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Assessing the legacy of red mud pollution in a shallow freshwater lake: long-term chemical recovery in the water column

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Abstract

Little is known about chemical and ecological recovery following red mud leachate pollution in fresh waters. This is confounded by a lack of knowledge on the chemical composition of red mud leachate and the changes in composition that occur as a result of interactions with sediments and freshwater organisms during transport through aquatic ecosystems. We used over 30 years of data from a shallow lake (Kinghorn Loch, Fife, Scotland) with a well-documented history of several decades of red mud leachate pollution to characterise the chemical loads (during a pollution period of 1981-1983), resultant impacts on surface water chemistry (comparison between 1983 and 2009) and recovery trajectories following leachate diversion (1983-2010) of constituents that pose a risk to the environment. Between 1981 and 1983, the input of leachate resulted in loads of total aluminium (Al), total arsenic (As), total vanadium (V) and phosphate ($\text{PO}_4\text{-P}$) to the lake of 107, 2.3, 3.3 and 2.3 g m^{-2} (lake surface area) yr^{-1} , respectively. During the same period, the lake acted as a sink of Al, As, V and $\text{PO}_4\text{-P}$ retaining 63.6, 0.6, 0.8 and 1.6 $\text{g m}^{-2} \text{yr}^{-1}$, respectively. We used General Additive Modelling to assess the response trajectories and recovery end points of these constituents. Our results demonstrate the complexity of sediment-pollutant interactions during pollutant transport through the aquatic environment and provide insight into likely recovery trajectories in other aquatic ecosystems following red mud contamination. The $\text{PO}_4\text{-P}$, total As and total V surface water concentration recovery times, defined statistically as the point on the time series beyond which no further significant decrease in concentrations were observed, ranged from 18 to 26 years. Total Al concentrations continued to decrease significantly following the end of the monitoring period in 2010. In Kinghorn Loch, the legacy of red mud pollution continues to represent an environmental risk, demonstrating the importance of long-term monitoring and management strategies following similar pollution events.

Key words: aluminium, arsenic, lake, phosphorus, recovery, vanadium

Introduction

The International Aluminium Institute, representing over 60% of global aluminium production industries report estimates of the global stock of red mud waste at 3,000 million tonnes (in 2010; Power et al., 2009, World Aluminium, 2015) with global production of about 120 million tonnes yr⁻¹. The effects of red mud pollution on aquatic ecosystems was demonstrated following a dam failure of a waste containment reservoir in October 2010 in Ajka, West Hungary. This resulted in the release of c.1 million m³ red mud waste (Burke et al., 2012) which impacted a catchment area of 3078 km² (Klebercz et al., 2012). The highly alkaline pollution (pH 13.5) reached the Torna Creek and River Marcal, passed through the River Rába and entered the Danube, Europe's second longest river (Schöll and Szövényi 2011). Calcium sulphate was applied over large areas to reduce the effects of elevated pH in contaminated rivers and streams in following the incident in Hungary (Enserink 2010). Research soon after the spill focused on short-term chemical and ecological impacts in aquatic ecosystems and on the potential human health effects associated with airborne red mud particles. This showed a recovery in pH in the river systems almost 2 months after the pollution event, which decreased with distance from the source of pollution from c. pH 13 (at the site closest to the pollution source area) to c. pH 8 downstream. The presence of elevated concentrations of arsenic (As), molybdenum (Mo) and vanadium (V) in water and As, V, chromium (Cr), cobalt (Co) and nickel (Ni) in river sediment was limited to the Torna Creek and part of the upper Marcal River. The results indicated that in aquatic ecosystems with low residence times and well oxygenated surface sediments, red mud constituents including oxyanion forming elements (e.g. As, V, Cr) were contained within solid phase complexes and represented limited ecological threat. However, in depositional zones, where reducing redox conditions may be common, the liberation of such contaminants may be expected (Mayes et al., 2011).

To date, no study has been published documenting the longer term (i.e. years to decades) recovery of any freshwater ecosystem, i.e. lotic or lentic, following red mud pollution. This information is critical for the development of effective monitoring and management strategies by the industry (World Aluminium, 2015). We propose that the current estimates of days to months for chemical recovery (of As, V, aluminium (Al) and P) for all freshwater ecosystems based on Mayes et al. (2016) are insufficient to cover all ecosystem types. Specifically, we hypothesise that chemical recovery following red mud pollution in lakes (i.e. high residence time depositional freshwater environments) will exhibit a long recovery time (i.e. similar to years and decades commonly observed for P in lakes; Sharpley et al., 2013) in comparison to the rapid recovery times (i.e. days to months) reported for fluvial systems following the Ajka incident (Mayes et al., 2016). Our understanding of P recovery in lakes following management for eutrophication indicates that recovery times can reach many decades as a result of internal biogeochemical cycling, especially in ecosystems with high retention times (i.e. lakes, wetlands and groundwater; Spears et al. 2012; Sharpley et al. 2013).

