



Flow dependent water quality impacts of historic coal and oil shale mining in the Almond River catchment, Scotland



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ABSTRACT

The Almond River catchment in Central Scotland has experienced extensive coal mining during the last 300 years and also provides an example of enduring pollution associated with historic unconventional hydrocarbon exploitation from oil shale. Detailed spatial analysis of the catchment has identified over 300 abandoned mine and mine waste sites, comprising a significant potential source of mine related contamination. River water quality data, collected over a 15 year period from 1994 to 2008, indicates that both the coal and oil shale mining areas detrimentally impact surface water quality long after mine abandonment, due to the continued release of Fe and SO_4^{2-} associated with pyrite oxidation at abandoned mine sites. Once in the surface water environment Fe and SO_4^{2-} display significant concentration-flow dependence: Fe increases at high flows due to the re-suspension of river bed Fe precipitates ($\text{Fe}(\text{OH})_3$); SO_4^{2-} concentrations decrease with higher flow as a result of dilution. Further examination of Fe and SO_4^{2-} loading at low flows indicates a close correlation of Fe and SO_4^{2-} with mined areas; cumulative low flow load calculations indicate that coal and oil shale mining regions contribute 0.21 and 0.31 g/s of Fe, respectively, to the main Almond tributary. Decreases in Fe loading along some river sections demonstrate the deposition and storage of Fe within the river channel. This river bed Fe is re-suspended with increased flow resulting in significant transport of Fe downstream with load values of up to 50 g/s Fe. Interpretation of major ion chemistry data for 2005–2006 indicates significant increases in Ca^{2+} , Mg^{2+} and HCO_3^- in coal mined areas probably as a result of the buffering of proton acidity in mine waters; in the oil shale areas Na^+ and Cl^- become increasing dominant possibly associated with increased urbanisation and saline pore water discharge from unprocessed oil shale waste. The study demonstrates the importance of considering the cumulative impact of point and diffuse contamination sourced from numerous small coal and oil shale mine sites on surface water quality.

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1. Introduction

Production of heavily mineralised discharge waters is a phenomenon observed world-wide at active and abandoned mine sites (e.g. Ahmad, 1974; Hedin et al., 1994; Banks et al., 1997b; Wood et al., 1999; Blowes et al., 2003). Mine closure commonly results in increased concentrations of dissolved ions, particularly Fe and SO_4^{2-} , in mine discharge waters due to the dissolution of pyrite oxidation products formed, principally, during the operational phase of the mine (Cairney and Frost, 1975; Bowen et al., 1998; Younger, 2000a). Waste rock brought to the surface in the process of mining can also produce similar mine waters, via pyrite oxidation, on exposure to atmospheric O_2 and precipitation (Bell, 1996; Banks et al., 1997a; Rees et al., 2002; Lottermoser, 2010; Nordstrom,

2011). When discharged at the surface, mine waters can have serious environmental consequences for water quality in recipient streams and rivers (Younger, 1995; Banks et al., 1997a; Jarvis and Younger, 1997). Oxidation and precipitation of Fe forms ochreous precipitates in the surface water column which, once settled, smother river beds and impact river ecology (Edwards and Maidens, 1995).

The processes of pyrite oxidation, carbonate buffering (which reduces acidity in mine waters, Hedin et al., 1994; Banks et al., 1997b; Wood et al., 1999) and Fe precipitation in surface waters is well characterised for individual coal mine sites (e.g. Chen et al., 1999; Younger, 2000a). The environmental impact of oil shale mining, however, is poorly characterised. The Almond River catchment in Central Scotland, provides an example of enduring water pollution from historic oil shale exploitation, which has particular significance due to the modern day interest in unconventional hydrocarbon exploitation, potentially in the remaining shales (DECC, 2011), and concerns about associated pollution.

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Oil shale and coal-bearing rocks have similar pyrite content, normally around 1–2% (Louw and Addison, 1985), and both are associated with marine deposition (Francis, 1983). Pyrite oxidation and carbonate buffering reactions are, therefore, likely to be principal controls on oil shale mine water chemistry (Erg, 2005). Within Scotland, oil shale mine waste differs to coal mine waste as follows: exhumed oil shale was heated to extract the organic fraction of the shale as a form of crude oil (Carruthers et al., 1927). This produced two oil shale mine wastes: (1) overburden mine waste, derived from the mining process, which may contain pyrite, (2) processed waste likely to lack pyrite due to the application of heat during processing. In the Almond River catchment, the oil shale mine waste sites, which can rise up to 95 m (Harvie, 2004, 2005), are dominated by orangey red burnt processed waste. However, discrete layers and sections of waste piles are formed from the first, generally black, unprocessed shale overburden. Therefore, the oil shale waste sites are a composite of the volumetrically dominant processed oil shale, which is unlikely to produce seriously contaminated runoff, and the unprocessed oil shale mine waste likely to contain pyrite and potentially produce Fe- and SO_4^{2-} -bearing waters.

In recent years significant advances have been made in the assessment of mine water hazard and impact as well as in remediation technology design to reduce the impact of point source mine water contamination on surface water and groundwater (e.g. Heal and Salt, 1999; Younger, 2000a,b; Gandy and Younger, 2003; Jarvis et al., 2006). Some studies, such as that undertaken by Mayes et al. (2008), indicate that water quality in mined catchments is heavily influenced by diffuse mine water inputs. However, impacts on water quality on the river catchment scale from mine water contamination are less well studied than the impact of individual coal mines. Recent European (Water Framework Directive, 2000/60/EC) and national legislation (Water Environment and Water Services Act (Scotland) 2003) encourages consideration of water quality pressures on the river catchment scale and the scientific community is increasingly advocating this scale of approach to deal with mine-related contamination (e.g. Kimball et al., 1999, 2002; España et al., 2005; Mayes et al., 2008).

The aim of this paper is to assess the impact of historic coal and oil shale mining on surface water quality and characterise the flow dependency of mine water contaminants in the surface water environment. This is done by the construction of a GIS data base of historic mines in the catchment and correlating this to the source and transport of mine-related contamination in surface water under variable flow conditions. Over 15 years of surface water quality data from 19 points in the catchment, with corresponding river flow data, are analysed focusing specifically on Fe and SO_4^{2-} , as the products of pyrite oxidation at mine sites, supported by pH, dissolved O_2 and major ion data.

2. Study area

The Almond River catchment is located in the Central Belt of Scotland, UK, between Glasgow and Edinburgh (Fig. 1). The catchment comprises approximately 370 km² of mixed urban and semi-agricultural land, of which up to 50%, by land area, has been affected by variable amounts of historic mining activity. Both coal and oil shale were mined in the catchment; coal from pre 17th century to the mid-1980s and oil shale from the 1860s to the 1960s. The mining industries and the legacy of abandoned mine sites has resulted in significant impacts on surface water and groundwater quality in the catchment. Surface water quality is amongst the worst in Scotland (Pollard et al., 2001) and the overall quality status of surface water and groundwater is classified by the Scottish Environment Protection Agency (SEPA) as poor (SEPA, 2008). Previous studies have presented data from coal mine water discharges

in the Almond including Polkemmet, Riddochill (Chen et al., 1999; Ó Dochartaigh et al., 2011) and Cuthill (Younger, 2001), and indicate that waters are generally net alkaline with elevated Fe concentrations of up to 50 mg/L.

Historic mining was intensive and widespread with over 300 sites relating to the extraction or disposal of mined or quarried mineral resources, the majority of which relate to coal and oil shale mining, although lesser amounts of ironstone, limestone, slate, sandstone, metals and clay were also mined. Mine waters and the resulting surface water and groundwater contamination are not associated with every mine site; however, the number and density of abandoned mine sites in the catchment gives an indication of the scale of the potential environmental impact (Fig. 2).

