Environ Earth Sci (2016) 75:340
DOI 10.1007/s12665-015-5191-z

ORIGINAL ARTICLE

Inorganic carbon dynamics and CO_2 flux associated with coal-mine drainage sites in Blythedale PA and Lambert WV, USA

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Received: 19 December 2014 / Accepted: 24 October 2015 / Published online: 12 February 2016
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Abstract Drainage from coal mines, where carbonate dissolution is driven by sulfuric acid, can result in a net transfer of geologically-bound carbon to the atmosphere. The flux and downstream evolution of dissolved inorganic carbon (DIC) is presented for two coal mine sites that discharge high concentrations of DIC (3.7–4.5 mM C) producing a total flux of DIC from the mine from 13 to 249 kg-C/year (18–364 metric tons of CO_2/year). More than 65 % of the total DIC is lost via CO_2 evasion with the remaining DIC is exported downstream as dissolved species. The fate of the DIC depends upon the pH of the water which is controlled by evasion of CO_2, the concentration of pre-existing alkalinity, carbonate precipitation and dissolution, and metal hydrolysis reactions. The CO_2 concentrations and fluxes from the study sites are comparable to those estimated from literature data for other coal mine sites in the Appalachian region. The total flux estimated from a dataset of 140 coal mines was comparable in magnitude to the CO_2 emissions from a small coal-fired power plant. The extent of CO_2 degassing from mine waters is poorly constrained because (1) flux estimates can be biased low when acid waters are excluded in alkalinity-based estimates; (2) flux estimates can be biased high if non-carbonate alkalinity is present in the mine waters; and (3) mine waters react rapidly following discharge hampering the measurement process. The study sites presented illustrate the impact of coal mining as an anthropogenic influence on carbon cycling; however, more data are necessary to fully estimate the importance of this impact on regional scales.

Keywords Dissolved inorganic carbon (DIC) · Carbon dioxide (CO_2) · CO_2 evasion, carbonate geochemistry, coal mine drainage

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Introduction

Terrestrial waters play a critical role in the release and transfer of geologically-bound carbon to the oceans (Butman and Raymond 2011). This process may be enhanced in regions where the legacy of coal mining has generated sulfate-rich waters. When sulfuric acid drives carbonate dissolution, it enhances carbonate weathering because, per mole of acid, sulfuric acid can dissolve twice as many moles of calcite than carbonic acid (Table 1; Eqs. 1, 2).

The reaction of sulfuric acid with carbonate rocks has been increasingly recognized as an important process in terrestrial weathering (Calmels et al. 2007; Hercod et al. 1998; Lerman and Wu 2006; Millot et al. 2003; Rice and Herman 2012; Telmer and Veizer 1999) and in creating some karst systems (Palmer 2007). Natural sources of sulfuric acid include oxidation of deep-sourced H_2S, volcanic activity, and dissolution of aluminum and iron sulfides. According to Calmels et al. (2007), sulfate-driven weathering of carbonates is "significantly underestimated" in the Canadian Mackenzie River Basin. In a study of a watershed in Texas, Hercod et al. (1998) concluded that pyrite oxidation accounted for nearly half of the flux of dissolved inorganic carbon (DIC) from the watershed although only trace pyrite was present. Sulfuric acid-driven

Table 1 Controlling reactions and equations for carbonate geochemistry

Chemical reaction	Equation no.	Description	% of C in products from $CaCO_3$
$H_2SO_4 + 2CaCO_3 \leftrightarrow 2HCO_3^- + 2Ca^{+2} + SO_4^{-2}$	(1a)	Dissolution of calcite by sulfuric above (1a) and below (1b) pH ~6.4	100
$H_2SO_4 + CaCO_3 \leftrightarrow H_2CO_3^* + Ca^{+2} + SO_4^{-2}$	(1b)		100
$H_2CO_3 + CaCO_3 \leftrightarrow 2HCO_3^- + Ca^{+2}$	(2a)	Dissolution of calcite by carbonic acid a bove (2a) and below (2b) pH ~6.4	50
$H_2CO_3 + 2H^+ + CaCO_3 \leftrightarrow 2H_2CO_3^* + Ca^{+2}$	(2b)		50
$CO_2(g) + H_2O \leftrightarrow H_2CO_3^*$	(3)	Hydration of CO_2 gas	
$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$	(4)	Dissociation of carbonic acid	
$HCO_3^- \leftrightarrow H^+ + CO_3^{-2}$	(5)	Dissociation of bicarbonate	
$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$	(6)	Mass balance on the carbonate species (definition of dissolved inorganic carbon)	

$H_2CO_3^*$ is the sum of the carbonic acid and the dissolved CO_2; the later accounts for >99.9 % of the $H_2CO_3^*$ (Stumm and Morgan 1996) therefore $H_2CO_3^* \cong$ dissolved CO_2 and can be used as a measure of the dissolved CO_2 concentration

dissolution of carbonates is a well-studied process of cave formation: well-known caves attributed to this process include Carlsbad and Lechuguilla Caves in New Mexico and Frasassi Cave in Italy (Palmer 2007).

