., 2011). In local aquatic ecosystems, with a short residence time and well oxygenated surface sediment layer, oxyanion forming contaminants (e.g. arsenic (As), chromium (Cr) and vanadium

(V)) were found within solid-phase complexes, representing little ecological threat. However, the processes driving the long-term fate of red mud constituents in fresh waters following such pollution events have not been quantified directly using either field or experimental data. This knowledge is expected to be particularly important for achieving effective recovery of longer retention time aquatic ecosystems, such as lakes, where the residence time of pollutants can far exceed those in rivers and streams (Sharpley et al., 2013; Spears et al., 2012).

Sediments play an important role in regulating seasonal phosphorus (P) dynamics in shallow lakes (Søndergaard et al., 2003). Cycling of P, as well as As, between sediments and overlying waters, is driven by redox conditions, adsorption and desorption mechanisms, and by mineral phase solubility (Kleeberg and Kozerski, 1997; Søndergaard et al., 2003; Toevs et al., 2008). Loosely adsorbed inorganic and organic fractions and redox sensitive forms of P adsorbed to iron (Fe) are considered potentially mobile (Søndergaard et al., 2003). Phosphate (PO_4-P) release can occur due to the dissolution of iron oxyhydroxides during anoxic conditions (Smolders et al., 2006), when Fe(III) is reduced to Fe(II) and both Fe and P are released into porewaters (Søndergaard et al., 2003). P can also be bound to other inorganic components, such as aluminium (Al), calcium (Ca), manganese (Mn), or clay (Søndergaard et al., 2003). Similarly to P, the diffusion of soluble As from sediment into overlying waters is limited by sorption of arsenite (As(III)) and arsenate (As(V)) to Fe, Mn and Al oxyhydroxides (Toevs et al., 2008; Whitmore et al., 2008). During the reduction of Fe oxyhydroxides in sediments under anoxic conditions, As(V) can be converted to As(III) and released to the porewaters. When waters overlying the sediment are well aerated, dissolved As(III) is likely to be co-precipitated with oxidised forms of Fe or Mn (Whitmore et al., 2008). Vanadium, like P and As, can be adsorbed to Fe oxides (Wällstedt et al., 2010). Vanadium occurs in many oxidation states; V(V) is expected to dominate in oxidising water environments and V(IV) in reducing conditions (Minelli et al., 2000). The conversion between V species depends on redox potential, pH, and V concentration (Minelli et al., 2000), but there is only limited evidence in the literature from which the behaviour of V in lakes can be predicted. In addition to redox potential, a number of environmental conditions are likely to regulate the mobilisation of red mud constituents in lake bed sediment, including water temperature, light, pH, organic matter, and bacterial activity (Czop et al., 2011).

Case studies in which the pollution history is sufficiently documented to allow field observations over recovery time scales (i.e. years to decades) in lakes are rare. Here, we assess the long-term persistence and cycling between the lake bed sediment and the overlying water column of P, As, and V in Kinghorn Loch, a shallow monomictic freshwater lake in the UK, 30 years after the diversion of red mud leachate away from the lake. This was achieved through a 12-month field campaign, examining concentrations of these red mud leachate pollutants in the surface water of the lake and in the water above the lake sediment in order to provide evidence of internal loading and any seasonal variation. To assess the mechanisms of release we conducted a complementary laboratory experiment designed to trigger the release of redox sensitive species from the lake sediment to the overlying water. Thus, in this paper we tested the following specific hypotheses: (1) that release of redox-sensitive red mud constituents (P, As and V) from the bed sediments of Kinghorn Loch can still occur 30 years after pollution was controlled, and (2) that dissolved oxygen (DO) concentrations in the water column can control this pollutant release from the lake bed sediment to the overlying water.

2. Methods

2.1. Study site

Kinghorn Loch is a small freshwater lake with surface area 11.3 ha, a mean depth of 4.5 m and a maximum depth of 12.8 m, situated in Fife, Scotland, UK (56°10′N; 3°11′W). The estimated water residence time is eight months (Edwards, 1985). The lake received leachate from a nearby red mud landfill site from 1947 to 1983 when the discharge was diverted (Edwards, 1985). The leachate consisted of a highly alkaline solution of sodium hydroxide (NaOH) and carbonate, with a mean pH of 12.1. It contained high concentrations of dissolved Al, As, V, orthophosphate, sulphate and chloride (Cl), whilst red mud solids, sporadically released to the lake, accounted for most of the input of Fe (Edwards, 1985). A long-term monitoring programme of the lake water chemistry measured in the outlet of Kinghorn Loch was initiated in 1980 by the Forth River Purification Board and continued by the Scottish Environment Protection Agency (SEPA).

2.2. Water sample collection - field campaign

A one-year field campaign was conducted to assess cycling of P, As, and V in Kinghorn Loch. Monthly water sampling was carried out from a boat from May 2012 to April 2013 at a site chosen within the lake's deepest part (at c.12 m water depth). Single 500 mL samples of lake surface water and 50 mL samples of bottom water (water 1 cm above the lake bed sediment, taken from a sediment core) were collected in polypropylene acid washed bottles and sterile polypropylene centrifuge tubes, respectively. Sediment cores were collected using a HTH gravity corer. DO concentration, pH, conductivity and water temperature were measured in situ in both the surface water and bottom water samples on each sample occasion, using a Hach HQ40d Portable Multi-Parameter Meter and probes (Hach Lange, Salford, UK). The collected water samples were subsequently analysed for concentrations of P, As and V (PO_4-P, total P (TP), dissolved and total As and V) as well as concentrations of four elements, Al, Ca, Fe and Mn, thought to be important in regulating cycling, either through redox or pH mediated processes. Due to the different sample preparation and storage requirements for the various groups of elements, each water sample was divided into four sub-samples and analysed as outlined in section 2.5.