We tested this hypothesis using long-term monitoring data documenting chemical recovery in Kinghorn Loch, UK, following red mud pollution control in 1983 (Olszewska et al., 2016). The specific objectives of the study were to: (1) quantify the composition of red mud leachate entering Kinghorn Loch during the peak pollution period in comparison to an unpolluted surface water inlet (i.e. 1981 to 1983); (2) quantify the loads of Al, As, V and phosphate ($\text{PO}_4\text{-P}$), and their retention by the lake; and (3) quantify recovery trajectories of red mud pollutants following diversion of the leachate between 1983 and 2010. This information was used in conjunction with environmental quality standards to assess the long-term environmental risk associated with these pollutants and to revise estimates of recovery time in freshwater ecosystems in general.

99 **Methods**

100 **Study site description**

101 Kinghorn Loch is a small lake of area 11.3 ha, mean depth 4.5 m and maximum depth 12.8
102 m, situated in Fife, Scotland (56°10'N; 3°11'W). For several decades the lake received
103 leachate from the nearby Whinnyhall landfill site where red mud waste from the Burntisland
104 plant of British Aluminium (BA) Ltd. was stored from 1944 (Fig. 1). This plant was in
105 operation from 1917 and by 1980 its production had risen to 120,000 t of alumina and
106 140,000 t of red mud waste per year, primarily through processing of bauxite from Awaso,
107 Ghana (Edwards, 1985). The landfill was drained through a series of ditches and culverts
108 which fed a retention pond of 60 m³ capacity and 6 hours hydraulic retention time. The pond
109 was retained by a concrete dam with a V-notch flow-measuring weir delivering leachate
110 directly to Kinghorn Loch. Reports of failure of this retention pond to reduce loads of
111 suspended solids were common due to poor maintenance where the sluice plate was removed,
112 spilling solids and aqueous waste directly to the loch in pulses. This drainage system
113 delivered highly alkaline leachate from the landfill site to Kinghorn Loch, mixed with rain
114 and spring waters, from 1947 to 25 May 1983, when the discharge was diverted away from
115 the lake in a collaborative effort to improve water quality by BA Ltd. and the Forth River
116 Purification Board (FRPB). A second inflow to the loch, the North inlet was not
117 contaminated with leachate and represents background conditions for the catchment.

118 **Pollutant retention in Kinghorn Loch**

119 The frequency and nature of the sampling and analyses of the leachate, inlets and the outlet of
120 Kinghorn Loch are summarised in Table 1. It was assumed that the results from the Kinghorn
121 Loch outlet represented surface water conditions in the lake. The collection of water samples
122 and discharge measurements for the determination of pollutant loads was conducted between

April 1981 and September 1984 at weekly to fortnightly frequency. Discharge at the North and leachate inlets and downstream of the lake outlet were assessed by stage boards calibrated to discharge as described by Edwards (1985). Water samples were taken at mid-depth in running water in 1 and 10 L polythene or polypropylene bottles for metal and metalloid analysis and 1 L glass bottles for analysis of other determinands. The polythene and glass bottles were cleaned in 50% v/v nitric acid solution and 50% v/v chromic acid solutions, respectively, and rinsed with deionised water prior to sample collection.

Physico-chemical parameter measurements and sample filtration were conducted in the laboratory after sample collection. pH values were determined using a Radiometer PHM 63 meter. Alkalinity was measured by titrating 100 mL samples against a standardised 0.05 M sulphuric acid solution to pH 4.5, with leachate samples being diluted 1/10 with deionised water prior to the titration.

Water samples for the determination of dissolved calcium (Ca), magnesium (Mg), fluoride (F) and silica (SiO₂) concentrations were filtered through Whatman GF/C filters. Nitrate (NO₃-N), ammonium (NH₄-N), chloride (Cl), SiO₂, orthophosphate (PO₄-P), boron (B) and sulphate (SO₄-S) were determined using air segmented continuous flow analysis with photometric detection performed on a Technicon AutoAnalyzer II system based on the assay reviewed by the Standing Committee of Analysts (HMSO, 1980a). Detection limits for NO₃-N, NH₄-N, Cl, SiO₂, B and SO₄-S were 0.01, 0.04, 1.0, 0.1, 0.04, 2 mg L⁻¹, respectively. Detection limit for PO₄-P was 0.01 mg L⁻¹ for the analysis of inlet and outlet samples, and 0.1 mg L⁻¹ for the analysis of leachate. Fluoride concentrations were determined using an ion selective electrode with a separate standard calomel reference electrode, with a limit of detection of 0.01 mg L⁻¹.