2.1. Geology

The Almond River catchment geology is dominated by a series of thick marine and deltaic Carboniferous aged sedimentary deposits (Table 1), part of the larger sedimentary sequence which composes the rocks of the Midland Valley, Scotland. The sediments appear in depositional cycles representing changes in the depositional regime of the Carboniferous aged sedimentary basin in which they were deposited. Principally, these cycles represent regressions from shallow marine to terrestrial environments coupled with periodic rises in sea level and local and regional subsidence defined by the Southern Uplands and Highland Boundary faults. The present day complex outcrop structure (Fig. 1) was caused by significant folding and faulting associated with a complex structural and volcanic history in the region (Francis, 1983; Cameron and Stephenson, 1985). The geology of the catchment is significant because it provides the framework for the mine site distribution, the pyrite source minerals for the production of mine water contamination and the carbonate minerals which buffer acidity. However, while carbonate buffering results in the majority of Scottish mine waters being net-alkaline (Younger, 2001), buffering capacity is unlikely to result from calcite dissolution as limestones are relatively rare in the coal bearing formations (Table 1), and where present are generally dolomitic. The principal buffering capacity is likely to originate instead from ankerite ($\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$), a common secondary mineral on coal fracture surfaces (Thomas, 2002) which acts as a net consumer of acidity, but also as a potential source for iron in mine waters (Younger, 2004).

2.2. Mine distribution

The scale and distribution of mining and the resulting mine waste across the Almond catchment is not uniform and several distinct areas of mining activity can be identified (Fig. 2). Coal mining dominated in the SW of the catchment, targeting coals in the Scottish Coal Measures, Passage Formation and Limestone Coal Formation. Oil shale mining dominated in the central east of the catchment targeting the 6 workable oil shale horizons, the Pumpherton, Camps, Dunnet, Champfleurie, Broxburn and Fells seams in the West Lothian Oil Shale Formation (Kerr, 1994). The clear geographic divide between the coal and oil shale dominant mining regions is identified by the dashed line in Fig. 2.

2.3. Mine history

Early mining in the catchment targeted shallow accessible coal and oil shale seams and produced only small amounts of mine waste. Deeper mining, which produced increased mine waste and mine water volumes, came later as the result of advances in water technology (Duckham, 1970) and increased demand in the coal market (Hassan, 1976).

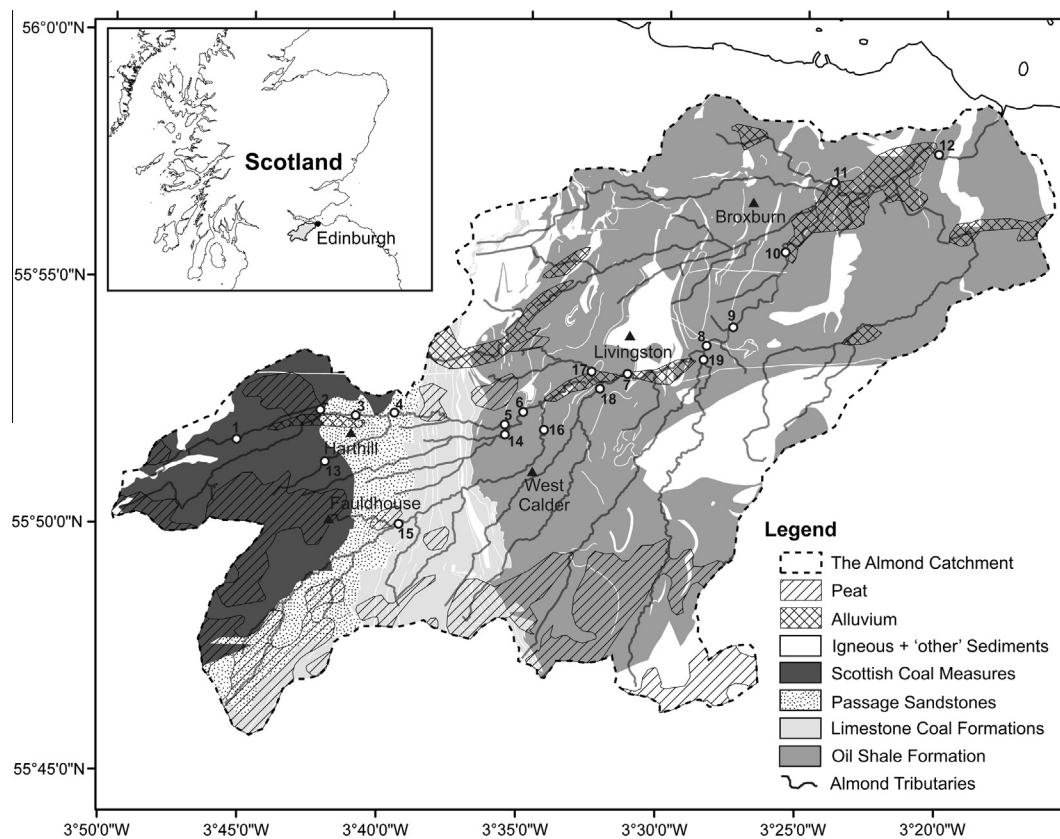


Fig. 1. Geology and surface water monitoring network in the Almond River catchment. 1–19 indicate surface water sampling sites on Almond tributaries. Derived from BGS digital geological mapping at 1:50,000 scale, British Geological Survey © NERC. Contains Ordnance Survey data © Crown Copyright. Licence No. 100021290.

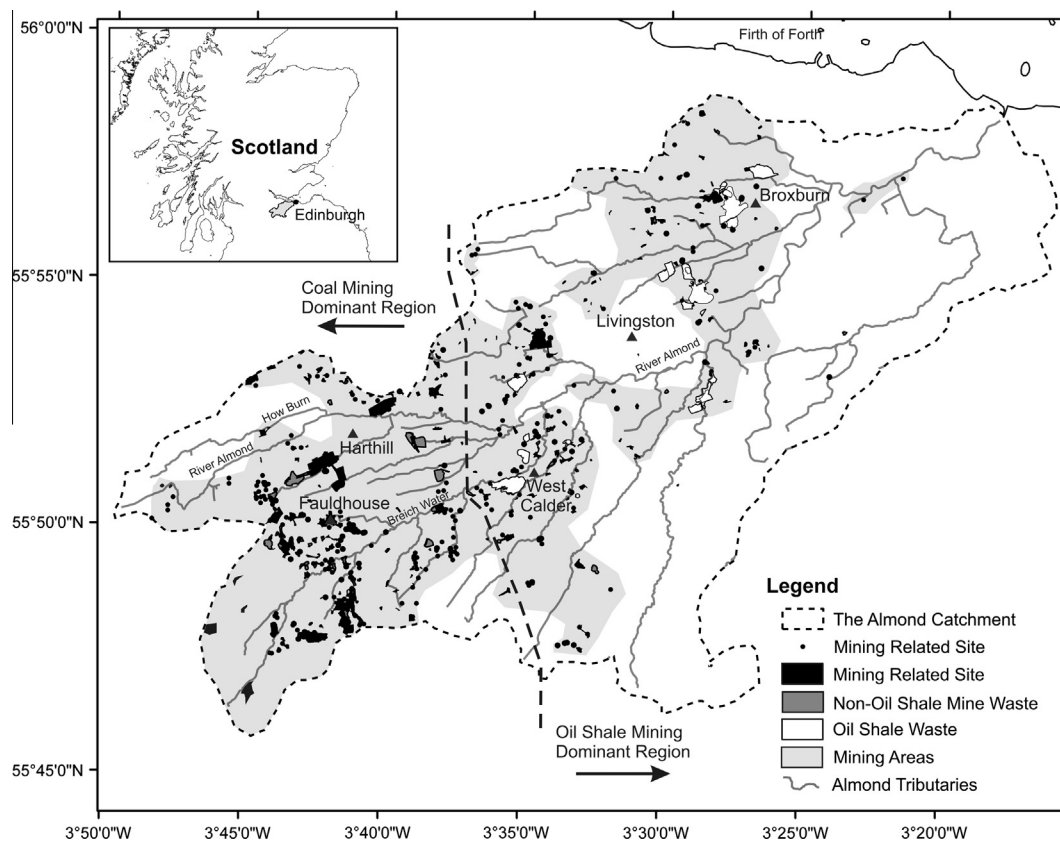


Fig. 2. Mine site distribution in the Almond River catchment. Contains Ordnance Survey data © Crown Copyright. Licence No. 100021290.