2.3. Sample collection – laboratory experiment

Ten sediment cores for the laboratory experiment were collected by boat (within an area of ~10 m^2) from the deepest point of the lake using a HTH gravity corer on 31 July 2012. The cores had an internal diameter of 65 mm and consisted of c.25–33 cm depth of sediment and 14–21 cm of overlying water and were transported to the laboratory within 2 h of collection. DO concentration, conductivity, pH and water temperature were measured in situ at the sample site and in the collected sediment cores using a Hach HQ40d Portable Multi-Parameter Meter and probes (Hach Lange, Salford, UK).

2.4. Oxygen manipulation laboratory experiment

The oxygen manipulation experiment was conducted in a controlled temperature room in which the temperature was set at the lake water temperature measured 1 m above the sediment (10.3 °C) at the time of the sediment core collection. Collected sediment cores were randomly assigned to oxic and anoxic treatments. Air was bubbled through the overlying water in five of the sediment cores (Tetratec Whisper AP 200 pump, TetraWerke, Melle,

Germany) to create an oxic treatment and nitrogen gas (N_2) was bubbled through the overlying water in the other five sediment cores to create an anoxic treatment. Cores were continually bubbled with air or N_2 for eight days. The seven-day experimental period started after a 24-h acclimatisation period. DO, conductivity, pH and temperature were measured in the water overlying each core, as outlined above. Measurements were conducted first after the acclimatisation period and then between 14:30–15:30 on every day of the experiment. 50 mL water samples were collected daily (after measurement of the water physico-chemical parameters) from 1 cm above the sediment surface using a syringe. The sampled water was replaced with 50 mL filtered (through Whatman GF/F filter) lake surface water collected at the same time as the sediment cores and stored at the same temperature. This experimental set-up follows that described by Spears et al. (2008).

2.5. Analyses of water samples from the field campaign and the laboratory experiment

PO$_4$-P and TP concentrations in the water samples were determined using the acid-molybdenum-blue colorimetric method (Murphy and Riley, 1962), preceded by a persulphate digestion of samples for determination of TP (as described in Eisenreich et al., 1975). Samples for determination of dissolved metals and metalloids were filtered through a Millex syringe-driven 0.45 μm filter, prior to preservation with 1% v/v nitric acid. Samples for total metal and metalloid determination were preserved with 1% v/v nitric acid, followed by a 16 h digestion at 80 °C in an oven, prior to analysis. Concentrations of metals and metalloids were determined by ICP-MS using an Agilent 7500ce. Detection limits for Al, As, Ca, Fe, Mg, Mn and V, and were 0.92, 0.45, 0.31, 0.10, 0.0005, 0.03 and 0.05 μg L^{-1}, respectively. A Certified Reference Material (NIST SRM 1643e Trace Elements in Water) was employed as a quality control check. The Al, As, Ca, Fe, Mg, Mn and V concentrations measured in the CRM were within 34, 19, 25, 24, 34, 7 and 15%, respectively, of the certified values. A detailed description of the PO$_4$-P and TP, and the metal and metalloid analysis methods is provided in Supplementary Information A1 & A2.

2.6. Statistical analyses

Monthly field observations (n = 12) were allocated to seasons (winter: Dec 2012–Feb 2013; spring: Mar–May 2013; summer: Jun–Aug 2012; autumn: Sep–Nov 2012) and two-way analysis of variance (ANOVA, total degrees of freedom = 23, α = 0.05) was applied to examine the variation in concentrations of pollutants (P, As and V) and conductivity, DO, pH and temperature in the lake water between the four seasons and between the two sample collection depths. Due to conditions in the lake water column varying from stratified to mixed during the year, the pollutant concentration-sample collection depth relationship may change across seasons. Therefore, the sample collection depth-season interaction term was added to the models. Assessing residuals showed violation of homogeneity (an important assumption in analysis of variance; Zuur et al., 2010) for the PO$_4$-P, TP, dissolved V, pH and temperature measurements, indicating variation across seasons and depths in the spread of values of these parameters. Log$_{10}$ transformations were applied to these datasets, but the residuals still indicated homogeneity violation. Hence, a statistical technique that allows for heterogeneity - generalised least squares (GLS; Zuur et al., 2009) - was applied to analyse these datasets. For each of the five response variables, four GLS models - a model with a no variance covariate and three models with heterogeneity incorporated as VarIdent variance structure (allowing a different variance per stratum either for season, water depth, or combined

season-water depth) - were produced and the best model was chosen by comparing Akaike's Information Criterion (AIC) values. If a model term was non-significant in the model output, the model was re-run without the term and the AIC values were used to compare the simplified and full version of the models. Models with the lowest AIC values were selected for further analysis. Planned multiple regression following stepwise multiple regression was conducted to examine the relationships between pollutant concentrations (PO$_4$-P, TP, dissolved and total As, dissolved and total V) and potential explanatory variables (conductivity, DO, pH and temperature) in both surface water and bottom water. Explanatory variables used in the models were selected by running first a stepwise regression model to choose variables that did not correlate (p > 0.15) with each other. Only significant relationships (p < 0.05) were included in the final regression models. The normality assumption was examined with a normal probability plot of the residuals and an Anderson-Darling test. All data were log$_{10}$ transformed to meet the normality criteria.