Samples of leachate, inlets and outlet for dissolved metal and metalloid analyses were filtered through 0.1 µm polycarbonate filter membranes. 1 M spectrophotometric grade hydrochloric

acid was used to adjust pH to 2-4 in leachate samples for metal determination and 2 cm³ L⁻¹ of hydrochloric acid was added to preserve all samples prior to analysis. The samples were evaporated on a hotplate to approximately 80 cm³ and made up to 100 cm³ with deionised water, concentrating the samples of leachate and North inlet by 10 and 100 times, respectively. Dissolved and total metal and metalloid concentrations, apart from cadmium (Cd) and lead (Pb), were determined using flame atomic absorption spectrophotometry (Instrumentation Laboratories IL357 equipped with an IL254 autosampler) and based on the method described in HMSO (1980b). Limits of detection for Al, Ca, Cr, copper (Cu), iron (Fe), Mg, manganese (Mn), nickel (Ni), potassium (K), sodium (Na), V, As and zinc (Zn) were 0.5, 0.005, 0.03, 0.01, 0.01, <0.002, 0.005, 0.02, 0.004, 1.0, 0.3, 0.005, 0.005 mg L⁻¹, respectively. Cd and Pb were measured by graphite furnace atomic absorption spectrophotometry, with detection limits of 0.005 mg L⁻¹ for Cd and 0.5 mg L⁻¹ for Pb. Total suspended solids (TSS) were determined by the removal of suspended matter from samples using vacuum filtration, followed by drying at 105°C and reweighing. The limit of detection for TSS was 2.5 mg L⁻¹.

The load of red mud associated contaminants to Kinghorn Loch was estimated using mean discharge and determinand concentration data for each inlet and outlet in the 1981-1984 monitoring period outlined above. Annual loads were calculated for Al, total As, total V, and PO₄-P prior to leachate diversion and used to estimate retention expressed relative to lake surface area.

Analysis of surface water and outlet determinands for analysis of long-term responses

Surface water pH in Kinghorn Loch was measured by FRPB and BA Chemicals Ltd. between 1954 and 1981 typically up to 4 times per year. The methodology for pH used by BA Chemicals Ltd. during this period is unreported, although we believe that water samples were collected from the outlet prior to pH determination in a laboratory. The Scottish Environment

Protection Agency (SEPA) and FRPB (its predecessor) measured pH weekly between 1981 and 1984, and a suite of determinands monthly thereafter on water samples collected from the outlet, using standard methods (Table 1 and 2). Since no obvious discrepancy was apparent between the pH values measured by FRPB and BA Chemicals Ltd. data prior to 1981, we assume the methods were comparable.

Statistical analysis

A direct comparison was made between a wide suite of measured determinands to in 2009 (post-diversion conditions) versus 1983 (i.e. pre-diversion conditions). Low frequency of sampling in 2010 was the reason for using data from 2009 to represent post-diversion water quality. Data exploration showed violation of normality assumption. Therefore, a non-parametric Mann-Whitney-Wilcoxon test, which allows for normality violation, was used to assess the significance ($P < 0.05$) of the difference between the two years. The frequency of sampling and analysis by SEPA differed between the two years and was between 5 to 53 (depending on the determinand) in 1983 and 12 in 2009. Due to lack of measurements of Ca, Mg and Fe in 1983, data from 1981 were used for comparison for these determinands.

We used General Additive Models, assuming normal errors (GAMs, Hastie & Tibshirani, 1990; Wood, 2006), to determine the timing of recovery following diversion for determinands for which long-term data were available over a suitable time series. The endpoint of recovery was determined in two ways: (1) the year in which no further significant decrease in concentration was detected, as assessed using GAMs, and (2) the year in which the determinand concentration dropped below relevant ecological quality standards (where available) for the last time in the dataset.