Table 1

Geology and economic geology of the main Carboniferous deposits of the Almond River catchment. 'Map Reference' refers to Fig. 1 (after Francis, 1983; Cameron and Stephenson, 1985).

Period	Group	Formation	Description	Map reference
Upper Carboniferous	Coal Measures (Scotland)	Middle Coal Measures	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	Scottish Coal Measures
		Lower Coal Measures	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	
	Clackmannan Group	Passage Formation	Mainly sandstones with fireclays and thin siltstones, mudstones, ironstones and thin coals	Passage Sandstones
		Upper Limestone Formation	Cyclic sequences of sandstones, siltstones, mudstones, marine limestones and a few coals	Limestone Coal Formations
		Limestone Coal Formation	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	
Lower Carboniferous	Strathclyde Group	Lower Limestone Formation	Cyclic sequences of sandstones, siltstones, mudstones, marine limestones and a few coals	
		West Lothian Oil Shale Formation	Mainly sandstones with siltstones, mudstones and oil-shales, thin coal seams and limestones	
	Inverclyde group	Gullane Formation	Sandstone, grey and green siltstone and mudstone	'Other' sediments
		Ballagan Formation	Sandstone, grey and red siltstone, mudstone and dolomitic limestone	
		Kinneswood Formation	Sandstone with siltstone and mudstone	

During the 19th century coal mining in Scotland saw considerable investment and growth; however, this was not reflected until after the 1840s in the mines of the Lothian coal fields (Hassan, 1976) and the Almond River catchment. After the 1840s, modernisation of the coal and transport industries and changes in the industrial and social landscape facilitated growth (Hassan, 1976). Around this time in the 1850s innovations in hydrocarbon extraction technologies, by James Young, resulted in the mining and exploitation of oil shale deposits in the catchment and the growth of the oil shale industry. The coal and oil shale industries in the area produced one of the most heavily mined catchments in the UK, which contained Scotland's most productive coal mine, Polkemmet (Oglethorpe, 2006).

Opencast, shallow and deep mining was utilised over the lifetime of the coal industry. Most opencast mines were limited in their extent and were generally reinstated upon closure; no mine pit lakes occur in the catchment. Shallow coal mines were generally older, locally operated mines which, although numerous, were limited financially in their working depth, due to the expense of mining equipment and water pumps. Deeper mines such as, Polkemmet 1916–1984 (Shaft 2, 470 m), Whitrigg 1900–1972 (Shaft 5, 323 m) and Riddochhill 1890–1968 (Shaft 1, 289 m) came later in the early to mid-20th century and were managed initially by large private companies and then by the National Coal Board following nationalisation in 1947 (Oglethorpe, 2006). The volumes of mine waste produced from coal mining, although environmentally significant, due to a generally acidic nature, were smaller than the neighbouring oil shale industry.

The oil shale industry employed opencast, shallow and deep mining methods. The majority of early oil shale mines were opencast; however, 'inclined' or 'drift' type mines became common place as the industry developed. Pits or shafts, which were typically between 120 and 210 m, were used to intersect drift mines or to access deeper shale seams (Kerr, 1994). Oil shale was mined and transported to the oil shale processing sites, of which there were over 100 at the peak of the industry, then the oil shale waste was deposited in large accumulations, known locally as 'binges'. Almost the entire mined volume of the oil shale industry was deposited as waste following the extraction of the oil shales' ~14% organic content (Yen and Chilingarain, 1976). The 'binges' also contain a significant proportion of black unprocessed shale waste originating from the mining process. Estimates suggest there are 150 million tonnes of waste within West Lothian resulting from the oil shale industry (McAdam et al., 1992).

Oil shale mining went into decline in the early 20th century, due to competition from American oil, finally closing in the 1960s after the withdrawal of over 40 years of government tax relief (Louw and Addison, 1985). Coal mining continued until widespread UK closure began in the 1980s. Mine closure in the catchment has resulted in the production of numerous coal and oil shale mine discharge waters from both subsurface mines and surface waste deposits.

2.4. Previous environmental assessments and management

The environmental impact of mining on the quality of river waters in the catchment today is both significant and widespread (SEPA, 2008). Historically, impacts were noted back in the 1870s, when fish stocks in the river were almost completely wiped out (Brock, 1892; Pollard et al., 2001).

Improvements in working practices at mine sites and the decline in the processing of oil shale is likely to have improved water quality in the river waters in the latter half of the 20th century. However, closure of the coal mines in the 1980s only increased the environmental threat as the cessation of dewatering activities had the potential for the surface break out of Fe-rich mine waters (Younger, 1994; Wood et al., 1999). The deep Polkemmet colliery is still pumped today to prevent the dissolution of pyritic salts into rising groundwaters; pumped waters are then treated, prior to discharge, to limit the environmental impact on the recipient surface waters. Many of the smaller, older collieries were probably allowed to flood and produce mine waters which break out uncontrollably at surface following closure. Little to no environmental management was put in place during the closure of oil shale mining activities as all were closed prior to the 1960s. Significant advances have been made in recent years in improving water quality through mine water treatment schemes and remedial activities at old opencast and mine waste sites. However, historically the impact of mining activities was one of the principal factors in downgrading quality classifications on a large number of the Almond River catchment's tributaries (Campbell et al., 1996).

3. Data and methods

Extensive and detailed datasets of the geology and hydrogeology, water quality and land use history of the Almond River catchment were acquired from the British Geological Survey (BGS), Scottish Environment Protection Agency (SEPA) and West Lothian Council (WLC), respectively.

3.1. Spatial analysis

Mine datasets provided by WLC and the BGS were refined through field observations and analysis of historic data sources (Winter, 2001; Mac Donald et al., 2003). Mine location data were refined to identify the dominant mine type (i.e. subsurface, open-cast or mine waste site) and mined mineral resource. Historic land use data were then compared, in ARC GIS, to the geological and hydrogeological data. Principal mining areas relating to different mined resource were identified. Spatial comparison of field data and surface water quality datasets was then undertaken.

3.2. Water quality data

Comprehensive monthly to two-monthly sampling, dating back to 1994, is undertaken by SEPA at 19 monitoring points (Fig. 1) on tributaries in the catchment; 1–12 on the main Almond tributary, 13–19 on second order tributaries. Sampled waters are analysed, by SEPA, for a number of analytical suites tailored to SEPA's requirements with respect to different water pressures including mining, urban drainage and sewage treatment. The data used in this study was extracted from this wider water quality dataset in order to specifically consider mine water related water quality pressures. In general Fe_{tot} , pH and dissolved O_2 are available at all the monitoring points 1–19 in the catchment, SO_4^{2-} was available at selected monitoring points (1–6, 10 and 12) on the main Almond tributary. The Fe_{tot} is Fe determined in an unfiltered river water sample and, therefore, considers all the Fe species in the sample, both dissolved and solid. Since 2007, a sample of Fe sampled through a 0.45 μm filter has also been collected, $\text{Fe} < 0.45 \mu\text{m}$, which is generally considered to only contain dissolved Fe species. This is used to consider differences in Fe speciation in river waters.