A repeated measures one-way analysis of variance (ANOVA; total degrees of freedom = 69, α = 0.05) was conducted on the results of the laboratory experiment to test the effects of oxic and anoxic conditions on the release of elements from sediment into overlying water and also to assess the effects of the treatments on water column conductivity, pH and temperature. Statistical analyses were conducted using R version 2.15.2. (http://www.r-project.org), with the exception of the planned multiple regression, which was carried out using Minitab statistical software version 16 (Minitab Ltd., Coventry, UK).

3. Results

3.1. Field measurements: conductivity, oxygen, pH, and temperature profiles

In the one-year field campaign, seasonal mean concentrations of DO (±SD of the means) ranged from 1.55 ± 0.78 mg L^{-1} (bottom water, summer) to 13.2 ± 2.07 mg L^{-1} (surface water, spring; Table 1). Mean DO values were similar in the surface and the bottom waters in autumn and higher in the surface compared to the bottom waters in winter, spring and summer. The greatest difference in DO between the two water depths occurred in summer during stratification. The effects of season, depth and interaction between these two variables on DO concentrations were significant (Table 1).

Mean seasonal values of pH were very similar in the surface and the bottom waters throughout most of the year with the exception of summer, in which the highest seasonal mean pH (9.14 ± 0.03) was recorded in the surface water and the lowest seasonal mean pH (7.69 ± 0.11) was recorded in the bottom water. Statistical analysis indicated significant effects of season, depth and interaction between these two variables on water pH.

The lowest mean conductivity value was observed in the surface water and the highest values in the bottom waters. During spring, autumn and winter conductivity values were slightly lower in the surface compared with the bottom waters. All three explanatory variables were found to have a significant effect on conductivity.

Seasonal mean water temperature varied throughout the year from 2.87 ± 0.55 °C (surface water, winter) to 16.6 ± 1.42 °C (surface water, summer). The difference in temperature between the two water depths in autumn and spring was small. The greatest difference in water temperature was measured in summer, which was the only season when stratification occurred (i.e. in July and August). Summer was the only season that was found to have a significant effect on water temperature.

Table 1
Means (n = 3 monthly samples), standard deviations and results of two-way ANOVA and GLS analyses of pH, conductivity ($\mu S\ cm^{-1}$), temperature (°C) and DO ($mg\ L^{-1}$) across seasons at 2 water column depths in Kinghorn Loch at the deepest site (12 m) from May 2012 to April 2013.

	Winter				Spring				Summer				Autumn				Season	Depth	Interaction
	Surface		Bottom		Surface		Bottom		Surface		Bottom		Surface		Bottom				
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	F-value	F-value	F-value
pH	8.57	0.12	8.50	0.09	8.84	0.35	8.82	0.28	9.14	0.03	7.69	0.11	8.47	0.36	8.53	0.11	4.44*	292***	65.8***
Conductivity	421	17.7	432	22.0	431	13.7	441	1.41	360	16.5	457	10.4	399	7.21	403	5.51	7.06**	29.9***	15.0***
Temperature	2.87	0.55	3.1	0.82	7.77	3.90	6.77	3.14	16.6	1.42	14.0	0.71	9.03	2.35	9.43	2.35	175***	1.22	2.38
DO	11.4	0.18	8.78	3.51	13.2	2.07	11.4	2.43	12.1	0.96	1.55	0.78	10.5	1.03	10.1	0.91	10.9**	30.4***	11.0**

*significant at $p < 0.05$/** significant at $p < 0.01$/*** significant at $p < 0.0001$.

3.2. Field measurements: water column pollutant concentrations

Fig. 1 shows monthly concentrations of P, As and V throughout the monitoring period in both the surface and the bottom waters of Kinghorn Loch.

Seasonal mean concentrations of PO_4-P and TP (Table 2) ranged from 5.90 ± 1.90 (surface water, spring) to $75.9 \pm 30.2\ \mu g\ L^{-1}$ (bottom water, spring) and from 22.7 ± 4.41 (surface water, spring)

to $198 \pm 125\ \mu g\ L^{-1}$ (bottom water, spring), respectively. Season and the interaction between season and depth had a significant effect on PO_4-P, whilst season and depth had a significant influence on TP (Table 2).

Seasonal mean dissolved and total As concentrations varied from $6.82 \pm 0.43\ \mu g\ L^{-1}$ (surface water, winter) to $23.5 \pm 1.83\ \mu g\ L^{-1}$ (bottom water, summer) and from $8.88 \pm 1.77\ \mu g\ L^{-1}$ (surface water, winter) to $25.7 \pm 4.72\ \mu g\ L^{-1}$ (bottom water, summer), respectively.

