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

1 **Assessing the legacy of red mud pollution in a shallow freshwater lake: long-term**

2 **chemical recovery in the water column**

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24   **Abstract**

25   Little is known about chemical and ecological recovery following red mud leachate pollution

26   in fresh waters. This is confounded by a lack of knowledge on the chemical composition of

27   red mud leachate and the changes in composition that occur as a result of interactions with

28   sediments and freshwater organisms during transport through aquatic ecosystems. We used

29   over 30 years of data from a shallow lake (Kinghorn Loch, Fife, Scotland) with a well-

30   documented history of several decades of red mud leachate pollution to characterise the

31   chemical loads (during a pollution period of 1981-1983), resultant impacts on surface water

32   chemistry (comparison between 1983 and 2009) and recovery trajectories following leachate

33   diversion (1983-2010) of constituents that pose a risk to the environment. Between 1981 and

34   1983, the input of leachate resulted in loads of total aluminium (Al), total arsenic (As), total

35   vanadium (V) and phosphate (PO_4-P) to the lake of 107, 2.3, 3.3 and 2.3 g m^{-2} (lake surface

36   area) yr^{-1}, respectively. During the same period, the lake acted as a sink of Al, As, V and

37   PO_4-P retaining 63.6, 0.6, 0.8 and 1.6 g m^{-2} yr^{-1}, respectively. We used General Additive

38   Modelling to assess the response trajectories and recovery end points of these constituents.

39   Our results demonstrate the complexity of sediment-pollutant interactions during pollutant

40   transport through the aquatic environment and provide insight into likely recovery trajectories

41   in other aquatic ecosystems following red mud contamination. The PO_4-P, total As and total

42   V surface water concentration recovery times, defined statistically as the point on the time

43   series beyond which no further significant decrease in concentrations were observed, ranged

44   from 18 to 26 years. Total Al concentrations continued to decrease significantly following the

45   end of the monitoring period in 2010. In Kinghorn Loch, the legacy of red mud pollution

46   continues to represent an environmental risk, demonstrating the importance of long-term

47   monitoring and management strategies following similar pollution events.

48   **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 m^3 red mud waste (Burke et al., 2012) which impacted a catchment area of 3078 km^2 (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).

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74   To date, no study has been published documenting the longer term (i.e. years to decades)

75   recovery of any freshwater ecosystem, i.e. lotic or lentic, following red mud pollution. This

76   information is critical for the development of effective monitoring and management strategies

77   by the industry (World Aluminium, 2015). We propose that the current estimates of days to

78   months for chemical recovery (of As, V, aluminium (Al) and P) for all freshwater ecosystems

79   based on Mayes et al. (2016) are insufficient to cover all ecosystem types. Specifically, we

80   hypothesise that chemical recovery following red mud pollution in lakes (i.e. high residence

81   time depositional freshwater environments) will exhibit a long recovery time (i.e. similar to

82   years and decades commonly observed for P in lakes; Sharpley et al., 2013) in comparison to

83   the rapid recovery times (i.e. days to months) reported for fluvial systems following the Ajka

84   incident (Mayes et al., 2016). Our understanding of P recovery in lakes following

85   management for eutrophication indicates that recovery times can reach many decades as a

86   result of internal biogeochemical cycling, especially in ecosystems with high retention times

87   (i.e. lakes, wetlands and groundwater; Spears et al. 2012; Sharpley et al. 2013).

88   We tested this hypothesis using long-term monitoring data documenting chemical recovery in

89   Kinghorn Loch, UK, following red mud pollution control in 1983 (Olszewska et al., 2016).

90   The specific objectives of the study were to: (1) quantify the composition of red mud leachate

91   entering Kinghorn Loch during the peak pollution period in comparison to an unpolluted

92   surface water inlet (i.e. 1981 to 1983); (2) quantify the loads of Al, As, V and phosphate

93   (PO_4-P), and their retention by the lake; and (3) quantify recovery trajectories of red mud

94   pollutants following diversion of the leachate between 1983 and 2010. This information was

95   used in conjunction with environmental quality standards to assess the long-term

96   environmental risk associated with these pollutants and to revise estimates of recovery time

97   in freshwater ecosystems in general.