River loads of Fe and SO_4^{2-} are calculated using daily flow readings from SEPA's 4 flow gauging stations in the catchment (Whitburn, Almond Wier, Almondell and Cragiehall). Flow readings at the monitoring points (Q_c) are calculated by multiplying the flow reading at the nearest gauging station (Q_g) by a correction factor calculated from the relative catchment area ratio of the monitoring point (C_c) and nearest gauging station (C_g).

$$Q_c = Q_g(C_c/C_g). \quad (1)$$

Where the catchment ratio (C_c/C_g) is close to 1 then the flow estimates and the associated load calculations are most accurate. This is generally the case for monitoring points 1–12 due to the proximity of monitoring points to gauging stations. Monitoring points

13–19 have lower catchment ratios and, therefore, give less accurate flow estimations and load calculations. As a result interpretations based on the load calculations are generally only made using data from monitoring points 1–12, data from points 13–19 are used only to support these interpretations.

The concentration and load of contaminants are considered under low flow and high flow conditions in the river catchment. Low flow is defined here as flow values falling below the 30th percentile for the distribution of flow values recorded at each monitoring point during the monitored period (1994–2008 Fe, 1994–2006 SO_4^{2-}); high flows are those flow values above the 90th percentile in the distribution.

Additional data on the concentration of major ions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , HCO_3^- , SO_4^{2-} and NO_3^-) were also available for the years 2005–2006 for monitoring points 1–12. This has been used to look at variations in the bulk river water chemistry in the Almond River.

4. Results and discussion

4.1. Water quality

Iron and SO_4^{2-} data for the 19 surface water monitoring points in the catchment (12 on the main Almond tributary, 7 on smaller second and third order tributaries) are summarised in Table 2. Data indicate Fe and SO_4^{2-} in surface waters of the Almond basin are elevated compared to other rivers in Scotland (e.g. Soulsby et al., 2005; SEPA, 2008). Neal et al. (2011) presents average concentration data (Fe 0.13–0.54 mg/L, SO_4^{2-} 6–116 mg/L) for river water in areas with similar geology but which are largely un-mined. In comparison average Fe and SO_4^{2-} concentrations in the Almond River waters are notably higher (Fe 0.64–2.64 mg/L, SO_4^{2-} 96.2–244 mg/L). This is likely to be a consequence of mine water discharge at the numerous mine sites in the catchment. The elevated concentration of Fe > 0.5 mg/L also indicates that river water ecology throughout the catchment is likely to be adversely impacted by Fe-rich precipitate formation (Jarvis and Younger, 1997; Younger, 2000b).

4.2. Flow dependency

Concentrations of Fe_{tot} and SO_4^{2-} in Almond surface waters (monitoring points 1–19) when plotted against river flow at the time of sampling show significant flow dependence (Fig. 3). Iron_{tot} concentrations increase with increased flow while SO_4^{2-} concentrations decrease with increased flow. River water pH was also found to be flow dependent with lower pH values recorded at increased

Table 2
Concentration and load of Fe_{tot} and SO_4^{2-} in Almond surface waters.

Fe_{tot}	1	2	3	4	5	6	7	8	9	10	11	12
Median (mg L^{-1})	1.27	1.20	1.59	1.30	0.88	1.18	1.30	1.02	0.92	0.79	0.78	0.68
Mean (mg L^{-1})	2.37	1.60	1.67	1.49	1.07	1.21	1.26	1.13	1.07	0.95	0.93	0.81
Max (mg L^{-1})	19.70	17.00	6.36	8.12	4.71	5.13	4.97	4.41	4.18	5.95	6.18	4.17
Low flow (g s^{-1})	0.01	0.04	0.09	0.07	0.07	0.10	0.31	0.39	0.39	0.26	0.28	0.37
High flow (g s^{-1})	3.06	4.68	9.45	9.71	10.10	15.38	30.16	50.27	46.62	49.06	50.40	34.74
SO_4^{2-}												
Median (mg L^{-1})	91.90	127.50	131.50	178.55	176.00	177.00	n.d.	n.d.	n.d.	124.00	n.d.	114.00
Mean (mg L^{-1})	96.22	132.13	132.45	244.19	230.74	192.44	n.d.	n.d.	n.d.	120.60	n.d.	113.89
Max (mg L^{-1})	196.00	240.00	217.00	686.00	572.00	525.00	n.d.	n.d.	n.d.	202.00	n.d.	186.00
Low flow (g s^{-1})	2.38	9.25	20.59	49.42	53.89	62.88	n.d.	n.d.	n.d.	161.19	n.d.	230.28
Fe_{tot}	13	14	15	16	17	18	19					
Median (mg L^{-1})	0.68	0.68	0.96	2.48	0.40	1.22	0.80					
Mean (mg L^{-1})	1.09	1.55	2.64	2.08	0.64	1.34	1.05					
Max (mg L^{-1})	6.15	33.00	5.83	19.00	3.93	7.82	6.44					
Low flow (g s^{-1})	0.01	0.04	0.31	0.21	0.01	0.06	0.04					
High flow (g s^{-1})	0.67	4.00	5.27	15.74	1.17	6.90	4.17					