Coal mining can be considered an anthropogenic form of mechanical and chemical weathering that exposes sulfide minerals to the atmosphere and consequently generates sulfuric acid (Calmels et al. 2007; Rice and Herman 2012). If the sulfuric acid interacts with carbonate rocks, either insitu or added as exogenous material for treatment, DIC is added to the water (Geroni et al. 2012; Younger et al. 2002). Depending upon the pH of the solution, DIC exists primarily as dissolved CO_2 ($H_2CO_3^*$), HCO_3^-, or CO_3^{-2}. The governing chemical reactions between these species and a mass balance statement for DIC are provided on Table 1. If the pH of the mine water is low enough to produce dissolved CO_2 from the DIC, and the partial pressure of CO_2 in the water (P_{CO2}) exceeds the atmospheric background pressure, then CO_2 can degas and transfer carbon from the aqueous to the atmospheric reservoir.

The mine water–carbonate interaction can occur inside the mine, in waste piles, or in streams and retaining ponds. Field and laboratory studies have shown that the addition of low-pH mine waters to neutral-pH streams can lower the stream pH sufficiently to convert DIC into CO_2 resulting in degassing and a loss of CO_2 from the system (Atekwana and Fonyuy 2009; Fonyuy and Atekwana 2008a; Hercod et al. 1998; Webb and Sasowsky 1994). The outcome depends on the DIC concentration, the buffering capacity of the receiving stream, and the capacity of the mine water to generate acidity via precipitation of metal hydroxides. The degassing of CO_2 and ensuing rise in pH are sometimes incorporated into the treatment design to enhance metal removal (Cravotta 2007; Cravotta and Trahan 1999; Geroni et al. 2012; Younger et al. 2002). On a more regional scale, the long-term impacts of mining can be seen over decadal scales in larger watersheds (Raymond and Oh 2009).

This study demonstrates the detailed release, speciation and evolution of DIC from two coal-mine drainage discharges. The flux of carbon released from the sites was determined along with means of export (CO_2 evasion flux to the atmosphere versus export of dissolved carbonate species). These fluxes are also compared to values estimated from site and regional data reported in the literature. The results illustrate the importance of carbon release associated with mine-waters and current limitations in the estimation of carbon flux in these settings.

Methods and procedures

Sample collection and analysis

The pH, electrical conductivity (EC), and temperature were measured using a YSI hand meter (YSI, Inc. Yellow Springs, OH). The meter was calibrated daily using two buffers for pH (4 and 7) and a 1.417 mS/cm EC standard. A limited number of samples were analyzed in the field for ferrous iron (Fe^{2+}) using a Hach DR2800 field spectrophotometer following the ferrozine method (Stookey 1970). Using this procedure, Fe^{2+} was determined four times for each sample; the relative standard deviations (RSD, the standard deviation divided by the mean expressed as a percentage) for the replicate measurements were always less than 9 %. The mean Fe^{2+} concentrations were used for assessing acidity as discussed below.

A carbonation meter (CarboQC; Anton Paar GmbH, Graz, Austria) was used to measure dissolved CO_2 in the

field (Vesper and Edenborn 2012). The meter is a commercially-available instrument used in the beverage industry for the determination of dissolved CO_2 in water, soda and beer (Anton Paar 2010). The meter works by sealing a water sample in a volumetric chamber and changing the chamber volume with a piston. The CO_2 concentration is calculated based on the differences in temperature and pressure at two volumes. DIC was also measured in the field using the carbonation meter. In this method the DIC was converted into CO_2 through the addition of a high ionic-strength, low-pH citrate solution, and then CO_2 was determined in the buffer-sample mixture. The DIC was calculated based on the measured CO_2, the pH of the buffer-sample mixture, and the dilution caused by adding the buffer (Vesper et al. 2015). The samples for CO_2 and DIC were collected in 140-mL syringes that were filled under water so that no air bubbles were introduced in the sampling process.

Water samples for laboratory analysis were collected as grab samples and filtered into 125-mL bottles through a Whatman GD/X 0.045-µm syringe filter. Samples for elemental analysis were preserved with trace-metal grade nitric acid and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 3000 Radial View spectrometer following US EPA method 200.7. Samples for anion analysis were kept cold prior to analysis on a Dionex ion chromatography system.

The discharge from the source was measured following the method of Buchanan and Somers (1969) at stream locations where the water was deep enough to allow the measurement to be made. A Swoffer propeller-meter (Velocity Meter 3000) was used to measure velocity at 60 % of depth over a cross-section perpendicular to flow direction. The RSDs for replicate measurements were <5 % for the higher discharge values and <20 % for the lower discharge values. Discharge was assumed to be constant throughout the site over each sampling period.