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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

123   April 1981 and September 1984 at weekly to fortnightly frequency. Discharge at the North

124   and leachate inlets and downstream of the lake outlet were assessed by stage boards

125   calibrated to discharge as described by Edwards (1985). Water samples were taken at mid-

126   depth in running water in 1 and 10 L polythene or polypropylene bottles for metal and

127   metalloid analysis and 1 L glass bottles for analysis of other determinands. The polythene and

128   glass bottles were cleaned in 50% v/v nitric acid solution and 50% v/v chromic acid

129   solutions, respectively, and rinsed with deionised water prior to sample collection.

130   Physico-chemical parameter measurements and sample filtration were conducted in the

131   laboratory after sample collection. pH values were determined using a Radiometer PHM 63

132   meter. Alkalinity was measured by titrating 100 mL samples against a standardised 0.05 M

133   sulphuric acid solution to pH 4.5, with leachate samples being diluted 1/10 with deionised

134   water prior to the titration.

135   Water samples for the determination of dissolved calcium (Ca), magnesium (Mg), fluoride

136   (F) and silica (SiO_2) concentrations were filtered through Whatman GF/C filters. Nitrate

137   (NO_3-N), ammonium (NH_4-N), chloride (Cl), SiO_2, orthophosphate (PO_4-P), boron (B) and

138   sulphate (SO_4-S) were determined using air segmented continuous flow analysis with

139   photometric detection performed on a Technicon AutoAnalyzer II system based on the assay

140   reviewed by the Standing Committee of Analysts (HMSO, 1980a). Detection limits for NO_3-

141   N, NH_4-N, Cl, SiO_2, B and SO_4-S were 0.01, 0.04, 1.0, 0.1, 0.04, 2 mg L^{-1}, respectively.

142   Detection limit for PO_4-P was 0.01 mg L^{-1} for the analysis of inlet and outlet samples, and 0.1

143   mg L^{-1} for the analysis of leachate. Fluoride concentrations were determined using an ion

144   selective electrode with a separate standard calomel reference electrode, with a limit of

145   detection of 0.01 mg L^{-1}.

146   Samples of leachate, inlets and outlet for dissolved metal and metalloid analyses were filtered

147   through 0.1 μm polycarbonate filter membranes. 1 M spectrophotometric grade hydrochloric

148   acid was used to adjust pH to 2-4 in leachate samples for metal determination and 2 cm^3 L^{-1}

149   of hydrochloric acid was added to preserve all samples prior to analysis. The samples were

150   evaporated on a hotplate to approximately 80 cm^3 and made up to 100 cm^3 with deionised

151   water, concentrating the samples of leachate and North inlet by 10 and 100 times,

152   respectively. Dissolved and total metal and metalloid concentrations, apart from cadmium

153   (Cd) and lead (Pb), were determined using flame atomic absorption spectrophotometry

154   (Instrumentation Laboratories IL357 equipped with an IL254 autosampler) and based on the

155   method described in HMSO (1980b). Limits of detection for Al, Ca, Cr, copper (Cu), iron

156   (Fe), Mg, manganese (Mn), nickel (Ni), potassium (K), sodium (Na), V, As and zinc (Zn)

157   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},

158   respectively. Cd and Pb were measured by graphite furnace atomic absorption

159   spectrophotometry, with detection limits of 0.005 mg L^{-1} for Cd and 0.5 mg L^{-1} for Pb. Total

160   suspended solids (TSS) were determined by the removal of suspended matter from samples

161   using vacuum filtration, followed by drying at 105°C and reweighing. The limit of detection

162   for TSS was 2.5 mg L^{-1}.

163   The load of red mud associated contaminants to Kinghorn Loch was estimated using mean

164   discharge and determinand concentration data for each inlet and outlet in the 1981-1984

165   monitoring period outlined above. Annual loads were calculated for Al, total As, total V, and

166   PO$_4$-P prior to leachate diversion and used to estimate retention expressed relative to lake

167   surface area.

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

169   Surface water pH in Kinghorn Loch was measured by FRPB and BA Chemicals Ltd. between

170   1954 and 1981 typically up to 4 times per year. The methodology for pH used by BA

171   Chemicals Ltd. during this period is unreported, although we believe that water samples were

172   collected from the outlet prior to pH determination in a laboratory. The Scottish Environment

173   Protection Agency (SEPA) and FRPB (its predecessor) measured pH weekly between 1981

174   and 1984, and a suite of determinands monthly thereafter on water samples collected from the

175   outlet, using standard methods (Table 1 and 2). Since no obvious discrepancy was apparent

176   between the pH values measured by FRPB and BA Chemicals Ltd. data prior to 1981, we

177   assume the methods were comparable.