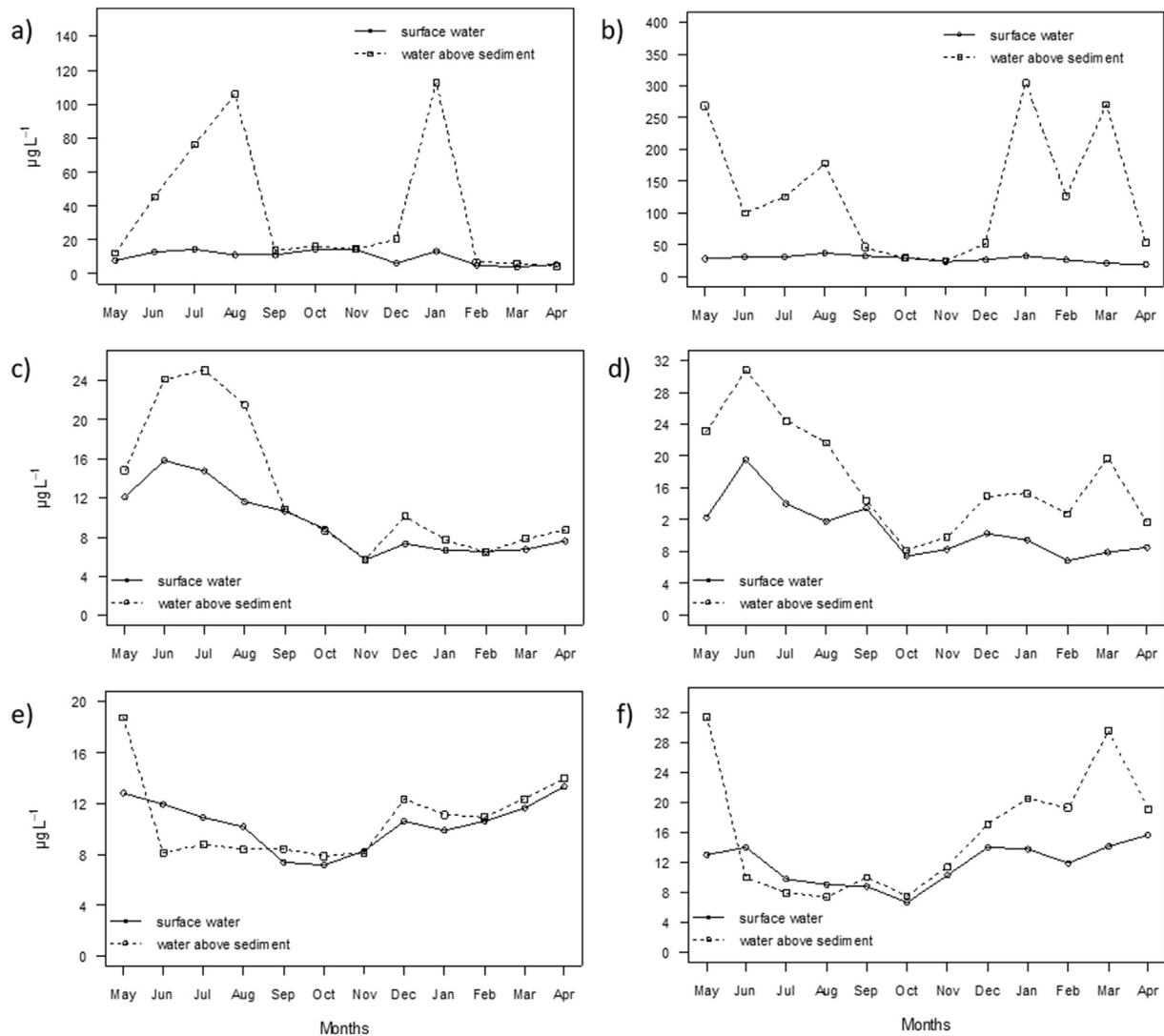**Fig. 1.** Monthly pollutant concentrations (PO_4-P (a), TP (b), dissolved (c) and total As (d), dissolved (e) and total V (f)) in surface water and water 1 cm above the sediment in Kinghorn Loch at the deepest site (12 m) from May 2012 to April 2013.

Table 2
Means (n = 3 monthly samples), standard deviations and results of two-way ANOVA and GLS analyses of PO_4-P, TP, dissolved and total As, dissolved and total V concentrations (μg L^{-1}) across seasons at 2 water column depths in Kinghorn Loch at the deepest site (12 m) from May 2012 to April 2013.

Pollutant		Winter				Spring				Summer				Autumn				Season	Depth	Interaction
		Surface		Bottom		Surface		Bottom		Surface		Bottom		Surface		Bottom				
		mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	F-value	F-value	F-value
Dissolved	As	6.82	0.43	8.09	1.86	8.80	2.90	10.5	3.79	14.1	2.20	23.5	1.83	8.37	2.55	8.40	2.55	27.6***	9.74**	4.67**
	V	10.4	0.42	11.5	0.77	12.6	0.85	15.0	3.35	11.0	0.88	8.42	0.32	7.60	0.58	8.14	0.28	40.5***	0.00	10.3**
	PO_4-P	8.53	4.51	46.7	57.5	5.90	1.90	7.80	4.14	12.9	1.50	75.9	30.2	13.4	1.79	15.1	1.08	19.2***	3.48	4.49**
Total	As	8.88	1.77	14.3	1.41	9.59	2.38	18.2	5.90	15.2	4.01	25.7	4.72	9.73	3.26	10.8	3.25	9.27**	18.7**	1.95
	V	13.2	1.11	19.0	1.75	14.3	1.29	26.7	6.65	10.9	2.68	8.46	1.37	8.57	1.82	9.67	1.94	21.5***	12.8**	7.49**
	P	28.9	3.04	162	130	22.7	4.41	198	125	33.4	3.25	135	39.6	29.0	4.11	34.1	11.3	3.99*	15.0**	1.83

*significant at $p < 0.05$/** significant at $p < 0.01$/*** significant at $p < 0.0001$.

Results indicated significant effects of season and depth on both dissolved and total concentrations of As, although the interaction between the two explanatory variables was significant only for dissolved As.