Calculation of acidity, alkalinity and saturation indices

Acidity is generated in mine waters when Al, Fe and Mn precipitate as hydroxides (Younger et al. 2002). The estimated potential metal-acidity produced by hydrolysis can be calculated as follows:

$$\mathrm{Acid_{MA}} = 2\left[\mathrm{Fe^{+2}}\right] + 3\left[\mathrm{Fe^{+3}}\right] + 2\left[\mathrm{Mn^{+2}}\right] + 3\left[\mathrm{Al^{+3}}\right] \quad (7)$$

where $\mathrm{Acid_{MA}}$ is the calculated metal acidity in eq/L, and the concentrations of Fe^{2+}, Fe^{+3}, Mn^{2+}, and Al^{+3} in filtered water samples are in mol/L. This value accounts for potential acidity generated if and when the metals precipitate as hydroxides and is commonly used in assessment of mine waters (Skousen et al. 2002). The equation as modified above does not account for acidity in other forms (e.g., protons) which is typically small in comparison to the metal acidity. Iron was not speciated in all of the collected samples, but in the 10 samples that were, Fe^{2+} accounted for at least 83 % of the iron detected. For consistency, $\mathrm{Acid_{MA}}$ was calculated for the samples assuming that all iron was in the Fe^{2+} species; there was less than 5 % error in the calculated acidity from this assumption.

The primary acid-consuming reaction in the high-DIC waters is the dissolution of carbonate rocks which creates carbonate alkalinity ($\mathrm{ALK_{CARB}}$); this value was calculated based on results for the speciation of DIC:

$$\mathrm{ALK_{CARB}} = \Sigma[\text{bicarbonate species}] + 2\Sigma[\text{carbonate species}] \quad (8)$$

where $\mathrm{ALK_{CARB}}$ is in eq/L, and the bracketed molar concentrations of the bicarbonate and carbonate species are calculated using Minteq (Allison et al. 1991) based on full water chemistry and the DIC. The calculated $\mathrm{ALK_{CARB}}$ is used because titrated alkalinities may include colloidal hydroxides (Adams 2012). Saturation indices for calcite (SI_C) and dolomite (SI_D) are also obtained from the Minteq model.

CO_2 calculations

Excess CO_2 is the ratio of the measured concentration of dissolved CO_2 to the dissolved concentration in equilibrium with atmospheric background. Estimation of the CO_2 lost to the atmosphere (evasion) cannot be calculated solely from the difference in upstream and downstream CO_2 concentrations because some of the CO_2 may be lost due to conversion to HCO_3^- as the pH rises. Therefore, flux and evasion are estimated based on DIC so that conversions between carbonate species do not affect the calculation.

The carbon mass balance for the studied sites has two inputs and two outputs (Fig. 1); the DIC lost due to CO_2 evasion can be determined by rearranging the mass balance as follows:

$$\mathrm{DIC_{EVAS}} = \mathrm{DIC_{IN}} + / - \mathrm{DIC_{RX}} - \mathrm{DIC_{EX}} \quad (9)$$

where $\mathrm{DIC_{EVAS}}$ is the flux of DIC from evasion of dissolved CO_2 to the atmosphere, $\mathrm{DIC_{IN}}$ is the DIC flux from the portal, $\mathrm{DIC_{RX}}$ is the flux of DIC into and out of the system due to in-stream reactions, and $\mathrm{DIC_{EX}}$ is the DIC exported from the study site in the dissolved form (Fig. 1).