178   **Statistical analysis**

179   A direct comparison was made between a wide suite of measured determinands to in 2009

180   (post-diversion conditions) versus 1983 (i.e. pre-diversion conditions). Low frequency of

181   sampling in 2010 was the reason for using data from 2009 to represent post-diversion water

182   quality. Data exploration showed violation of normality assumption. Therefore, a non-

183   parametric Mann-Whitney-Wilcoxon test, which allows for normality violation, was used to

184   assess the significance ($P < 0.05$) of the difference between the two years. The frequency of

185   sampling and analysis by SEPA differed between the two years and was between 5 to 53

186   (depending on the determinand) in 1983 and 12 in 2009. Due to lack of measurements of Ca,

187   Mg and Fe in 1983, data from 1981 were used for comparison for these determinands.

188   We used General Additive Models, assuming normal errors (GAMs, Hastie & Tibshirani,

189   1990; Wood, 2006), to determine the timing of recovery following diversion for

190   determinands for which long-term data were available over a suitable time series. The

191   endpoint of recovery was determined in two ways: (1) the year in which no further significant

192   decrease in concentration was detected, as assessed using GAMs, and (2) the year in which

193   the determinand concentration dropped below relevant ecological quality standards (where

194   available) for the last time in the dataset.

195   For the GAM analysis, the aim was to identify relationships between the concentrations with

196   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 PO_4-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.

218   **Results**

219   **Red mud loading to Kinghorn Loch**

220   Prior to the diversion of the red mud leachate from Kinghorn Loch pH and alkalinity at the

221   leachate inlet were 12.1 and 4125 mg L^{-1} (i.e. mean values 1981-1983), respectively,

222   compared to 8.1 and 133 mg L^{-1}, respectively, for the north inlet (Table 3). The leachate inlet

223   was characterised by high concentrations of Al, V, As, Zn, Cu, Pb, Cr, Cd, Fe, K, Cl, F, SO_4-

224   S, Na, PO_4-P and TSS compared to the north inlet. North inlet water contained higher

225   concentrations of Ca and Mg compared to the leachate inlet. The load from the leachate inlet

226   of total Al, As, V and PO_4-P to the lake during the period January 1981 to May 1983 was

227   107, 2.3, 3.3 and 2.3 g m^{-2} yr^{-1}, respectively. The annual retention of Al, As, V and PO_4-P was

228   63.6, 0.6, 0.8 and 1.6 g m^{-2} yr^{-1}, respectively.

229   **Lake water chemical responses following red mud leachate diversion**

230   pH in Kinghorn Loch outlet water increased until the diversion of the leachate in 1983,

231   reaching a value of 10.5 (Fig. 2). Following diversion, pH decreased in the first few years

232   before clear seasonal patterns emerged (higher pH values in summers, lower in winters), with

233   pH fluctuating between 7.5 and 9.5. All measured determinands in the lake outlet water were

234   significantly lower in 2009 than in 1983, with the exception of total Ca and Mg which had

235   significantly higher concentrations in 2009 than in 1983 (Table 4, Figs. 3-4). Concentrations

236   of total Fe, As and V were < 1 mg L^{-1} in 1983 and, together with total Al, decreased to < 0.1

237   mg L^{-1} in 2009. Concentrations of PO_4-P decreased from 0.076 to 0.012 mg L^{-1} between 1983

238   and 2009.

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

240   The time series of concentrations of total Al, total As, total V and PO$_4$-P before and after the

241   diversion are shown (Fig. 4). For all these determinands, concentrations decreased following

242   the diversion in May 1983 until 1985 after which the rate of decrease slowed, with occasional

243   high concentrations occurring. GAMs showed that the recovery times were determinand-

244   specific and that the effects of season were significant for total V and pH. Our analysis

245   indicated that no further significant decrease in pH values occurred 5 years following

246   leachate diversion (Table 5). Declines in PO$_4$-P concentrations ceased in 2007 and, although

247   not directly comparable, PO$_4$-P concentrations were below the suggested Trophic State Index

248   value for TP of 0.024 mg L^{-1} (Carlson et al., 1996) by 1986 (0.020 mg L^{-1}). For total Al, the

249   significant decrease in concentrations was maintained until the end of the observation period

250   in 2009 when the Al concentration still exceeded the ecological quality standard of 0.015 mg

251   L^{-1} (SEPA Supporting Guidance, 2013). Total As concentrations declined following leachate

252   diversion for a period of 22 years, with concentrations falling below the water quality

253   guideline of 0.050 mg L^{-1} (UK Standards for Protection of Aquatic Life; EEC, 1976) in 2006.