Seasonal mean concentrations of dissolved V ranged between 7.60 ± 0.58 μg L^{-1} (surface water, autumn) to 15.0 ± 3.35 μg L^{-1} (bottom water, spring), whilst total V concentrations varied from 8.46 ± 1.37 μg L^{-1} (bottom water, summer) to 26.7 ± 6.65 μg L^{-1} (bottom water, spring). Season and the interaction between season and depth were found to have a significant influence on the variation in V (dissolved and total) with depth having a significant effect only on total V concentrations.

Whilst the highest PO_4-P and As concentrations occurred in the bottom water in summer, dissolved and total V concentrations were highest in the bottom water in spring and V was the only element among the three for which the dissolved and total concentrations in summer were higher in the surface water than in the bottom water. For As, P and V the smallest differences between the mean seasonal concentrations (both dissolved and total) in the surface and the bottom waters occurred in autumn.

Concentrations of dissolved and total Al, Fe, Mn and total Ca were higher in the bottom water in all seasons (Supplementary Information, Table B.1). The highest dissolved and total Mn and dissolved Fe concentrations were observed in summer, whilst the highest total Al, Ca and Fe occurred in spring and winter.

3.3. Field measurements: relationship between water column pollutant concentrations and physico-chemical parameters

DO was significantly positively correlated with dissolved V in the surface water and negatively correlated with dissolved As and PO_4-P in bottom water, accounting for 45% of the variation in V, 72% in As and 49% in PO_4-P concentrations (Table 3). There was a significant positive correlation between pH and dissolved and total concentrations of As in the surface water and between pH and total V in the bottom water (34, 39 and 59% of variation explained, respectively).

3.4. Oxygen manipulation laboratory experiment: conductivity, pH and temperature profiles

A significant difference between the DO concentrations measured under the two experimental treatments (Table 4) demonstrated that they were effective in developing and maintaining distinct oxic and anoxic conditions. Mean DO concentrations under the oxic treatment (11.0 ± 0.35 mg L^{-1}; Table 4) were similar to surface water conditions in Kinghorn Loch at the time of sampling (11.6 mg L^{-1}). DO concentrations under the anoxic treatment (0.66 ± 0.19 mg L^{-1}) were similar to the anoxic conditions in the lake bottom water (0.20 mg L^{-1}). Conductivity, pH and

water temperature values were significantly different under oxic and anoxic treatments. Conductivity and water temperature (difference less than 0.37 °C) were significantly higher in cores supplied with air, whilst pH was significantly higher in cores treated with N_2 (Table 4). The conductivity and pH in the experimental cores contrasted with the field measurements, where higher pH and lower conductivity were recorded in the oxygenated surface water compared to the anoxic bottom water in Kinghorn Loch. Conductivity under the oxic treatment and pH under both treatments were higher than recorded in the Kinghorn Loch field measurements.

3.5. Oxygen manipulation laboratory experiment: water column pollutant concentrations

Differences in pollutant concentrations between treatments were measured on every day of the experiment (Fig. 2). PO_4-P and TP (Fig. 2a and b) concentrations throughout the seven-day incubation period were significantly higher under anoxic conditions than oxic (Table 4). Similar differences were observed for As, with dissolved and total concentrations (Fig. 2c and d) significantly higher in anoxic conditions. Dissolved and total V (Fig. 2e and f) also differed significantly under different redox conditions. However, in contrast to P and As, V concentrations were higher under oxic conditions compared with anoxic. Both dissolved and total V concentrations decreased during the experiment under oxic conditions. Among the three measured red mud leachate contaminants, the difference between the mean concentrations under oxic and anoxic conditions was smallest for As (dissolved and total) and greatest for P, with mean PO_4-P and TP concentrations three times higher under anoxic conditions compared with the oxic treatment (Table 4, Fig. 2). Mean dissolved and total concentrations of the four tested pollutant-binding elements, i.e. Al, Ca, Fe, and Mn, did not differ significantly between the experimental treatments (Table 4). However, concentrations of Al, Fe and Mn (with the exception of dissolved Al) were higher under anoxic conditions.

4. Discussion

This case study represents the first detailed evidence of the long-term persistence and cycling of P, As, and V associated with the historical red mud pollution of a freshwater lake. Thirty years after the control of the red mud leachate in 1983, the lake bed sediments are still acting as a source of As, P and V. As, V and P showed significant seasonal variations within the water column of the lake, with higher concentrations occurring in the bottom waters. There were also significant differences in the pollutant concentrations measured between the oxic and anoxic experimental laboratory treatments. These findings are generally consistent with other investigations of the behaviour of P (Smolders et al., 2006;

Table 3
Results of planned multiple regression following stepwise multiple regression to examine the relationship between pollutant concentrations (PO$_4$-P, TP, dissolved and total As, dissolved and total V) and potential explanatory variables (pH, DO, conductivity and temperature) in both, surface water and bottom water. Planned multiple regression was conducted at alpha = 0.05. Only significant results are reported. NS = not significant.