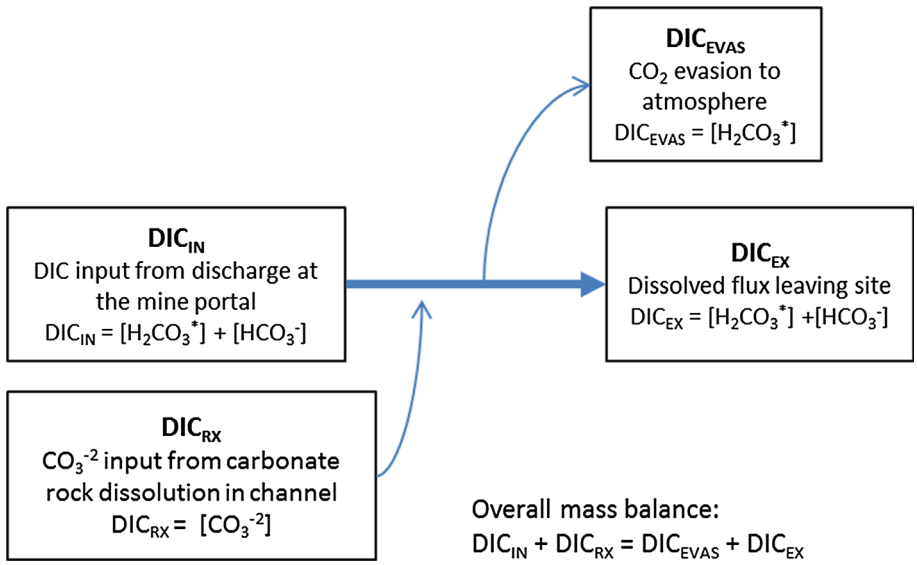

Fig. 1 The mass balance of DIC for the study sites. The DIC discharged at the mine portal (DIC_{IN}) and the dissolved species exported from the site (DIC_{EX}) are a combination of dissolved CO_2 gas ($H_2CO_3^*$) and the bicarbonate ion (HCO_3^-) with the relative concentrations of the two species controlled by the pH; DIC lost to gas evasion (DIC_{EVAS}) is in the form of dissolved gas; and the DIC generated from the dissolution of limestone in the discharge channel (DIC_{RX}) is in the form of the carbonate ion (CO_3^{-2})

Site 1: Iron Falls

Site description

The Iron Falls site is approximately 32 km southeast of Pittsburgh, Pennsylvania near the town of Blythedale. The mine is at the base of the Pittsburgh Formation of the Monongahela Group, a Pennsylvanian rock unit (Pullman-Swindell Pullman-Swindell 1977) in the western limb of the Irwin Syncline (Capo et al. 2000).

The coal mine portal is partially sealed but water continues to discharge from around the portal seal and, to a lesser degree, from several adjacent pipes. Five meters from the portal is a waterfall with a drop of approximately 10.5 meters. At the base of the falls the stream flows down slope for ~ 180 m before discharging into the Youghiogheny River. Water samples were collected at the portal and over the entire distance from the portal to the confluence with the river (Fig. 2). A set of longitudinal samples were collected at Iron Falls in July 2012 and again in June 2013 (Tables 2, 3). Additional CO_2 and/or DIC data were obtained between 2009 and 2014.

Water chemistry at Iron Falls

Water flowing from the Iron Falls portal (F000) in 2012 and 2013 had slightly acidic pH (5.9 and 6.0) and contained dissolved CO_2 approximately 240 times in excess of atmospheric equilibrium concentrations (Table 2). Periodic samples collected between 2009 and 2014 indicate that the mine has been consistently discharging water high in CO_2 since at least 2009 (Fig. 3). Based on $\delta^{13}C$ for three samples obtained from the Iron Falls portal in 2009 and 2010, Sharma et al. (2013) estimated that the carbon source was primarily from limestone dissolution.

Downstream from the portal, DIC, CO_2, metal concentrations, and $ACID_{MA}$ decreased while the pH increased (Table 2; Fig. 4). The loss of DIC and increase in pH are attributed to CO_2 evasion. The decrease in iron concentrations and metal acidity occur as oxygen in-gasses, iron is oxidized, and ferric hydroxide precipitates:

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_{3(solid)} + 2H^+. \quad (10)$$

As the mine discharge flows over the 10.5-m high waterfall (Figs. 2, 4), agitation and mixing with air enhances the degassing process; in the 2012 and 2013 sample sets, approximately 90 % of the CO_2 was lost over the waterfall. In-gassing by oxygen also increases in waterfalls causing the ferrous iron to precipitate as $Fe(OH)_3$ which causes Fe concentrations to decrease between the portal and the base of the waterfall (Table 3). The $ACID_{MA}$ continued to decrease downstream at Iron Falls as iron precipitated from solution. Although the precipitation of hydrolysable metals releases protons, the pH remained approximately constant over the downstream reaches; this is attributed to the pH increases with CO_2 degassing and the pre-existing carbonate alkalinity buffering the system against the free protons generated during metal hydrolysis. In 2012, the system remained net-acid throughout the stream reach while in 2013 it was generally net-alkaline (Fig. 4). The water was undersaturated with respect to calcite and dolomite over the entire distance (Table 3); the SI_C values varied from −1.18 to −2.32.

The estimated CO_2-evasion fluxes at Iron Falls were 67–272 kg-C/day (Table 4). The CO_2 concentrations at