254   Depending on the season, it took from 18 to 26 years for the total V concentrations to stop

255   significantly decreasing, with the shortest recovery period observed for autumn and the

256   longest for spring and winter. Concentrations of total V measured in autumn decreased to

257   below the water quality guideline of 0.020 mg L^{-1} for total V (UK Standards for Protection of

258   Aquatic Life; EEC, 1976) in 2001, whilst spring concentrations only fell below the guideline

259   value in 2008.

260

261   **Discussion**

262   **Impacts of red mud leachate on lake chemistry**

263   The composition of the red mud leachate, which entered Kinghorn Loch between 1947 and

264   1983, posed four potential pressures on the aquatic environment: high pH, metal and

265   metalloid pollution, eutrophication and high salinity. The high loadings of contaminants

266   entering the lake (e.g. 107, 2.3, 3.3 and 2.3 g m^{-2} yr^{-1} of total Al, As, V and PO_4-P,

267   respectively) led to high concentrations of a range of metals (e.g. total Al - 7.30 mg L^{-1}, V –

268   0.49 mg L^{-1}), metalloids (e.g. As – 0.32 mg L^{-1}), PO_4-P (0.13 mg L^{-1}) and chloride (38.0 mg

269   L^{-1}) in the loch water. The concentrations of some pollutants in the water column in 1983

270   greatly exceeded ecological quality standards for fresh waters. Specifically, the

271   concentrations of PO_4-P and total As were approximately 3 and 5 times higher than the

272   relevant environmental guidelines, whilst total V and total Al concentrations were 22 and 355

273   times higher, respectively, than the recommended ecological quality values. The pressures in

274   Kinghorn Loch, with the exception of eutrophication, were also observed in the river system

275   downstream of the Ajka red mud spill in Hungary in 2010 (Mayes et al., 2011; Ruyters et al.,

276   2011; Shöll and Szövényi, 2011).

277   **Recovery following red mud pollution**

278   The results of the GAM analyses indicated that chemical recovery in Kinghorn Loch took

279   decades to complete and is in agreement with our hypothesis based on P recovery following

280   eutrophication management. The time scale of the recovery differed among the determinands.

281   The shortest recovery period (5 years) was observed for pH. In contrast, analysis of the river

282   system affected by the Ajka red mud spill indicated rapid recovery in pH only 2 months after

283   the pollution accident at sites further downstream from the pollution source (Mayes at al.,

284   2011). The fast improvement in pH in this case was, however, a result of both acid dosing

285 and dilution of the contaminated water in the river system (Mayes et al., 2011), whereas no

286 remedial actions were taken in Kinghorn Loch. In addition, elevated pH in Kinghorn Loch

287 during the first few years following the cessation of pollution may have been influenced by

288 the enhanced phytosynthetic activity in the lake (Scheffer, 2004).

289 As a result of eutrophication caused by high P loading, intense phytoplankton blooms

290 occurred in Kinghorn Loch from the mid-1970s until 1985, when a collapse in the

291 phytoplankton activity was recorded (Edwards, 1985). These results indicate that the

292 recovery times reported following the Ajka spill are not representative of all freshwater

293 ecosystems. In addition, we report here significant differences in the long term recovery

294 times for Al, As, V, and PO_4-P ranging from 18 to 26 years, with significant seasonal effects

295 being reported for V. Sporadic peaks in contaminant concentrations can be observed even in

296 recent years in Kinghorn Loch indicating persistent environmental risk, especially associated

297 with PO_4-P, total V, As and Al. Olszewska et al. (2017), using laboratory controlled sediment

298 core incubations confirmed the release of P, As and V from bed sediments in recent years,

299 being controlled predominantly by redox conditions, competitive ion concentrations and pH.

300 Delayed recovery following pollution control has been well documented in the case of P in

301 lakes (Jeppesen et al., 2007; Søndergaard et al., 2003, Spears et al., 2012), and also for As

302 (Toevs et al., 2008; Whitmore et al., 2008) and V in fresh waters (Minelli et al., 2000).