	Pollutant concentration		P-value	Equation of line y = ….	R^2 (%)
Surface	Dissolved	As	0.047	−3.80 + 5.05 pH	34
		V	0.024	−0.171 + 1.10 DO	45
		PO$_4$-P	NS		
	Total	As	0.03	−3.55 + 4.85 pH	39
		V	NS		
		P	NS		
Bottom	Dissolved	As	0.001	1.40−0.433 DO	72
		V	NS		
		PO$_4$-P	0.019	1.95−0.758 DO	49
	Total	As	NS		
		V	0.004	−5.42 + 7.12 pH	59
		P	NS		

Table 4
Results of repeated measures one-way ANOVA analysis to assess the significance of the difference between pH, conductivity (µS cm^{-1}), temperature (°C), DO (mg L^{-1}), pollutant concentrations (PO$_4$-P, TP, dissolved and total As, dissolved and total V) and dissolved and total pollutant-binding elements (Al, Ca, Mn, Fe) under oxic and anoxic treatments during the 7-day incubation experiment. All concentrations are given in µg L^{-1} apart from for Ca (mg L^{-1}).

Measured variables		Oxic conditions		Anoxic conditions		F-value	P-value
		mean	s.d.	mean	s.d.		
Treatment variables	pH	8.36	0.16	9.18	0.21	335.1	<0.001
	Conductivity	401	163	305	5.50	12.03	0.001
	Temperature	9.76	0.42	9.39	0.14	23.65	<0.001
	DO	11.0	0.35	0.66	0.19	23310	<0.001
Pollutants (dissolved)	As	16.1	3.06	18.1	2.21	10.11	0.002
	V	9.36	3.35	4.04	0.89	82.39	<0.001
	PO$_4$-P	45.1	38.2	136	35.0	108.4	<0.001
	Al	44.1	181	20.1	26.1	0.60	0.440
	Ca	42.1	2.62	41.3	2.72	1.56	0.216
	Mn	173	305	248	77.4	1.95	0.167
	Fe	28.3	24.3	35.9	18.0	2.18	0.144
Pollutants (total)	As	20.3	3.23	24.8	4.35	23.96	<0.001
	V	10.4	3.43	4.84	0.91	84.73	<0.001
	TP	69.1	39.7	201	45.3	169.2	<0.001
	Al	33.3	15.4	36.0	5.39	0.923	0.340
	Ca	47.7	5.14	50.0	9.04	1.71	0.195
	Mn	243	336	289	85.9	0.60	0.443
	Fe	90.7	53.3	117	65.2	3.47	0.067

Søndergaard et al., 2003), As (Toevs et al., 2008; Whitmore et al., 2008) and V (Minelli et al., 2000) in aquatic environments. Our results are discussed in more detail below.

4.1. Evidence of redox-mediated cycling in phosphorus and arsenic

Low oxygen levels can affect the sediment sorption processes through the reduction of pollutant-binding Fe and other metal oxyhydroxides, resulting in the release of soluble forms of elements into the overlying water (Couture et al., 2010; Smolders et al., 2006; Whitmore et al., 2008). This mechanism was evident in the bottom waters of Kinghorn Loch in the summer months, when DO concentrations were at their annual lowest and corresponded with a period of thermal stratification. The concentrations of dissolved Fe and Mn at both water column depths were much higher in summer as were concentrations of dissolved and total As and PO$_4$-P, especially in the bottom waters of the lake. These field measurements were also confirmed by our laboratory experiments.

A number of previous studies have also observed seasonal variations in release of P from bed sediments related to changing DO concentrations, with an increase in sediment sorption capacity for P in winter and a decrease in summer (e.g., Kleeberg and Kozerski, 1997; Søndergaard et al., 1999; Spears et al., 2012). Significant differences in dissolved and total As and TP concentrations

between water depths in Kinghorn Loch indicate that the As and TP in the water column are predominantly provided by the lake bed sediment and are contained within the bottom waters during periods of thermal stratification. This is also apparent for PO$_4$-P, with the ANOVA results showing a significant influence of season on the relationship between concentration and water column depth. The multiple regression analysis did not show any significant correlation between surface water concentrations of P and measured physico-chemical parameters. However, the increased concentrations of dissolved and total As in surface waters were significantly positively related to pH. The highly significant positive correlation between pH and DO in the bottom waters (correlation coefficient = 0.899, p < 0.001) suggested that pH might act as a secondary driver of As and P cycling between the lake bed sediments and the overlying water column, although our experimental manipulations indicated that DO supply to bed sediments is likely to be the main driver of these processes in Kinghorn Loch.