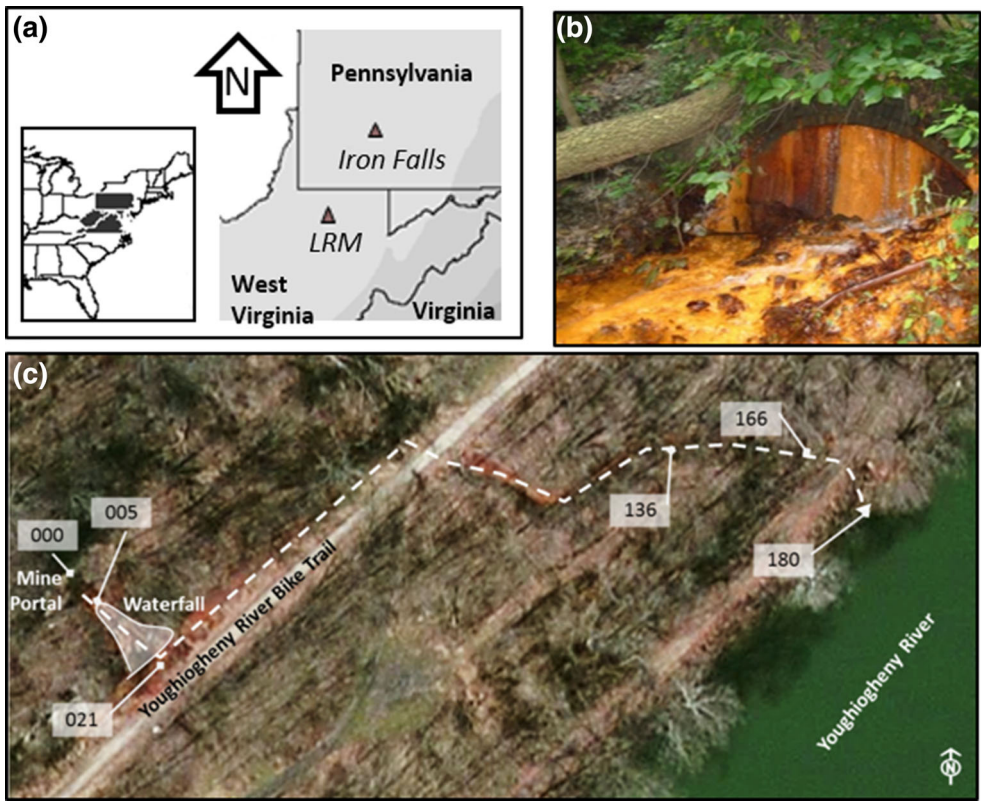

Fig. 2 Iron Falls site. **a** Location of sites in eastern US; **b** the discharge portal (sample location F000); **c** approximate sampling locations on aerial imagery. *Location labels* indicate meters from portal. Base image from Google Maps

Iron Falls were relatively constant; the range in flux was controlled by variations in discharge.

The distribution of CO_2 and HCO_3^- is controlled by pH. At Iron Falls there is no carbonate rock source external to the portal; however, past attempts at treating the mine water may have included adding carbonates to the mine system. Therefore, it is not certain if the DIC generated within the mine is from dissolution of carbonates within the geologic strata or from the addition of limestone during or after mining.

Site 2: Lamberts Run (LRM)

Site description

The LRM site is located approximately 4.5 km north of Clarksburg, WV (Figs. 2, 5). Lamberts Run flows northeast from the site until it joins the West Fork River near the town of Spelter, WV (Fig. 5). The Lamberts Run watershed is underlain by the upper Monongahela and upper Conemaugh Series, both of which are of Upper Pennsylvanian in age. The mine drainage likely comes from mining of the Pittsburgh coal which forms the base of the Monongahela Series. The Lamberts Run area was mined for at least 100 years (Hennen 1912); however, limited historic information is available regarding this site.

A passive treatment system was installed at this site in 2006 and included a portal seal, a limestone-lined channel, an altered natural wetland, a newly-constructed wetland, and a steel slag leech pit (Fig. 5). The natural wetland was altered using a series of baffles to increase the travel time of the drainage to promote precipitation of metals before discharge into West Fork River. The slag leech pit was designed to add alkalinity to the mine water, but little to no water flows from that unit. Water samples were collected from the portal and downstream locations (Fig. 5) in August 2012 and July 2013.

Water chemistry at LRM

Mine water samples were collected directly at the discharge point and had pHs of 3.13 and 5.28 with respective DIC concentrations of 3.7 and 5.2 mmol/L C (Table 2). At the lower pH, the DIC and CO_2concentrations were equal within the error of the measurement. At the higher pH, the bicarbonate ion contributed a greater proportion of the DIC. The DIC, CO_2, metal concentrations, and $ACID_{MA}$ decreased downstream of the portal. Over the same reach, the pH increased (Table 2; Fig. 4). The loss of DIC and rise of pH are attributed to CO_2 evasion while the decrease in iron concentrations and metal acidity are attributed to hydroxide precipitation.