303 Competition between P, As and V for adsorption to iron oxyhydroxides may lead to

304 preferential immobilisation of these pollutants in bed sediments (Wällstedt et al., 2010). High

305 pH can also have negative effects on immobilisation of some elements, e.g. P (Søndergaard et

306 al., 1999) and V (Naeem et al., 2007) and might therefore account for longer recovery times.

307 The likely impact of the elevated pH in Kinghorn Loch in the years immediately following

308 the diversion of the leachate, as well as the potential competition for sorption sites between

309 some red mud constituents, indicate that these interactions may be a dominant factor

310   regulating chemical recovery. However, uptake into biota may also be a major pathway of

311   internal cycling of red mud pollutants; significant accumulation of As species was reported in

312   tissues of macrophytes in Kinghorn Loch, as recently as 2013 (Olszewska et al., 2016).

313   Concentrations of most determinands were significantly lower in 2009 than in 1983, with the

314   exception of Mg and Ca, and PO_4-P, As and V concentrations were all below the relevant

315   ecological quality standards in 2009, although total Al was not. Mg and Ca concentrations

316   were significantly higher in 2009 than in 1983 (15.9 and 24.5 mg L^{-1} in 2009, respectively,

317   compared to 8.80 and 7.12 mg L^{-1} in 1983), although the major input of these two elements

318   was the unpolluted north inlet, characterized by high natural levels of water hardness. The

319   significantly lower concentrations of Mg and Ca in lake outlet water in 1983 were likely to be

320   a result of removal of any free Ca^{2+} and Mg^{2+} by reaction with the high carbonate alkalinity

321   coming from the leachate to form solid carbonates in the elevated pH conditions (Renforth et

322   al., 2009).

323   **Implications for management**

324   Mayes et al. (2011) reported rapid contaminant dilution, with the exception of depositional

325   hotspots, in the river system affected by the Ajka accident, indicating species-specific

326   transport rates through the system (Mayes et al., 2011). Although chemical recovery was

327   reported to be rapid, good ecological condition in the Torna Stream polluted in the Hungarian

328   accident is not expected to be achieved until 2021, some 11 years after the pollution event

329   (Kovács et al., 2012). Our results indicate that chemical recovery time may be significantly

330   longer in depositional zones with long hydraulic retention times. Ecological recovery times

331   may be longer still. The analysis of As content in five macrophyte taxa in Kinghorn Loch

332   conducted in 2013 showed that macrophytes contained relatively high concentrations of toxic

333   inorganic As, suggesting toxicological risk to higher trophic levels (Olszewska et al., 2016).

334   There appears to be a lack of evidence on available measures with which to mitigate the

335   environmental impacts of red mud pollution in lakes. In Hungary, calcium sulphate was

336   applied (Enserink 2010) to reduce the pH effects. In Kinghorn Loch, metal concentrations

337   remained elevated above environmental quality standards even after pH had recovered and so

338   pH control only may be insufficient to control the effects of complex potentially harmful

339   elements in fresh waters as confirmed also by Mayes et al. (2016).

340   Removal of contaminated sediments has been practiced as a measure for mitigating

341   environmental impacts of metals and nutrients in lakes with mixed effectiveness (Peterson,

342   1982; Phillips et al., 2015). Emerging geo-engineering techniques (Spears et al. 2013; Lürling

343   et al., 2016) developed for the simultaneous control of multiple elements may also represent

344   effective management tools in this respect for oxyanion forming elements (e.g. As, V, P),

345   although the development of this approach is in its early stages. Aeration of bottom waters

346   may also be effective in the control of redox sensitive elements, including As and P (Beutel

347   and Horne, 1999). Advances have been made recently in the development of materials with

348   which to deliver oxygen to lake bed sediments. Nykänen et al. (2012) have demonstrated at

349   the field scale the application of calcium peroxide to manipulate redox conditions at the bed

350   sediment surface which can lead to the reduction of P release to the water column (Lu et al.,

351   2017). However, oxidising conditions might result in undesirable response in V, leading to a

352   release of this metal from bed sediment, as shown by Olszewska et al. (2017). We call for a

353   more comprehensive assessment of such measures to support emergency response strategies