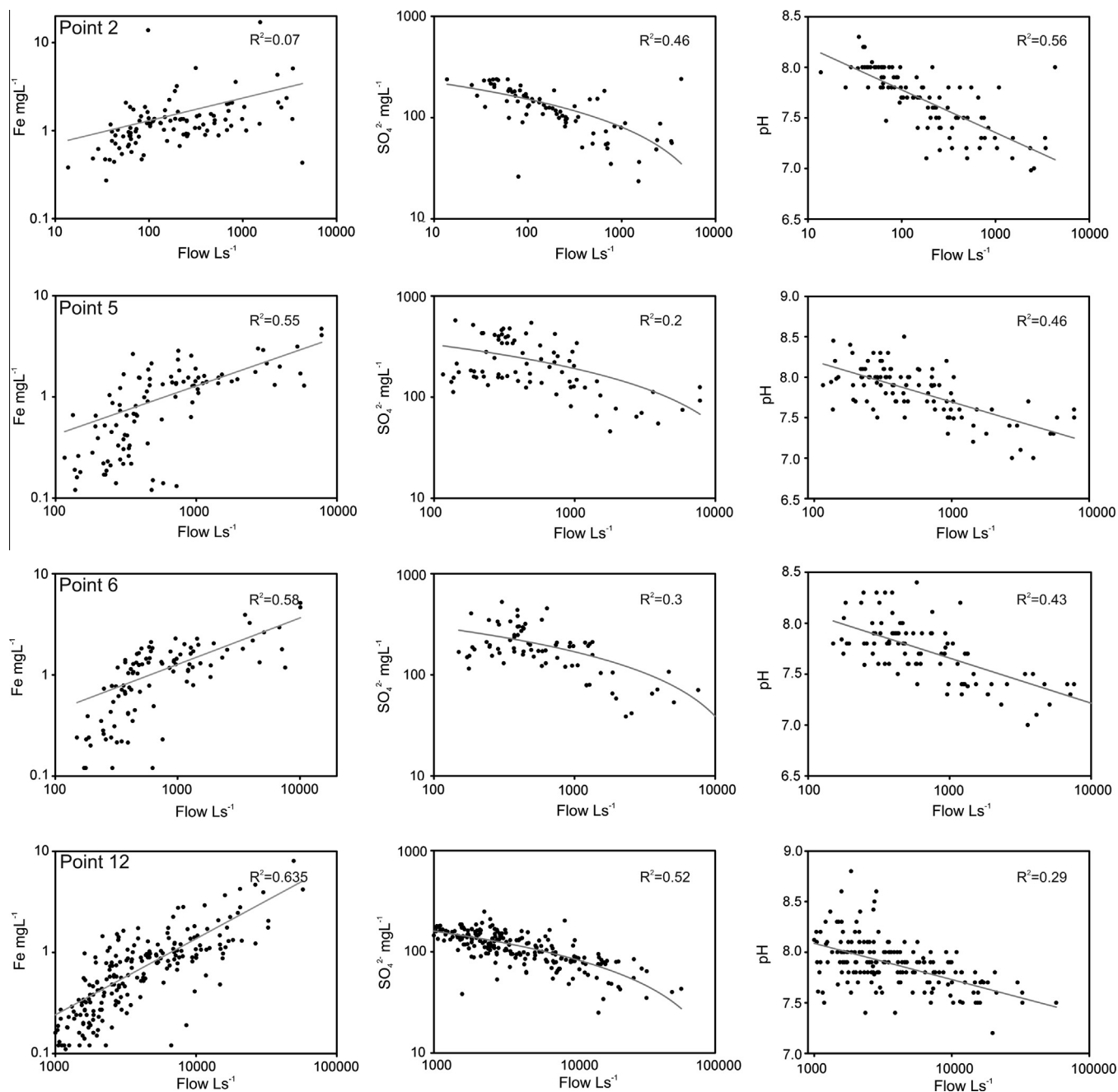


Fig. 3. Flow dependence of Fe_{tot} , SO_4^{2-} and pH in Almond surface waters. The power law regressions applied to Fe vs flow plots show better R^2 correlations at monitoring points with larger catchment areas (e.g. point 12) due to the dominance of re-suspended river bed Fe from heavily mined areas. Monitoring points with smaller catchment (e.g. point 2) areas show a poor flow dependent relationship due to the greater significance of individual mine sites as point sources of Fe on surface water Fe concentrations.

flow. All the monitoring points in the catchment were found to display these flow relationships.

At monitoring point 12 the relationship of Fe_{tot} to flow is approximated to a power law with an $R^2 = 0.635$. Flow dependence of Fe in surface waters has been observed, although over shorter monitoring periods with smaller distribution of flow values, in similar heavily mined catchments where it has been related to the re-suspension of diffuse sources of mine and non-mine related river bed Fe sediments (Mayes et al., 2008). The flow dependence of Fe and the widespread mining in the Almond is also considered to be indicative of diffuse stream bed Fe precipitate re-suspension. Precipitate formation when mine waters are discharged to the surface water environment produces Fe-rich solids suspended in the water column; some of this is transported downstream while a

large majority is deposited in surface waters close to the mine site. River beds covered in ochre are a common feature of the heavily mined areas in the catchment. However, because of the high density and long history of mining in the catchment, these river bed precipitates are considered to be almost ubiquitous throughout the main catchment rivers resulting in the flow dependency of Fe at all monitoring points.

Sulphate concentration shows an opposing flow dependent relationship, SO_4^{2-} concentrations are reduced with increased flow. Sulphate does not readily precipitate on exposure to O_2 and, therefore, does not commonly produce river bed precipitates. The flow dependence of SO_4^{2-} is likely to be caused by dilution; the mass of SO_4^{2-} in the river channel remains as a near constant while the river channel water volume and flow increase. The river water

pH shows a similar relationship to flow as SO_4^{2-} . This is considered to be related to the difference in river water source at high and low flow. Groundwaters are generally the dominant water source of river waters at low flow while at high flow rainfall and soil water sources dominate which have lower pH values than groundwaters. Scatter is observed in the flow dependent relationships potentially due to natural variability in (1) discharge rates from mine sites, (2) groundwater baseflow contribution, and (3) the frequency of higher flow events affecting Fe storage and re-suspension.

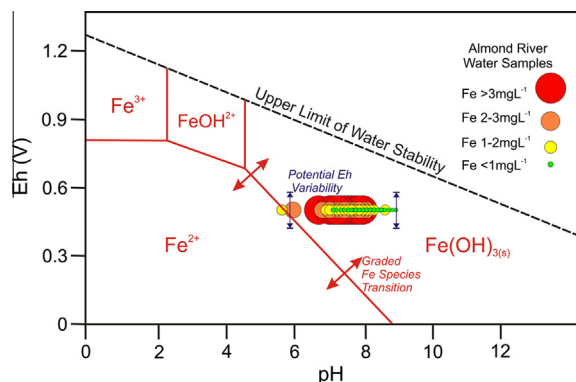


Fig. 4. Eh–pH diagram and Fe species stability in Almond surface waters.

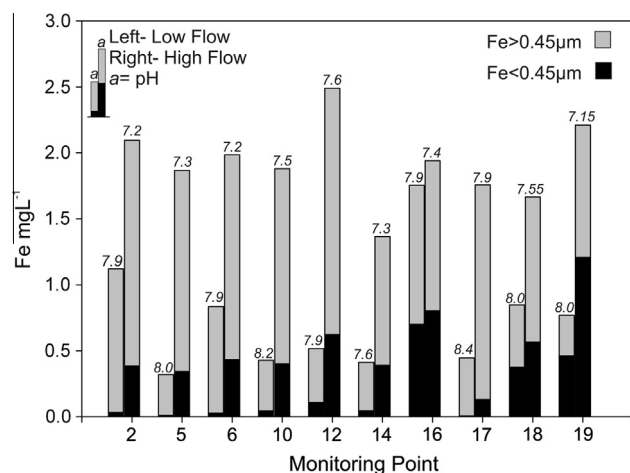


Fig. 5. Distribution of dissolved Fe, solid Fe and pH in Almond surface waters.

4.3. Fe speciation

As stated above, Fe in mine waters discharged to O_2 -rich river waters has a tendency to form $\text{Fe}(\text{OH})_3$ precipitates. Fig. 4 shows the Almond surface waters plotted on an Eh–pH diagram with Fe species stability fields. No Eh data were available for the samples so dissolved O_2 measurements, ranging from 6 to 13 mg/L, were used to estimate a mean Eh value of 0.5 V to plot the results. This generally plots waters in the $\text{Fe}(\text{OH})_3$ region, although some of the higher Fe values are approaching the transition towards the Fe^{2+} region. This is significant because the transition is generally graded between the Fe stability regions (Freeze and Cherry, 1979).

Since 2007 SEPA have monitored river waters at a number of monitoring points for both Fe_{tot} and $\text{Fe} < 0.45 \mu\text{m}$. Fig. 5 shows the averaged low flow and high flow split between $\text{Fe} > 0.45 \mu\text{m}$ and $\text{Fe} < 0.45 \mu\text{m}$ and the corresponding pH. It should be noted that there is some indication that a $< 0.45 \mu\text{m}$ filter, which is generally accepted to filter out all the solid chemical species in a water sample, may allow small amounts of solid Fe complexes into the sample (Appelo and Postma, 2005). With this limitation in mind the diagram indicates that while Fe_{tot} increases at higher flow values related to the re-suspension of $\text{Fe}(\text{OH})_3$, described above, $\text{Fe} < 0.45 \mu\text{m}$ also increases indicating a greater proportion of the dissolved Fe species, Fe^{2+} . The reason for this $\text{Fe} < 0.45 \mu\text{m}$ increase is related to the reduction in pH at high flow, shown by the pH values on the diagram and the relationship in Fig. 3. The Eh–pH diagram of Almond waters suggests the lower pH causes the partial dissolution of the re-suspended $\text{Fe}(\text{OH})_3$ as Fe^{2+} . The hydrological conditions in the river catchment, therefore, not only cause the re-suspension of diffuse $\text{Fe}(\text{OH})_3$, but result in water chemistry changes which affect the behaviour of Fe in surface water.

The flow-concentration and pH relationships described above indicates that Fe and SO_4^{2-} concentrations in surface water will best represent the direct impact of mining on water quality at low flow. At higher flow the input of Fe from direct mine related inputs is likely masked by the re-suspension of diffuse sources of river bed Fe precipitates (Mayes et al., 2008). Iron concentrations at high flow may be useful as an indication of the amount and location of the 'stored' river bed Fe.

4.4. Iron and sulphate loading

Concentration data and averaged daily flow values were used to calculate the surface water load of Fe and SO_4^{2-} in river waters across the Almond River catchment (Table 2 – Fe load-points 1–19, SO_4^{2-} load-points 1–7, 10 and 12). Load is defined here as a measure of the total mass of Fe or SO_4^{2-} passing each monitoring point.