For the GAM analysis, the aim was to identify relationships between the concentrations with year after the diversion of the red mud leachate, with season included as a fixed effect in the

analysis, the following modelling strategy was employed. A Gamma error structure (log link function) was used in all models and an autocorrelation structure of AC1 (auto-regressive model of order 1) on year relative to the diversion of the leachate from the inlet was applied. The relationship between the response (pH and pollutant concentrations) and the explanatory variable (year relative to the diversion of the pollution) was allowed to be a smooth function instead of restricting the relationships to be linear. Due to the use of different smoothers for different seasons for V and the significance of the fixed effect of season in the pH analysis, separate models were fitted for different seasons for these two determinands. Data used in the models were for the period 1981 – 2009 (the last two years of the pollution input and the recovery period that followed). Based on the recommendations of Zuur et al. (2009) the response variables were not transformed prior to analysis. The changes in the red mud constituent concentrations were compared against relevant ecological quality standards. As there is no standard for PO₄-P or total phosphorus (TP) for Kinghorn Loch, the Trophic State Index for TP (Carlson et al., 1996) was used to provide ecological context for the lake water TP concentrations. Due to the lack of ecological quality standards for total As and Al, the results were compared against the standards for dissolved As and reactive Al, respectively. As such, our comparisons of total element concentrations against EQSs should be considered the worst case scenario. In reality the risk associated with dissolved components of the total element concentration will be lower. The models were fitted using the GAM function in the mgcv package (1.7-6) (Wood, 2011) and statistical analyses were conducted using R version 2.15.1. (R Core Team, 2012) available at <http://www.r-project.org>.

Results

Red mud loading to Kinghorn Loch

Prior to the diversion of the red mud leachate from Kinghorn Loch pH and alkalinity at the leachate inlet were 12.1 and 4125 mg L⁻¹ (i.e. mean values 1981-1983), respectively, compared to 8.1 and 133 mg L⁻¹, respectively, for the north inlet (Table 3). The leachate inlet was characterised by high concentrations of Al, V, As, Zn, Cu, Pb, Cr, Cd, Fe, K, Cl, F, SO₄-S, Na, PO₄-P and TSS compared to the north inlet. North inlet water contained higher concentrations of Ca and Mg compared to the leachate inlet. The load from the leachate inlet of total Al, As, V and PO₄-P to the lake during the period January 1981 to May 1983 was 107, 2.3, 3.3 and 2.3 g m⁻² yr⁻¹, respectively. The annual retention of Al, As, V and PO₄-P was 63.6, 0.6, 0.8 and 1.6 g m⁻² yr⁻¹, respectively.

Lake water chemical responses following red mud leachate diversion

pH in Kinghorn Loch outlet water increased until the diversion of the leachate in 1983, reaching a value of 10.5 (Fig. 2). Following diversion, pH decreased in the first few years before clear seasonal patterns emerged (higher pH values in summers, lower in winters), with pH fluctuating between 7.5 and 9.5. All measured determinands in the lake outlet water were significantly lower in 2009 than in 1983, with the exception of total Ca and Mg which had significantly higher concentrations in 2009 than in 1983 (Table 4, Figs. 3-4). Concentrations of total Fe, As and V were < 1 mg L⁻¹ in 1983 and, together with total Al, decreased to < 0.1 mg L⁻¹ in 2009. Concentrations of PO₄-P decreased from 0.076 to 0.012 mg L⁻¹ between 1983 and 2009.

Recovery trajectories for pH, phosphorus, aluminium, arsenic and vanadium

The time series of concentrations of total Al, total As, total V and PO₄-P before and after the diversion are shown (Fig. 4). For all these determinands, concentrations decreased following the diversion in May 1983 until 1985 after which the rate of decrease slowed, with occasional high concentrations occurring. GAMs showed that the recovery times were determinand-specific and that the effects of season were significant for total V and pH. Our analysis indicated that no further significant decrease in pH values occurred 5 years following leachate diversion (Table 5). Declines in PO₄-P concentrations ceased in 2007 and, although not directly comparable, PO₄-P concentrations were below the suggested Trophic State Index value for TP of 0.024 mg L⁻¹ (Carlson et al., 1996) by 1986 (0.020 mg L⁻¹). For total Al, the significant decrease in concentrations was maintained until the end of the observation period in 2009 when the Al concentration still exceeded the ecological quality standard of 0.015 mg L⁻¹ (SEPA Supporting Guidance, 2013). Total As concentrations declined following leachate diversion for a period of 22 years, with concentrations falling below the water quality guideline of 0.050 mg L⁻¹ (UK Standards for Protection of Aquatic Life; EEC, 1976) in 2006. Depending on the season, it took from 18 to 26 years for the total V concentrations to stop significantly decreasing, with the shortest recovery period observed for autumn and the longest for spring and winter. Concentrations of total V measured in autumn decreased to below the water quality guideline of 0.020 mg L⁻¹ for total V (UK Standards for Protection of Aquatic Life; EEC, 1976) in 2001, whilst spring concentrations only fell below the guideline value in 2008.