354   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 PO_4-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 PO_4-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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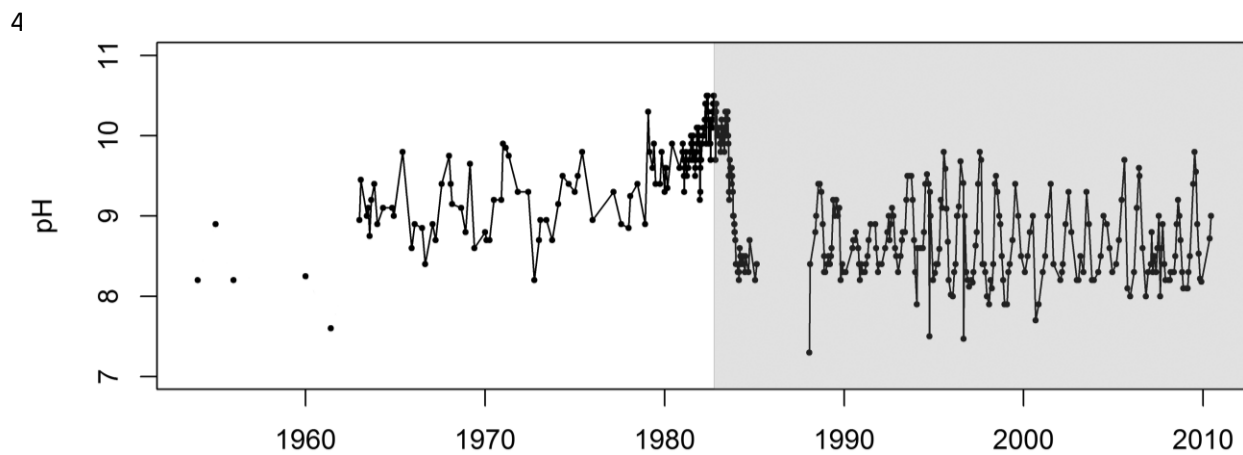
Fig. 1. Locations of the former production plant and landfill site, and current location of the treatment plant in relation to Kinghorn Loch (image courtesy of Google Earth, taken in 2010).

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.