Table 2 Field measurements and calculated carbonate alkalinity

Site and date	Sample location	Field measurements			DIC (mM-C)			CO_2 (mM-C)				ALK_{CARB}	
		Temperature (C)	pH	SC (mS/cm)	*n*	Mean	SD	*n*	Mean	SD	Excess CO_2	meq/L	mg/L as $CaCO_3$
Iron Falls 7/25/12	F000	12.7	5.91	1.56	3	6.35	0.05	3	3.72	0.07	239	1.66	83.0
	F005	12.8	5.73	1.54	2	5.39	0.06	3	2.82	0.07	182	1.02	51.2
	F021	14.3	6.44	1.53	3	2.57	0.05	3	0.36	0.03	24	1.42	71.0
	F136	14.2	6.46	1.52	3	2.34	0.07	3	0.41	0.02	28	1.32	65.9
	F166	13.8	6.45	1.51	3	2.14	0.01	3	0.31	0.01	21	1.19	59.5
Iron Falls 6/21/13	F000	12.6	5.99	1.62	3	6.39	0.08	3	3.67	0.09	236	1.90	94.8
	F005	12.6	6.09	1.61	3	5.77	0.04	3	3.06	0.03	196	2.01	100.3
	F021	13.9	6.59	1.52	3	2.69	0.05	3	0.30	0.08	20	1.70	85.2
	F136	14.0	6.58	1.58	3	2.62	0.06	3	0.43	0.02	29	1.65	82.3
	F180	13.6	6.09	1.56	4	2.02	0.09	4	0.40	0.22	27	0.71	35.4
LRM 8/6/12	LRM000	12.9	3.13	1.14	3	3.66	0.12	3	3.77	0.08	244	0.00	0.11
	LRM050	14.0	5.61	1.13	3	1.59	0.05	3	1.03	0.03	69	0.25	12.3
	LRM078	14.7	6.10	1.11	3	1.41	0.01	3	0.69	0.07	47	0.51	25.5
	LRM138	21.6	6.53	1.10	2	0.85	0.04	3	0.38	0.03	32	0.54	26.8
	LRM172	23.8	6.94	1.08	2	0.79	0.05	3	0.32	0.13	28	0.65	32.4
LRM 7/25/13	LRM000	13.0	5.28	1.19	3	5.22	0.18	3	4.51	0.08	293	0.40	20.0
	LRM010	13.1	5.47	1.21	3	5.22	0.06	3	3.80	0.14	247	0.60	30.0
	LRM050	13.3	5.65	1.20	3	2.99	0.06	3	1.51	0.03	99	0.49	24.5
	LRM078	13.9	6.17	1.17	3	1.99	0.11	3	0.94	0.03	63	0.79	39.3
	LRM138	18.6	7.02	1.57	3	1.21	0.07	3	0.27	0.05	21	1.01	50.6
	LRM172	15.1	6.82	1.15	3	1.20	0.02	3	0.17	0.01	12	0.90	45.0

For Iron Falls and LRM sites, the last 3 digits of the location name indicate the distance from the source in meters. Both SCAR samples were collected at the source. DIC and CO_2 measured on Anton Paar carbonation meter. Excess CO_2 is the ratio of the measured dissolved CO_2 to its temperature-corrected concentration in equilibrium with atmospheric pressure of P_{CO2} ($10^{-3.5}$ atm). ALK_{CARB} (carbonate alkalinity) is calculated according to Eq. (5)

SC specific conductance, *SD* standard deviation

The mine water flows through a limestone-lined channel in the 50 meters downstream from the portal (Fig. 5). Based the increase in Ca and Mg concentrations over this distance (approximately 18 %), the limestone is dissolving into the mine water. SI_C values ranged from −7.48 (LMR000) to −0.8 (LRM172) which is indicative of waters that are undersaturated and aggressively dissolving calcite. Between the portal (LRM000) and the end of the limestone channel (at LRM050), the SI_C increased which further supports that limestone is being actively dissolved. This dissolution releases CO_3^{-2} and acts as an in-stream source of DIC ($+DIC_{RX}$ in Eq. 9). The contribution of this CO_3^{-2} source was estimated as equal to the sum of the Ca and Mg molar concentrations over the same stream reach. Dissolution from the limestone-lined channel contributed 27 % of the DIC in 2012 and 7 % in 2013. The greater contribution in 2012 may be driven by the lower pH of the portal water at that time (Table 2). The ALK_{CARB} increase in this stream reach is a combination of carbonate released from rock dissolution plus a shift in the DIC from CO_2 to HCO_3^- as the pH increases. The rock dissolution should result in an increase in DIC over the first 50 meters; however, the DIC decreased over that distance because the loss of DIC by CO_2 evasion exceeds the addition of DIC from rock dissolution.

In the wetland reach (80–160 m; Figs. 4, 5), alkalinity may also be generated by biological processes such as sulfate reduction (Younger et al. 2002); further limestone dissolution is unlikely in this reach because the Ca and Mg concentrations do not increase. The solution was undersaturated with respect to calcite indicating that precipitation of calcite is unlikely to account for changes in the Ca and Mg concentrations.