Discussion

Impacts of red mud leachate on lake chemistry

The composition of the red mud leachate, which entered Kinghorn Loch between 1947 and 1983, posed four potential pressures on the aquatic environment: high pH, metal and metalloid pollution, eutrophication and high salinity. The high loadings of contaminants entering the lake (e.g. 107, 2.3, 3.3 and 2.3 g m⁻² yr⁻¹ of total Al, As, V and PO₄-P, respectively) led to high concentrations of a range of metals (e.g. total Al - 7.30 mg L⁻¹, V – 0.49 mg L⁻¹), metalloids (e.g. As – 0.32 mg L⁻¹), PO₄-P (0.13 mg L⁻¹) and chloride (38.0 mg L⁻¹) in the loch water. The concentrations of some pollutants in the water column in 1983 greatly exceeded ecological quality standards for fresh waters. Specifically, the concentrations of PO₄-P and total As were approximately 3 and 5 times higher than the relevant environmental guidelines, whilst total V and total Al concentrations were 22 and 355 times higher, respectively, than the recommended ecological quality values. The pressures in Kinghorn Loch, with the exception of eutrophication, were also observed in the river system downstream of the Ajka red mud spill in Hungary in 2010 (Mayes et al., 2011; Ruyters et al., 2011; Shöll and Szövényi, 2011).

Recovery following red mud pollution

The results of the GAM analyses indicated that chemical recovery in Kinghorn Loch took decades to complete and is in agreement with our hypothesis based on P recovery following eutrophication management. The time scale of the recovery differed among the determinands. The shortest recovery period (5 years) was observed for pH. In contrast, analysis of the river system affected by the Ajka red mud spill indicated rapid recovery in pH only 2 months after the pollution accident at sites further downstream from the pollution source (Mayes et al., 2011). The fast improvement in pH in this case was, however, a result of both acid dosing

and dilution of the contaminated water in the river system (Mayes et al., 2011), whereas no remedial actions were taken in Kinghorn Loch. In addition, elevated pH in Kinghorn Loch during the first few years following the cessation of pollution may have been influenced by the enhanced photosynthetic activity in the lake (Scheffer, 2004).

As a result of eutrophication caused by high P loading, intense phytoplankton blooms occurred in Kinghorn Loch from the mid-1970s until 1985, when a collapse in the phytoplankton activity was recorded (Edwards, 1985). These results indicate that the recovery times reported following the Ajka spill are not representative of all freshwater ecosystems. In addition, we report here significant differences in the long term recovery times for Al, As, V, and PO₄-P ranging from 18 to 26 years, with significant seasonal effects being reported for V. Sporadic peaks in contaminant concentrations can be observed even in recent years in Kinghorn Loch indicating persistent environmental risk, especially associated with PO₄-P, total V, As and Al. Olszewska et al. (2017), using laboratory controlled sediment core incubations confirmed the release of P, As and V from bed sediments in recent years, being controlled predominantly by redox conditions, competitive ion concentrations and pH.

Delayed recovery following pollution control has been well documented in the case of P in lakes (Jeppesen et al., 2007; Søndergaard et al., 2003, Spears et al., 2012), and also for As (Toevs et al., 2008; Whitmore et al., 2008) and V in fresh waters (Minelli et al., 2000). Competition between P, As and V for adsorption to iron oxyhydroxides may lead to preferential immobilisation of these pollutants in bed sediments (Wällstedt et al., 2010). High pH can also have negative effects on immobilisation of some elements, e.g. P (Søndergaard et al., 1999) and V (Naeem et al., 2007) and might therefore account for longer recovery times. The likely impact of the elevated pH in Kinghorn Loch in the years immediately following the diversion of the leachate, as well as the potential competition for sorption sites between some red mud constituents, indicate that these interactions may be a dominant factor

regulating chemical recovery. However, uptake into biota may also be a major pathway of internal cycling of red mud pollutants; significant accumulation of As species was reported in tissues of macrophytes in Kinghorn Loch, as recently as 2013 (Olszewska et al., 2016).

Concentrations of most determinands were significantly lower in 2009 than in 1983, with the exception of Mg and Ca, and PO₄-P, As and V concentrations were all below the relevant ecological quality standards in 2009, although total Al was not. Mg and Ca concentrations were significantly higher in 2009 than in 1983 (15.9 and 24.5 mg L⁻¹ in 2009, respectively, compared to 8.80 and 7.12 mg L⁻¹ in 1983), although the major input of these two elements was the unpolluted north inlet, characterized by high natural levels of water hardness. The significantly lower concentrations of Mg and Ca in lake outlet water in 1983 were likely to be a result of removal of any free Ca²⁺ and Mg²⁺ by reaction with the high carbonate alkalinity coming from the leachate to form solid carbonates in the elevated pH conditions (Renforth et al., 2009).