In contrast to P cycling, for which a large body of evidence is available, few studies of polluted lakes and none associated specifically with red mud pollution are available with which comparisons of As cycling in Kinghorn Loch can be drawn. However, an increased presence of dissolved As, due to the enhanced mobility of this element at high pH, was previously reported in streams in Sweden (Wällstedt et al., 2010). No evidence was reported for
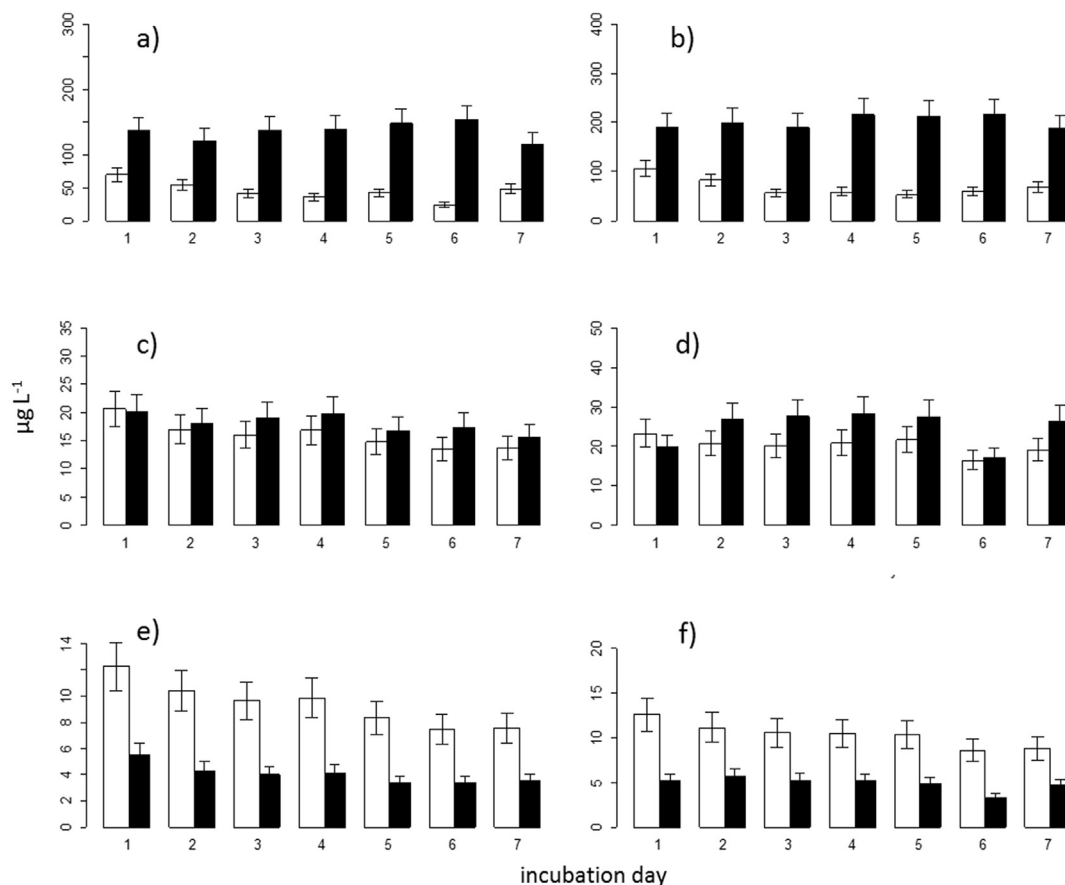
Fig. 2. Water column pollutant concentrations (PO_4-P (a), TP (b), dissolved (c) and total As (d), dissolved (e) and total V (f)) under oxic and anoxic treatments during the 7-day incubation experiment. Bars represent the mean of 5 cores from each treatment and error bars 1 standard deviation of the mean. White and black bars represent oxic and anoxic treatments, respectively.

significant sediment-water exchange of total As under stratified conditions in polluted Crowley Lake, USA, even though elevated As concentrations from 140 to 260 mg kg^{-1} were reported in surface bed sediments (Kneebone and Hering, 2000). The range of bed sediment As concentrations in Kinghorn Loch in 2010 was 86–185 mg kg^{-1} (Olszewska, 2016). The difference in As behaviour between the two lakes can be explained by immobilisation of As in bed sediments of Crowley Lake in the sulphide phase, which is stable under reducing conditions (Kneebone and Hering, 2000).

4.2. Evidence of multiple drivers of vanadium cycling

Adsorption to iron oxides together with redox potential have been shown to control strongly the aqueous geochemistry of V (Peacock and Sherman, 2004). In contrast with our expectations, significant differences in V concentrations, which occurred across both field and experimental measurements, indicated the highest V concentrations under oxic conditions. Furthermore, multiple regression analysis showed a significant positive relationship between dissolved V concentrations and DO concentrations in surface waters. The evidence from the oxygen manipulation experiment and the Kinghorn Loch field campaign indicate that the internal cycling of V in Kinghorn Loch differs from cycling of As and P, in not being controlled predominantly by redox processes.

Although interest in V behaviour in the environment is growing (Cappuyns and Swennen, 2014), the processes controlling seasonal changes in concentrations of dissolved V in freshwater ecosystems are still not well understood (Wang and Wilhelmy, 2009). The majority of reports in the literature have investigated the behaviour of V in controlled laboratory conditions, oceans, estuaries and groundwater (e.g. Audry et al., 2006; Blackmore et al., 1996; Cinti et al., 2015; Pourret et al., 2012; Wright et al., 2014).

Harita et al. (2005), in a laboratory experiment using water and sediment from Lake Biwa, Japan, demonstrated that the release of V from sediment observed under oxic conditions was a response to increased pH, which was the predominant driver of V mobilisation in this lake. Naeem et al. (2007) reported a strong effect of pH on V adsorption onto metal oxides in laboratory controlled conditions, with an increase in adsorption of V as pH increased from 2 to 4 and a linear decrease as pH rose from 4 to 11.6. The results of these studies help us to explain the results in Kinghorn Loch where the highest V concentrations in the bottom waters occurred during the season with the highest pH and under oxic conditions. pH varied significantly across the seasons and depths and regression analysis indicated a significant positive relationship between pH and total V concentrations in the bottom waters. This is, however, inconsistent with our experimental results in which adsorption of V was higher under the anoxic treatment characterised by a higher mean pH compared to the oxic treatment, although the difference in pH was low in comparison to the effective values reported by others above.