4

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.
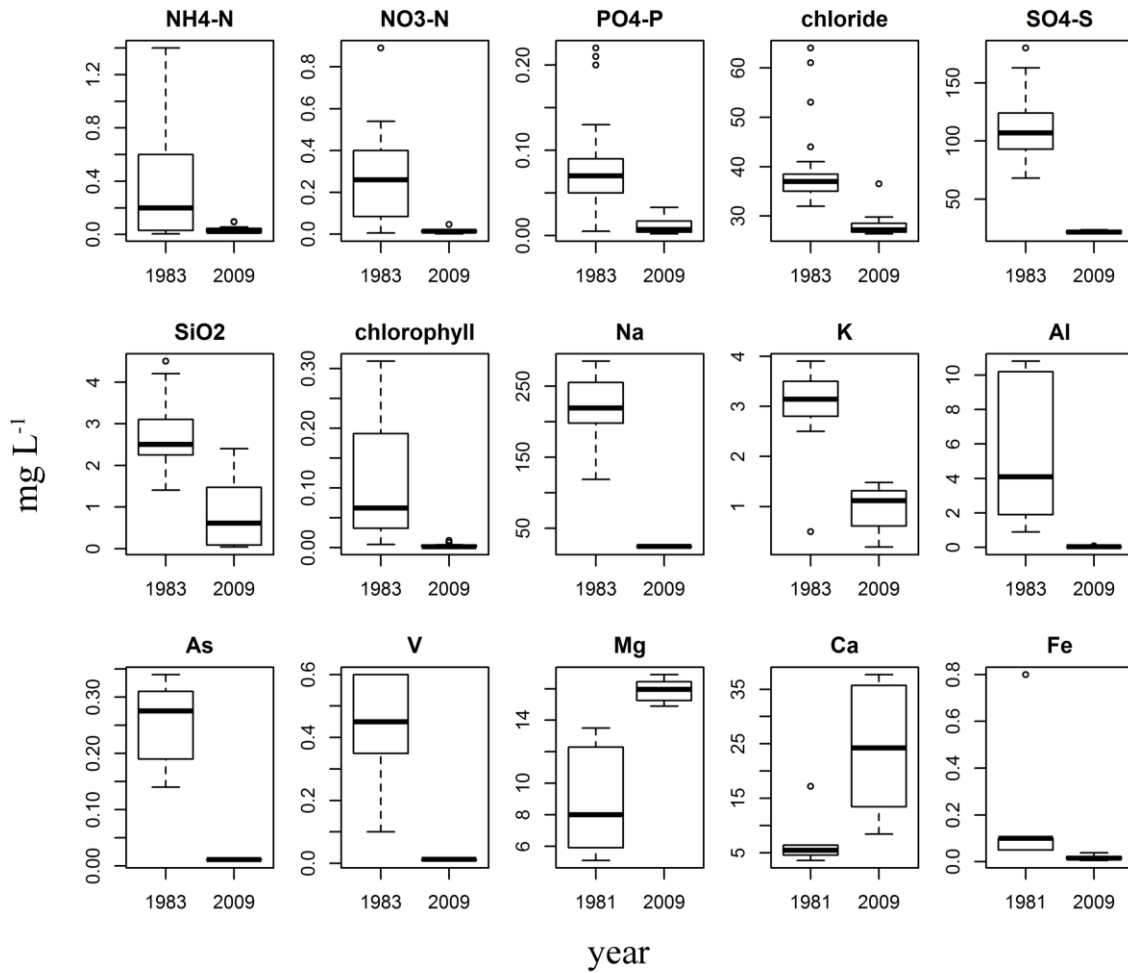
Fig. 4. pH, conductivity, alkalinity and TSS in Kinghorn Loch outlet in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery); recovery). Data are summarised as boxplots showing the median and 25th and 75th quartiles, with whiskers representing the values outside the middle 50% and outliers shown as dots.
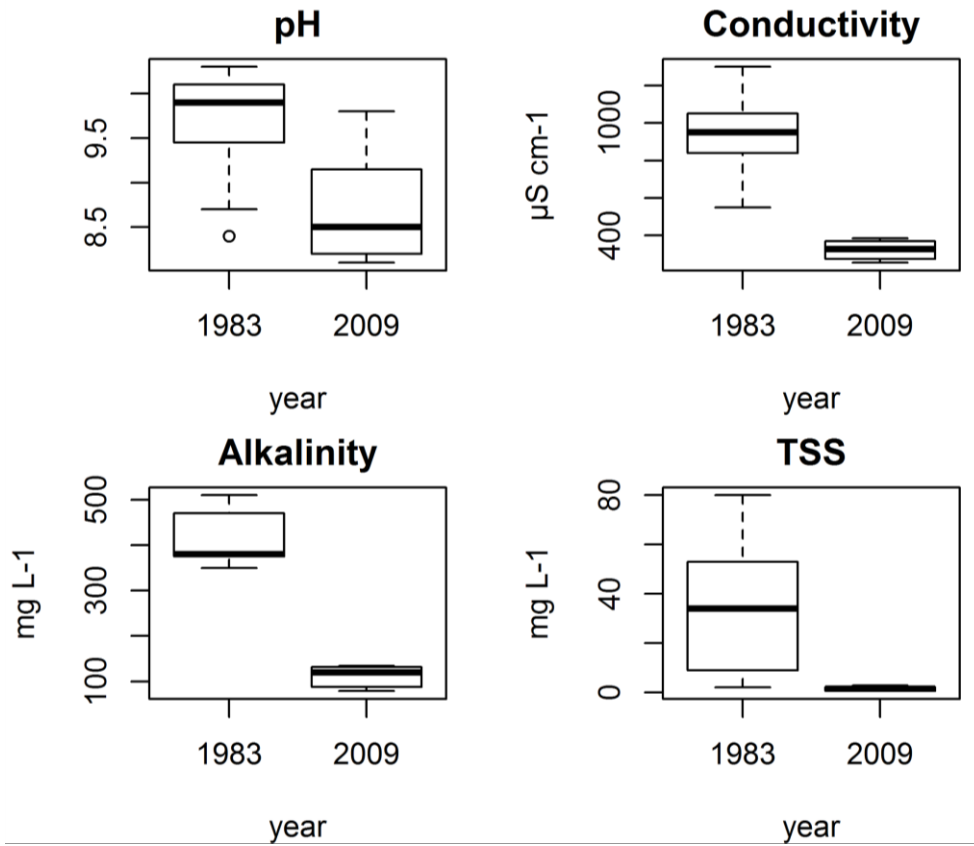
500 **Fig. 5.** Total arsenic (panel a), vanadium (panel b), aluminium (panel c) and orthophosphate
501 (PO4-P, panel d) concentrations in Kinghorn Loch outlet prior to (1981-1983) and following
502 (1984-2010) the diversion of the leachate from the loch inlet in 1983. Vertical dashed lines
503 indicate the cessation of red mud leachate input into the lake in 1983.