The CO_2-evasive flux at LRMin August 2013 was 13.3 kg-C/day (Table 4). Due to the treatment channel, DIC sources included all three carbonate species: dissolved

Table 3 Major element chemistry and calculated parameters

Site and date	Sample location	Major ions (mg/L)								$ACID_{MA}$		Saturation indices	
		Al	Ca	Fe	K	Mg	Mn	Na	SO_4	meq/L	mg/L as $CaCO_3$	Calcite (SI_C)	Dolomite (SI_D)
Iron Falls 7/25/12	F000	<0.01	107	55.4	3.28	44.5	1.05	168	566	2.02	101	−1.76	−3.78
	F005	<0.01	106	53.7	3.06	43.9	1.03	163	622	1.96	98.1	−2.32	−4.84
	F021	<0.01	107	45.3	3.21	43.3	1.02	165	564	1.66	82.9	−1.43	−3.04
	F136	<0.01	107	33.7	3.23	44.3	1.00	165	561	1.24	62.1	−1.44	−3.06
	F166	<0.01	107	31.4	3.15	44.6	0.99	165	552	1.16	57.9	−1.50	−3.18
Iron Falls 6/21/13	F000	<0.01	110	47.7	3.10	39.5	0.86	137	523	1.74	87.0	−1.762	−3.78
	F005	<0.01	109	46.7	3.11	39.8	0.85	138	622	1.70	85.2	−1.66	−3.58
	F021	<0.01	110	39.9	3.04	40.5	0.83	141	506	1.46	72.9	−1.18	−2.59
	F136	<0.01	108	29.6	3.14	40.3	0.80	140	517	1.09	54.5	−1.22	−2.65
	F180	<0.01	109	25.3	3.09	39.7	0.80	138	517	0.936	46.8	−2.07	−4.38
LRM 8/6/12	LRM000	1.59	132	6.19	3.40	52.3	3.64	32.9	597	0.531	26.5	−7.48	−15.2
	LRM050	0.28	159	2.46	3.70	59.5	2.71	28.5	600	0.218	10.9	−2.04	−4.30
	LRM078	<0.01	153	0.054	3.95	56.8	1.88	27.1	582	0.071	3.5	−2.04	−4.29
	LRM138	<0.01	153	0.054	3.95	56.8	1.88	27.1	570	0.071	3.5	−1.29	−2.69
	LRM172	0.07	152	0.054	3.93	56.0	1.15	26.8	561	0.052	2.6	−0.97	−2.58
LRM 7/25/13	LRM000	0.58	139	1.67	3.46	55.2	3.04	34.0	593	0.235	11.7	−3.92	−8.05
	LRM010	0.46	150	1.45	3.41	58.2	2.71	31.3	588	0.202	10.1	−5.64	−11.5
	LRM050	0.24	148	0.992	3.37	57.4	2.61	30.2	580	0.157	7.9	−2.55	−5.31
	LRM078	0.05	147	0.670	3.37	57.0	2.45	30.3	561	0.118	5.9	−1.81	−3.82
	LRM138	<0.01	144	0.019	3.37	55.2	0.96	29.9	563	0.036	1.8	−0.80	−1.73
	LRM172	<0.01	141	0.022	3.19	54.5	0.65	29.6	561	0.024	1.2	−1.10	−2.39

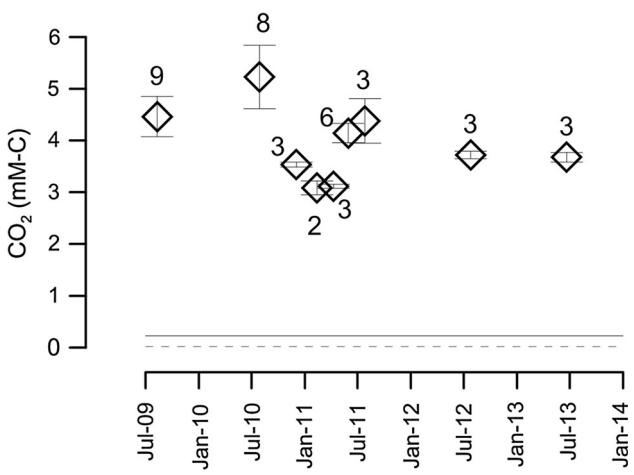

Fig. 3 CO_2 at the portal water at Iron Falls. All data based on direct readings using carbonation meter. *Numbers by symbols* indicate *n* for replicates. *Error bars* based on standard deviations from replicates. The *dashed line* is for dissolved CO_2 in equilibrium with atmospheric background (based on a log $P_{CO2} = -3.5$ atm). The *solid line* is the method detection limit (0.23 mmol/L)

CO_2, HCO_3^- and CO_3^{-2} (Fig. 6). The DIC left the site via CO_2 evasion and the downstream export of both dissolved CO_2 and HCO_3^-; CO_2 evasion dominated the output.

Discussion and interpretation

Comparison of carbon evasion and export between Iron Falls and LRM

The concentrations of dissolved CO_2 measured at the mine portals were similar at Iron Falls (F000) and LRM (LRM000) (3.7–4.5 mM); these concentrations are up to 300 times greater than what would be expected for water in equilibrium with atmospheric CO_2 (Table 2). The flux of DIC and loss of DIC via CO_2 evasion is higher at Iron Falls due to its higher discharge rate (Table 4).