However, Wright and Belitz (2010) indicated that, although the effect of pH on V concentrations can be evident in oxic ground-water, it was a less significant driver under anoxic conditions, perhaps due to V precipitation as insoluble oxyhydroxides and/or strong adsorption of reduced cationic species of V(IV and III) to negatively charged mineral surfaces. This may explain the lower V

concentrations under the anoxic treatment compared to oxic conditions observed in this study, despite pH being higher in the former. Moreover, Wright and Belitz (2010) reported significantly higher V concentrations in oxic compared to anoxic groundwater, similar to other studies of groundwater (Cinti et al., 2015; Wright et al., 2014). In addition, Wright et al. (2014) measured higher concentrations of V than As in oxic groundwater and the opposite in anoxic groundwater samples, indicating a different behaviour of As and V in response to varying redox conditions in aqueous systems. Cinti et al. (2015) suggested that mobilisation of V was favoured under oxidising conditions at near neutral pH due to the formation of the highly soluble V(V) oxyanion, whereas under reducing conditions relatively insoluble species of V(III) were prevalent. Our experimental results for V, as well as the summer field measurements at Kinghorn Loch, appear to be in agreement with these studies.

4.3. The role of competing ions

Competition for binding sites can be another factor controlling the cycling of V, as well as P and As. The extent of anion sorption depends on its relative affinity for the sorption material. Wällstedt et al. (2010) indicated that vanadate (VO_4^{3-}) should be more strongly adsorbed to ferrihydrite than PO_4^{3-}, which in turn shows higher adsorption strength than arsenate (AsO_4^{3-}). The results for dissolved As and PO_4-P in this study appear to reflect this relationship, with a greater difference between PO_4-P concentrations in oxic and anoxic conditions compared to As, suggesting that PO_4-P was more strongly absorbed by ferrihydrite. The V results, however, contradict a stronger adsorption of V compared to PO_4-P.

Blackmore et al. (1996), in a study assessing the removal of V from corrosion inhibitor effluent, showed that with decreasing concentrations of iron oxyhydroxides, the effect of pH and presence of PO_4-P on the extent of adsorption of VO_4^{3-} increased. Moreover, the study indicated that the presence of PO_4-P in aqueous solution at higher concentration than V will interfere severely with the adsorption of the latter, not only by competing for adsorption sites with V, but also by interfering with the co-precipitation process. The higher PO_4-P compared to dissolved V concentrations in Kinghorn Loch reported here suggest that competitive adsorption of PO_4-P could result in the persistence of V under oxidising conditions. This also appears to be in agreement with the increased concentrations of dissolved forms of V and As attributed to high PO_4-P concentrations (and also the effect of high pH) previously reported in streams in Sweden (Wällstedt et al., 2010). To better understand the mechanisms driving the internal cycling of V in Kinghorn Loch the interactions between pH, competitive ion concentration, and redox conditions need to be assessed further and speciation of V should be examined. What is clear is that the control of one element in isolation may result in unintended consequences on others and this should be considered in any long-term management plans.

4.4. Wider implications of the study

Our results indicate that contaminant cycling between the lake sediment and overlying waters of Kinghorn Loch has persisted since the diversion of red mud leachate in 1983. This study has demonstrated seasonal increases in the water column of red mud contaminants released from sediment with the highest concentrations appearing to be confined to the bottom waters of Kinghorn Loch. Nevertheless, the total As concentrations measured during the experiment and field campaign, as well as the total V measured in the laboratory experiment, did not exceed the Standards for Protection of Aquatic Life in the UK (50 µg L^{-1} (EEC, 1976) and 20 µg L^{-1} (EEC, 1976), respectively). These standards were not, however, met for total V in Kinghorn Loch for the bottom water sampled in spring 2013. TP concentrations measured during the experiment and field campaign also exceeded the Trophic State Index value of 24 µg L^{-1} for TP, above which a lake is classified as eutrophic (Carlson and Simpson, 1996). In addition, Olszewska et al. (2016) recently reported the presence of As species within tissues of aquatic plants in Kinghorn Loch that exceeded ecological guidelines and indicated legacy contamination in the food web.

Given these findings, it is clear that management actions to enhance natural recovery processes in red mud polluted water bodies should be considered. Sediment removal or chemical treatment have been considered in other studies. For example, materials have been developed with binding properties for the removal of As from drinking water (Kundu and Gupta, 2006; Partey et al., 2008; Zaspalis et al., 2007). Similar materials have been proposed for the control of P (Spears et al., 2013) as well as other metal contaminants in surface waters. The effectiveness of such measures in aquatic ecosystems impacted by red mud should be considered further. This is particularly important in the case of V, which is not substantially removed from red mud leachate by a range of neutralisation methods (Burke et al., 2013). One other potential approach for the control of P and As is aeration of bottom waters, as has been demonstrated for P (Beutel and Horne, 1999). However, given that our study indicates V will increase under oxic conditions, the simultaneous control of multiple pollutants remains challenging. To conclude, as has been demonstrated by this Kinghorn Loch study, there is a need to develop novel management measures to control these multiple, and potentially interacting, pollutants in order to reduce the long-term legacy effects.

5. Conclusions

- This study confirmed that the bed sediments of Kinghorn Loch still act as a source of As, P and V to the water column, 30 years after red mud pollution was diverted away from the lake.
- Higher concentrations of As, P and V were reported in the lake bottom waters compared with the surface waters; these differences were affected by both season and depth.
- Results from an intact sediment core laboratory incubation experiment and field measurements indicated elevated As and P concentrations in the lake water under anoxic conditions and raised V concentrations under oxic conditions.
- Whereas the main driver of As and P cycling in Kinghorn Loch was confirmed as being mediated by redox processes, the release of V from the lake sediments appeared to be controlled by the interaction of multiple factors, including competitive ion concentrations, pH and redox conditions.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2017.07.009.

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