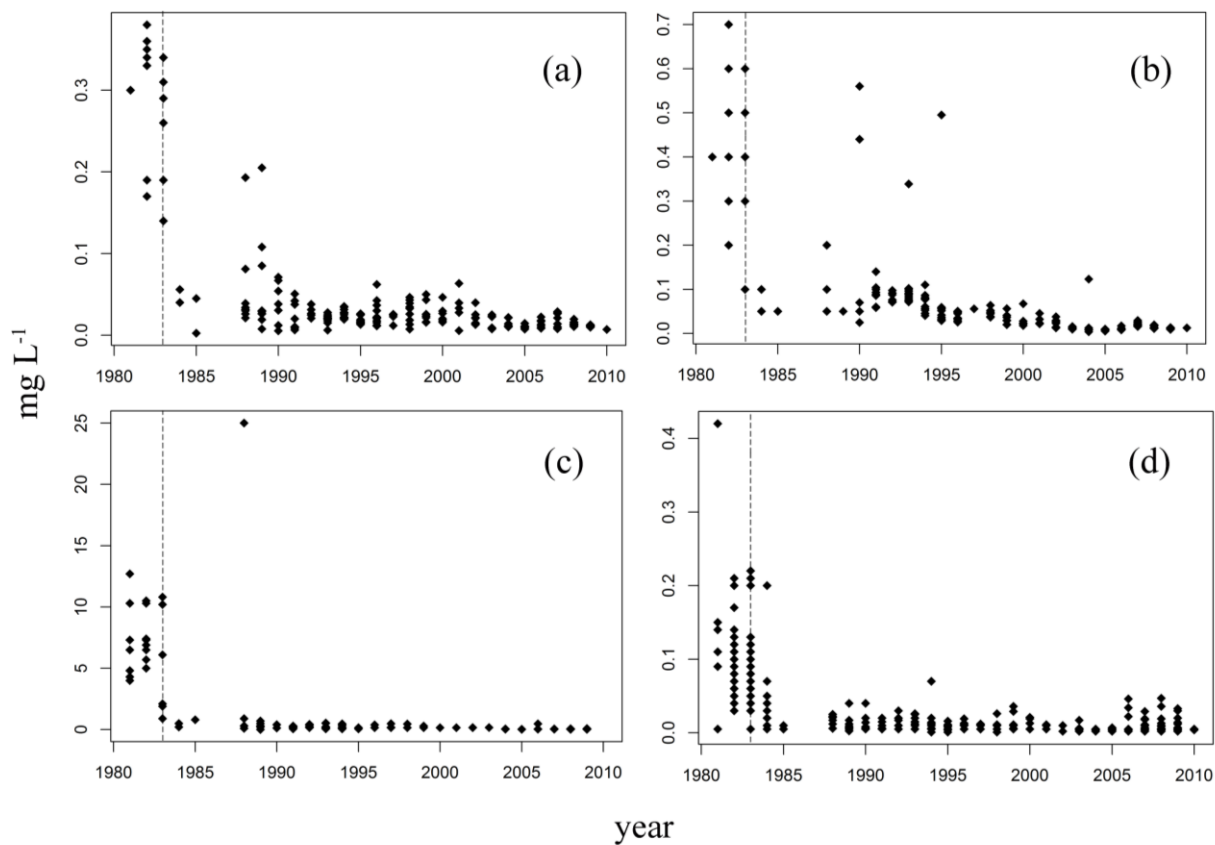
Table 1. Summary of leachate and Kinghorn Loch inlet and outlet sampling and analysis conducted to 2010.

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, Genéve
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 $CaCO_3$ (mg L^{-1})	417	69.1	5	112	22.9	11	55	0.002
Conductivity ($\mu S\ cm^{-1}$)	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 ($\mu g\ L^{-1}$)	108	94.2	37	3.15	3.53	12	437	< 0.001
(mg L^{-1})								
NH_4-N	0.359	0.405	50	0.036	0.030	12	464.5	0.003
NO_3-N	0.259	0.192	47	0.015	0.011	12	517	< 0.001
PO_4-P	0.076	0.045	47	0.012	0.011	11	507.5	< 0.001
SO_4-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
SiO_2	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	