Implications for management

Mayes et al. (2011) reported rapid contaminant dilution, with the exception of depositional hotspots, in the river system affected by the Ajka accident, indicating species-specific transport rates through the system (Mayes et al., 2011). Although chemical recovery was reported to be rapid, good ecological condition in the Torna Stream polluted in the Hungarian accident is not expected to be achieved until 2021, some 11 years after the pollution event (Kovács et al., 2012). Our results indicate that chemical recovery time may be significantly longer in depositional zones with long hydraulic retention times. Ecological recovery times may be longer still. The analysis of As content in five macrophyte taxa in Kinghorn Loch conducted in 2013 showed that macrophytes contained relatively high concentrations of toxic inorganic As, suggesting toxicological risk to higher trophic levels (Olszewska et al., 2016).

There appears to be a lack of evidence on available measures with which to mitigate the environmental impacts of red mud pollution in lakes. In Hungary, calcium sulphate was applied (Enserink 2010) to reduce the pH effects. In Kinghorn Loch, metal concentrations remained elevated above environmental quality standards even after pH had recovered and so pH control only may be insufficient to control the effects of complex potentially harmful elements in fresh waters as confirmed also by Mayes et al. (2016).

Removal of contaminated sediments has been practiced as a measure for mitigating environmental impacts of metals and nutrients in lakes with mixed effectiveness (Peterson, 1982; Phillips et al., 2015). Emerging geo-engineering techniques (Spears et al. 2013; Lüring et al., 2016) developed for the simultaneous control of multiple elements may also represent effective management tools in this respect for oxyanion forming elements (e.g. As, V, P), although the development of this approach is in its early stages. Aeration of bottom waters may also be effective in the control of redox sensitive elements, including As and P (Beutel and Horne, 1999). Advances have been made recently in the development of materials with which to deliver oxygen to lake bed sediments. Nykänen et al. (2012) have demonstrated at the field scale the application of calcium peroxide to manipulate redox conditions at the bed sediment surface which can lead to the reduction of P release to the water column (Lu et al., 2017). However, oxidising conditions might result in undesirable response in V, leading to a release of this metal from bed sediment, as shown by Olszewska et al. (2017). We call for a more comprehensive assessment of such measures to support emergency response strategies and longer-term mitigation options.

Conclusions

- A significant decrease of pH and concentrations of all red mud constituents occurred in Kinghorn Loch water after leachate was diverted from the loch inflow waters.
- The chemical recovery period of PO₄-P and total V, As and Al ranged from 22 to 26 years, depending on the determinand, and was 5 years for pH. Total Al concentrations had not reached the end-point of recovery after 26 years.
- Evidence of persistent cycling of PO₄-P total V, As and Al between bed sediments and the water column appears to be the major process regulating recovery.
- The higher retention time of standing waters can result in longer chemical recovery times following red mud pollution in lakes compared to rivers and streams.

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Fig. 1. Locations of the former production plant and landfill site, and current location of the treatment plant in relation to Kinghorn Loch (image courtesy of Google Earth, taken in 2010).

486 **Fig. 2.** Long-term trends in water pH in Kinghorn Loch. The shaded area represents the
487 period of recovery following diversion of leachate from the lake inlet.

Fig. 3. Concentrations of pollutants in Kinghorn Loch outlet in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery). Due to no measurements of Ca, Mg and Fe in 1983, data from year 1981 were used for these three determinands. Data are summarised as boxplots showing the median and 25th and 75th quartiles, with whiskers representing the values outside the middle 50% and outliers shown as dots.

Fig. 4. pH, conductivity, alkalinity and TSS in Kinghorn Loch outlet in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery); recovery). Data are summarised as boxplots showing the median and 25th and 75th quartiles, with whiskers representing the values outside the middle 50% and outliers shown as dots.

Fig. 5. Total arsenic (panel a), vanadium (panel b), aluminium (panel c) and orthophosphate (PO₄-P, panel d) concentrations in Kinghorn Loch outlet prior to (1981-1983) and following (1984-2010) the diversion of the leachate from the loch inlet in 1983. Vertical dashed lines indicate the cessation of red mud leachate input into the lake in 1983.

Table 1. Summary of leachate and Kinghorn Loch inlet and outlet sampling and analysis conducted to 2010.