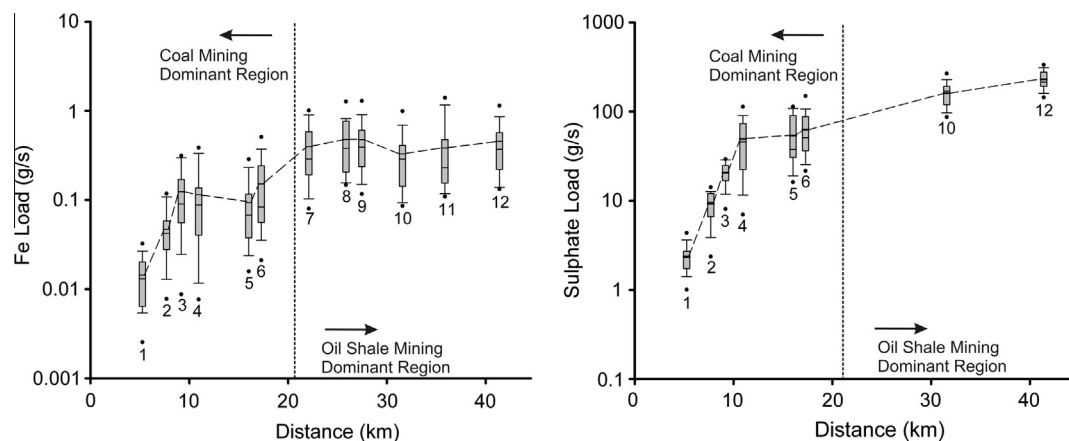


Fig. 6. Box plot of the distribution of Fe_{tot} and SO_4^{2-} at low flow.

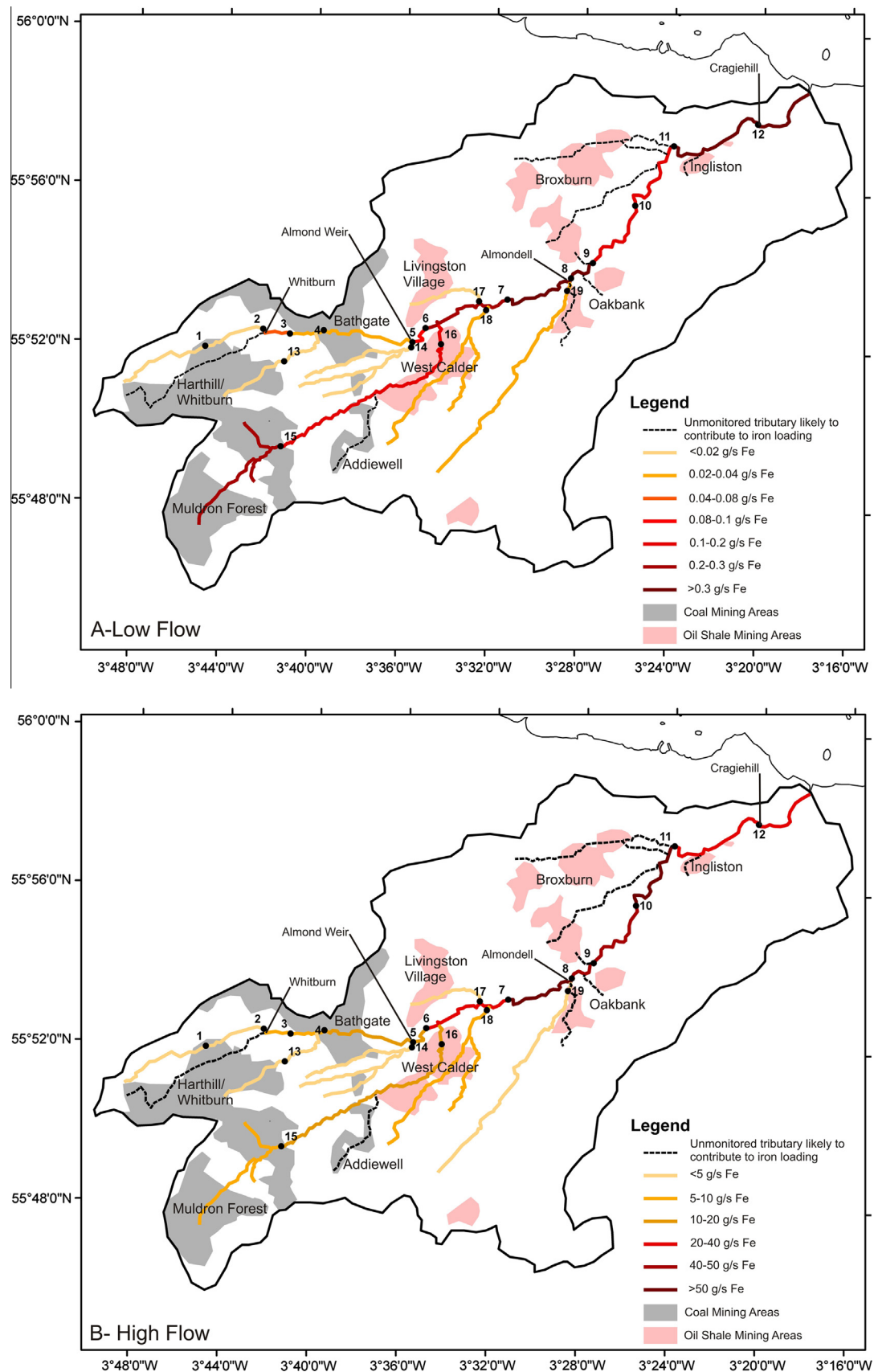


Fig. 7. Principal mining areas and iron loading under (A) low flow and (B) high flow in monitored tributaries.

Fig. 6 shows a box plot distribution of loading values for Fe and SO_4^{2-} at monitoring points 1–12, along the Almond River, during low flow events 1994–2008. The box plots for the load distribution at each monitoring point show the mean and 5th, 10th, 25th, 50th (median), 75th, 90th, 95th, percentiles. Geometric mean is used for the Fe loading values due to the power law relationship of Fe and flow outlined previously. The mean load value of the distribution at each point is joined by the dashed line to give a visual representation of the mean loading profile along the Almond River. An upward trend on the loading profile represents the input of fresh Fe or SO_4^{2-} , whilst a downward trend represents, in the case of Fe, deposition of $\text{Fe}(\text{OH})_3$ from the water column to the river bed, or for SO_4^{2-} , dilution.

The plots show between a 1 and 2 order magnitude increase in loading of both Fe and SO_4^{2-} from one end of the catchment (point 1) to the other (point 12). This is a clear indication of the discharge of Fe and SO_4^{2-} heavy mine waters, controlled by pyrite oxidation at numerous mine sites, and the resulting impact on the quality of surface water.

The geographic divide and distribution of coal and oil shale mining (Fig. 2) in the catchment allows the detailed interpretation of load increases calculated from water quality monitoring data. Fig. 7 displays the low (A) and high flow (B) Fe load distribution calculated at all 19 monitoring points across the Almond River catchment. Sulphate loading is not included in Fig. 7 as SO_4^{2-} data were not available at all monitoring points. A summary of the load difference and the relationship to specific regions of concern or 'hotspots' is presented in Table 3.

Coal and oil shale mines and mine wastes are all likely to contribute to point and diffuse mine contaminant sources within their respective areas. The close correlation between the load increase of both Fe and SO_4^{2-} (Fig. 6) and the main mining areas, even with the omission of SO_4^{2-} data for points 7, 8, 9 and 11, would seem to support this interpretation. However, in the oil shale areas only the black unprocessed shales found at the oil shale waste sites, and not the processed shales, will contribute Fe and SO_4 through the oxidation of pyrite. Other potential sources of Fe which may influence the observed results include urban drainage, potentially derived from anticaking agents used in road salts (Paschka et al., 1999) and sewage treatment works, as well as natural sources such as peat bogs (Fenner et al., 2001).