Time period	Frequency	Location	Measurements and analyses	Samples collected by:
1976-1981	up to 4 times per year	incoming leachate	pH, chemical composition	Forth River Purification Board (FRPB) and BA chemical Ltd.
1954-1981	up to 4 times per year	lake outlet	pH	FRPB and BA Chemical Ltd.
Apr 1981-Sep1984	weekly - fortnightly	incoming leachate	temperature, pH, conductivity,, major ions, trace elements (total and dissolved), TSS, chlorophyll a, discharge	Edwards (1985) and FRPB
Apr 1981-Sep 1984	weekly - fortnightly	North inlet	temperature, pH, conductivity, BOD, major ions, trace elements (total and dissolved), TSS, chlorophyll a, discharge	Edwards (1985) and FRPB
Apr 1981-Sep 1984	weekly - fortnightly	lake outlet	DO, temperature, pH, conductivity, alkalinity, BOD, COD, , major ions, trace elements (total and dissolved), TSS, chlorophyll a, discharge	Edwards (1985) and FRPB
1981-2010	weekly – 6 times per year	lake outlet	DO, temperature, pH, conductivity, alkalinity, BOD, COD, major ions, trace elements (total and dissolved), TSS, chlorophyll a	Scottish Environment Protection Agency (SEPA) and FRPB (its predecessor)

Table 1. Procedures used by SEPA for the analyses of Kinghorn Loch outlet water during the period 1981 to 2010.

Determinand	Procedure based on:
pH, alkalinity as CaCO ₃ , electrical conductivity	HMSO. 1981. The Determination of Alkalinity and Acidity in Water, 1981 - Methods for the Examination of Waters and Associated Materials. London.
Total Suspended Solids	HMSO. 1984. Suspended, Settleable and Total Dissolved Solids in Waters and Effluents, 1980 - Methods for the Examination of Waters and Associated Materials. London.
chlorophyll a	HMSO. 1983. The Determination of Chlorophyll a in Aquatic Environments, 1980. Methods for the Examination of Waters and Associated Materials. London; 13.2 ISO 10260: 1992(E). Water quality - Measurement of biochemical parameters – Spectrometric determination of the chlorophyll-a concentration. 9pp. International Organization for Standardization, Genève
NH ₄	HMSO. 1982. Ammonia in Waters, 1981 - Methods for the Examination of Waters and Associated Materials. London.
NO ₃ -N	HMSO. 1982. London. Oxidised Nitrogen in Waters 1981 - Methods for the Examination of Waters and Associated Materials. London.
PO ₄ -P	HMSO. 1981. Based on Phosphorous in Waters, Effluents and Sewages, 1980 - Methods for the Examination of Waters and Associated Materials. London.
chloride	HMSO. 1982. Chloride in Waters, Sewage and Effluents 1981 - Methods for the Examination of Waters and Associated Materials. London.
SO ₄ -S	HMSO. 1989. Based on Sulphate in Waters, Effluents And Solids (2nd Edition) 1988 - Methods for the Examination of Waters and Associated Materials. London.
SiO ₂	HMSO. 1981. Silicon in Waters and Effluents 1980 - Method For The Examination Of Waters And Associated Materials. London.
Metal and metalloids	HMSO. 1996. Inductively Coupled Plasma Spectrometry 1996, Methods for the Examination of Waters and Associated Materials. London.

Table 3. Mean values and loads for determinands measured (generally weekly to fortnightly) in Kinghorn Loch inlets and the outlet during the period 4 April 1981 to 24 May 1983. Bold values are from single spot samples. Filtered samples are shown in brackets with < denoting a value that is lower than the detection limit. Data from spot samples collected from Torna Creek (Hungary) on 1 December 2010 are shown for comparison (from Mayes et al., 2011).