4.5. Fe trends

Iron_{tot} concentrations in river waters at the 12 monitoring points on the main Almond tributary were considered in relation to time over the 1994–2008 sampling period in order to identify any potential temporal trends. Fig. 8 displays the trend of Fe_{tot} for each of the 1–12 main Almond River tributary monitoring points. Significant scatter is observed in the data related to the flow dependence of the $\text{Fe}(\text{OH})_3$ species in the surface waters, however, in general all the monitoring points, except Point 1, show a shallow upward trend in Fe concentration in the river waters from 1994 to 2008. A possible explanation for this is that although mining came to a close from 1960 to 1985 (depending on mined resource), it can take several decades before the main water quality impacts associated with mining occur due to extended groundwater recovery times in heavily mined areas. Indeed, the main interconnected 'pond' in the Whitburn area was still in a phase of groundwater recovery in the late 1990s (Chen et al., 1999). The uncontrolled discharge of mine waters to the surface water environment even from mines not directly connected to the Whitburn 'pond' may, therefore, have been delayed due to reduced groundwater levels in the region. When discharge does occur mine waters are initially in the 'vestigial acidity' phase when contaminant release and Fe concentrations are greatest, as described by Younger (1997). This vestigial acidity phase continues for several decades, hence why an upward trend is observed in recipient surface waters. As mine waters move into the 'juvenile acidity' phase Fe concentrations move to a lower asymptotic concentration (Younger, 2000a) and a general reduction in Fe in recipient surface waters might be expected.

4.6. Attenuation and cumulative loading

Some sections of the Almond River are dominated by the deposition of the $\text{Fe}(\text{OH})_3$ species on the river bed, while others show increases in Fe load related to mine discharge. The cumulative low flow Fe load increase and reduction, termed attenuation (Kimball et al., 2002), can be used to give a useful quantitative measure of the relative impact of coal and oil shale mining in the catchment. Kimball et al. (2002) and Mayes et al. (2008) define cumulative in-stream loading as the sum of all loadings in the reaches where a positive change in loading was measured. Cumulative in-stream

Table 3
Fe loads and mine source areas in the Almond catchment (source areas are shown in Fig. 7).

Monitoring points	Fe load difference (g/s)	Coal/oil shale	Source area	Comments
1 → 2	0.03	Coal	Harthill (North)	Direct input from mine sites along the How Burn tributary
2 → 3	0.05	Coal	Harthill and Whitburn	Influx of mine impacted waters from the unmonitored upper reaches of the Almond River prior to confluence with How Burn. Numerous coal mine waste and subsurface mines discharge waters in the surrounding area
3 → 4	−0.02	–	–	River bed deposition of Fe precipitates
4 → 5	0	Coal	Bathgate	Likely input from mine sites in the area possibly balanced by river bed deposition of Fe precipitates
5 → 6	0.03	Coal	Bathgate, Harthill and Whitburn	Large mines including Polkemmet and Whitrigg colliery
6 → 7	0.21	Coal and oil shale	West Calder, Addiewell, Muldron Forest and Harthill	Breich Water tributary is impacted by numerous coal mine and mine waste sites including Woodmuir Colliery and Levensat as well as oil shale mine and mine waste sites including the Westwood, Hermand and Five Sisters
7 → 8	0.08	Oil shale	Oakbank	Oakbank oil shale mines and large volumes of oil shale waste
8 → 9	0	Oil shale	Oakbank	Likely input from mine sites in the area possibly balanced by river bed deposition of Fe precipitates
9 → 10	−0.13	–	–	River bed deposition of Fe precipitates
10 → 11	0.02	Oil shale	Broxburn	Numerous oil shale mine sites, reinstated opencasts and 10s of millions of tons of oil shale waste
11 → 12	0.09	Oil shale	Ingliston	Possible direct discharge from oil shale workings directly below the Almond River

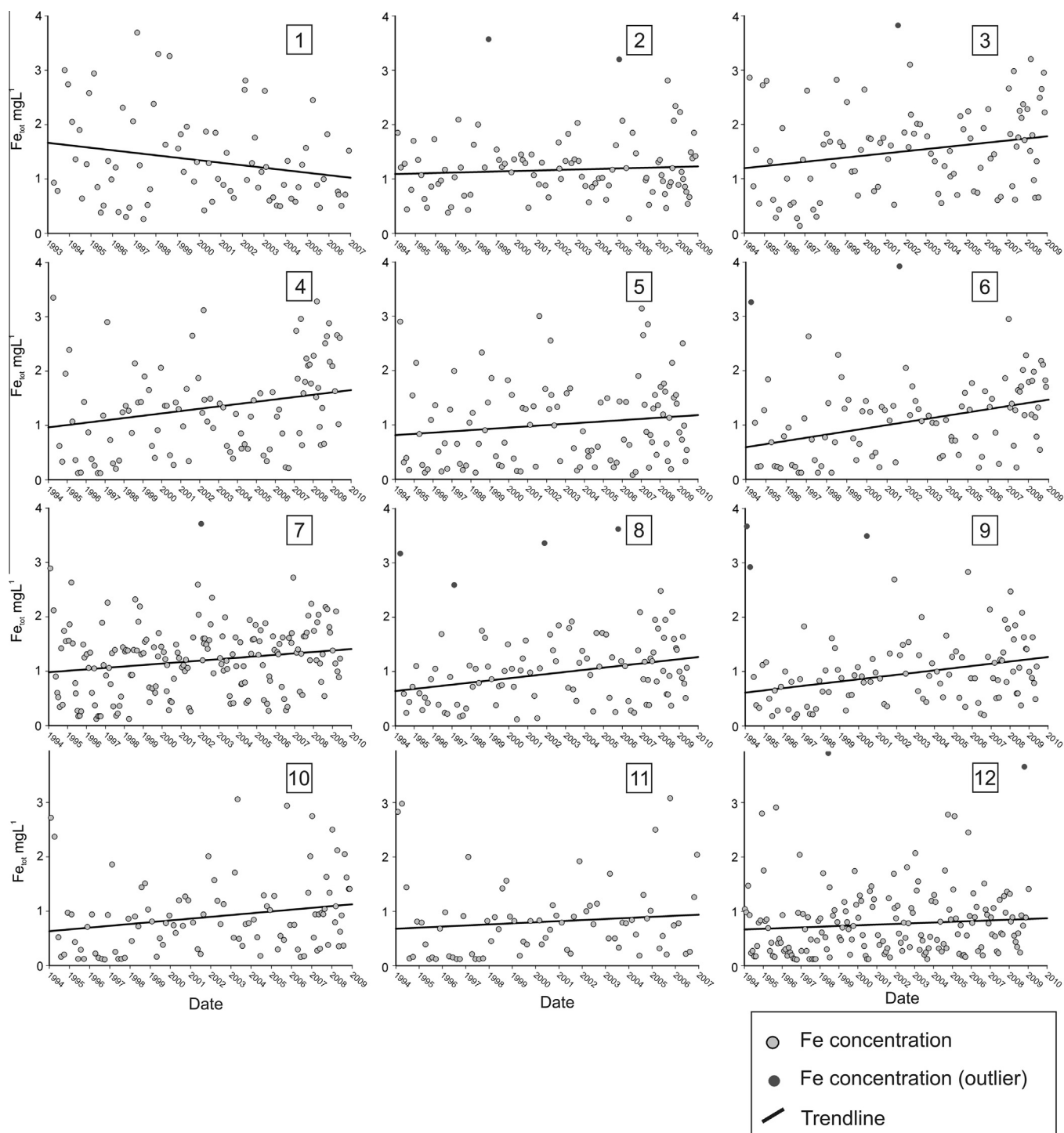


Fig. 8. Fe monitoring data 1994–2008 at 12 sample stations on the principal Almond tributary.

attenuation is taken as the sum of the loadings in all reaches that recorded a negative change in loading. The Almond River flowing between point 1 and 12 is considered in these calculations, smaller tributaries monitored with points 13–19 are omitted; except in the determination of the amount of increase directly attributable to oil shale mining between points 6 and 7. This is calculated on the assumption that the 'West Calder' oil shale area contributes approximately the same amount of low flow load at point 16 as point 18. Therefore, the load difference between point 6 and 7, attributed to oil shale mining, is calculated at 0.117 g/s (0.055 g/s on the point 16 and point 18 tributaries and 0.007 g/s on the point

17 tributary). The contribution of coal between point 6 and 7 is, therefore, calculated as 0.086 g/s; the difference between the oil shale load contribution and the total load increases between 6 and 7.

Omitting points 13–19 prevents a potentially unfair biased towards coal mining caused by the lack of Fe monitoring on tributaries closest to oil shale mining areas, particularly in the north of the catchment, as well as problems associated with flow estimation on these tributaries. It should be noted that both the loading and attenuation values are likely to be underestimations of the true values because deposition is also possibly occurring on river

Table 4

Cumulative low flow in-stream loading and attenuation on the main Almond tributary.

	Coal	Oil shale
Cumulative instream loading (g/s)	0.21	0.31
Cumulative instream attenuation (g/s)	0.154	

sections even where a load reduction is not observed. Table 4 indicates, whilst being mindful of the limitations discussed, that coal and oil shale mining regions both contribute significantly to Fe loading on the main Almond tributary and that oil shale, at 0.31 g/s, contributes more than the coal region, at 0.21 g/s. The cumulative in-stream attenuation of 0.154 g/s suggests that approximately 30% of the total load discharged to the Almond River is attenuated by deposition onto the river bed. This value agrees with the load reduction value observed between 15 and 16 (of 33%), which was not included in these calculations. As mentioned earlier, this value is likely to be much higher for the whole catchment as deposition is thought to be occurring on river beds even when a load reduction is not observed. This is supported by the observation that high flow load increases occur on the majority of monitored tributaries in the catchment (Fig. 7B): as in order for a significant high flow load increase to occur Fe precipitates must have been previously deposited on the river bed. Also, consideration of the difference in low flow and high flow load values indicates that load is increased in some cases by over 2 orders of magnitude (e.g. point 11 – 0.28–50.4 g/s) indicating the significance of re-suspension of diffuse stream bed sources of Fe at high flow.

If all the currently monitored tributaries in the catchment are considered it would appear coal, not oil shale, contributes more Fe loading to the catchment rivers, however, this is an unfair comparison because of the lack of monitoring in the one of the main oil shale mined areas – ‘Broxburn’. Nevertheless, the cumulative loading comparison is a useful one as it shows in a quantitative manner that Fe loading and water quality is significantly impacted by mine discharge inputs from both coal and oil shale mining.

4.7. Major ion water chemistry

The major ion chemistry for the Almond River water is displayed in Fig. 9; it indicates significant variation in water chemistry along the course of the river related to source. At point 1 the river water displays a Ca–HCO₃–dominant signature representing a significant component of groundwater entering the river. The Coal Measures Group, which underlies this section of the river,

displays elevated and moderately elevated concentrations of HCO₃ (median 456 mg/L; 10–90th percentile range 251–510 mg/L) Ca (10–90th percentile range 3.4–76.6 mg/L, median 50.2 mg/L) and Mg (10–90th percentile range 1.08–43.3 mg/L, median 19 mg/L), with local variations (Ó Dochartaigh et al., 2011) and is likely to be responsible through baseflow contribution for the Ca–HCO₃ dominance in surface waters. Between points 2–5, in the predominantly coal mined area, Ca, Mg and SO₄^{2−} are increasingly dominant, indicating a significant proportion of river water is likely to be sourced from coal mine water discharges (Younger, 2001; Ó Dochartaigh et al., 2011).

In the oil shale mined areas, points 6–12, which are significantly more urbanised, Na⁺ and Cl[−] are dominant. Discharge of Na⁺ and Cl[−] (up to 1000 mg/L) dominant mine waters has been recorded associated with shale spoil discharge elsewhere in the UK (Banks et al., 1997a). It is possible that the black unprocessed component of the oil shale mine wastes discharge NaCl-dominant waters flushed out from residual pore waters derived at depth and contained in the shale. This together with a component of sewage effluent discharge from sewage works and urban areas (Pollard et al., 2001) may explain the NaCl dominance of river water in the oil shale mined areas. Therefore while it is clear from Fe and SO₄^{2−} data, presented previously, that both coal and oil shale mined areas contribute contaminants to the environment, their influence on major ion chemistry of the Almond River water differs significantly.

5. Conclusions and recommendations

This catchment study has highlighted the scale and distribution of coal and oil shale mining in the Almond River catchment. In the study mine site source distribution were compared with surface water contaminant concentrations and loads calculated from over 15 years of monthly chemical analysis and flow data at 19 sites in the catchment. The results of this demonstrates (1) the continued detrimental impact of both historic coal and oil shale mining on water quality, (2) the diffuse nature of mine water pollution sourced from numerous mine sites within the river catchment, and (3) the flow dependent nature of mine contaminants in surface waters. Of particular significance is the demonstration of a previously poorly characterised relationship between historic unconventional hydrocarbon exploitation from oil shales in Scotland and significant detrimental water quality impact.

Further work on identifying and sampling discharges from both subsurface oil shale mines and mine wastes would help to further quantify the relationship between abandoned oil shale mining sites and reduced water quality. In addition, direct sampling of

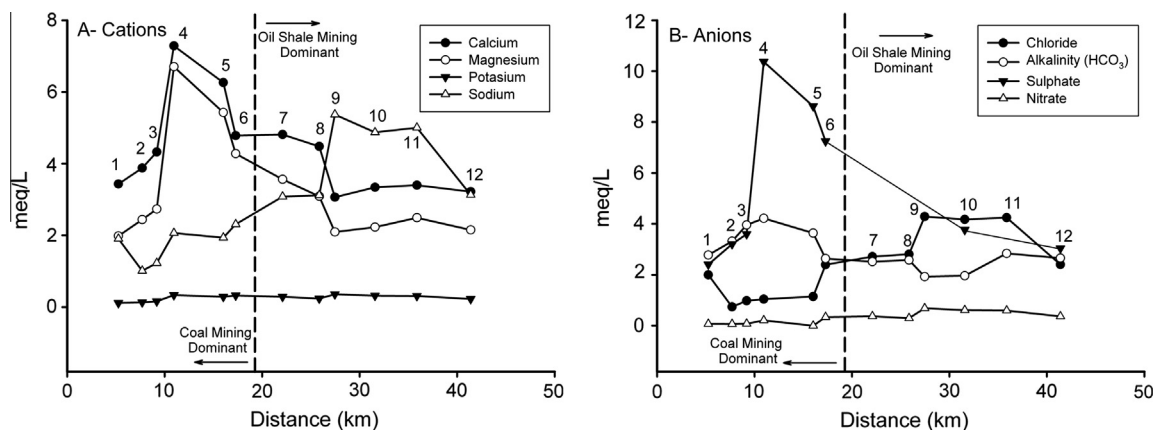


Fig. 9. Major ion chemistry of the Almond surface waters: (A) cations, (B) anions (mean low flow 2005–2006).

small coal mine and waste discharges could help to better separate the roles of point and diffuse mine contamination sources. Investigations into the specific nature and chemistry of river bed precipitates would be required to differentiate between diffuse Fe from mine and non-mine sources. This study has also highlighted the importance of regular and widespread sampling of water quality in catchments subject to diverse mining activities to identify the various significant sources of contamination.

The relationships presented here are directly applicable to other similar mined catchments in the UK and across the world. They indicate that a catchment view of mine water contamination should be engaged when assessing numerous, point and diffuse mine water contamination sources.

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