Determinand	Leachate inlet (mg L ⁻¹)	North inlet (mg L ⁻¹)	Loch outlet (mg L ⁻¹)	Leachate load (g m ⁻² yr ⁻¹)	Pollutant retention in the loch (g m ⁻² yr ⁻¹)	Torna site K1 (mg L ⁻¹)
pH	12.1	8.1	9.9			13.1
Alk	4125	133	427	3038		7160
TSS	87	6.2	31	66		
NH ₄ -N	(0.7)	(0.14)	(0.26)	(0.50)		
NO ₃ -N	(1.8)	(7.3)	(1.8)	(1.4)		
PO ₄ -P	(3.0)	(0.04)	(0.13)	(2.3)	1.6	
SO ₄ -S	154	23	44	114		727
Cl	68	26	38	52		83
SiO ₂ -Si	(7.1)	(4.6)	(1.2)	(5.1)	23.72	499 (0.67)
F	3.2	0.15	1.5	2.7		
Ca	7.2 (4.0)	51 (43)	11 (3.4)	4.8 (3.1)	232.7	1515 (1.3)
Mg	8.2 (0.10)	25 (22)	10 (4.3)	6.1 (0.72)	101.8	9.7 (0.001)
Na	(2007)	(21)	(252)	(1514)		(701)
K	(26)	(0.67)	(3.7)	(19)		115 (85)
Fe	0.51 (0.12)	0.19 (0.08)	0.13 (0.06)	0.30 (0.09)		10 (<0.01)
Al	138 (138)	0.38 (0.17)	7.3 (6.6)	107 (1.5)	63.6	1228 (659)
As	3.6	0.01	0.32	2.3	0.60	3.9 (3.61)
V	5.3	0.05	0.49	3.3	0.76	6.4 (5.7)
Zn	0.01					0.5 (0.05)
Cu	0.03					0.4 (0.31)
Pb	0.03					0.3 (0.04)
Mn	0.06					9.9 (<0.001)
Ni	0.06					0.3 (0.04)
Cr	0.11					0.4 (0.05)
Cd	0.01					0.1 (0.05)
B	0.82	0.06	0.13	0.59	0.14	1.0 (0.90)

Table 4. Results of Mann-Whitney-Wilcoxon tests to assess the significance of the difference between determinand values in lake outlet water in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery). Due to no measurements of Ca, Mg and Fe in 1983, data from year 1981 ^(a) were used for these three determinands.

Response variable	1983 (^a 1981)			2009			Test of difference	P-value
	Mean value	S.D.	n ₁	Mean value	S.D.	n ₂		
pH	9.70	0.526	53	8.69	0.625	11	512	< 0.001
Alkalinity as CaCO₃ (mg L⁻¹)	417	69.1	5	112	22.9	11	55	0.002
Conductivity (µS cm⁻¹)	936	148	53	325	49.3	12	636	< 0.001
Total Suspended Solids (mg L⁻¹)	32.8	23.2	53	1.44	0.921	12	632	< 0.001
Chlorophyll a (µg L⁻¹)	108	94.2	37	3.15	3.53	12	437	< 0.001
(mg L⁻¹)								
NH₄-N	0.359	0.405	50	0.036	0.030	12	464.5	0.003
NO₃-N	0.259	0.192	47	0.015	0.011	12	517	< 0.001
PO₄-P	0.076	0.045	47	0.012	0.011	11	507.5	< 0.001
SO₄-S	108	23.7	49	21.8	1.25	12	588	< 0.001
Chloride	38.0	6.23	47	28.3	2.788	12	541	< 0.001
SiO₂	2.66	0.738	50	0.858	0.913	12	555.5	< 0.001
Ca^a	7.12	5.05	6	24.5	11.5	12	4	0.001
Mg^a	8.80	3.60	6	15.9	0.686	12	0	< 0.001
Na	221	36.4	49	24.5	0.522	12	588	< 0.001
K	3.12	0.539	49	0.961	0.439	12	579	< 0.001
Fe^a	0.220	0.325	5	0.017	0.010	12	60	< 0.05
Al	5.33	4.38	6	0.034	0.018	12	72	< 0.001
As	0.254	0.072	8	0.011	0.001	12	96	< 0.001
V	0.438	0.177	8	0.012	0.002	12	96	< 0.001

Table 5. Summary of generalised additive modelling (GAM) results for red mud contaminant recovery trajectories in Kinghorn Loch outlet water. Optimal models for total V and pH predicted different recovery times for different seasons due to the use of separate smoothers for each season in the total V model and the significance of the fixed effect of season in the pH model.

Response variable	r ² adj	n	P-value	Deviance (%)	Recovery time (years)	End point value (mg L ⁻¹)	Season	Ecological quality guidelines (mg L ⁻¹)
PO ₄ -P	0.68	231	<0.001	60.8	24	0.004	-	0.024
Total Al	0.70	146	<0.001	87.5	26	0.020	-	0.015
Total As	0.79	192	<0.001	-	22	0.016	-	0.050
Total V	0.53	190	<0.001	83.2			-	0.020
					20	0.017	summer	
					18	0.018	autumn	
					26	0.010	winter	
					26	0.019	spring	
pH	0.58	237	<0.001	60.3				
					5	9.05	summer	
					5	8.57	autumn	
					5	8.28	winter	
					5	8.63	spring	