The physical characteristics of the two sites govern the location of the DIC loss. At Iron Falls, the greatest loss of DIC (ca. 90 %) took place as the mine drainage flowed over a waterfall (Fig. 4). This can be attributed to enhanced degassing at waterfalls; a process recognized at karst and travertine-depositing sites (Lorah and Herman 1988; Zhang et al. 2001). In contrast, at LRM the slope is more gradual and the loss of DIC was more evenly distributed from the portal downstream (Fig. 4).

Additional alkalinity sources may contribute to the DIC at LRM: dissolution of limestone in the drainage channel

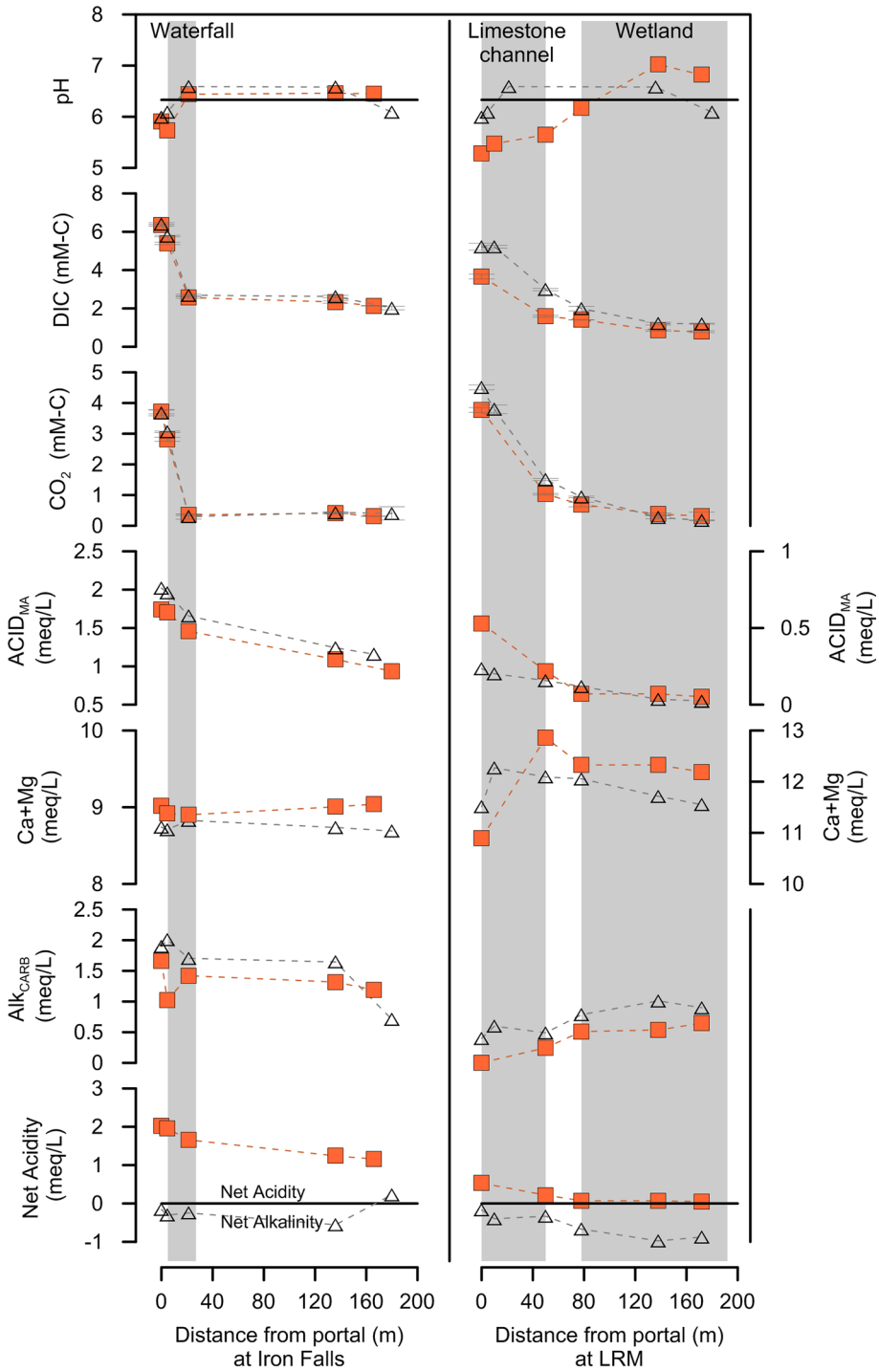

Fig. 4 Changes in measured and calculated parameters downstream from the portal at Iron Falls site (*left*) and LRM (*right*). 2012 data in *solid squares*, 2013 data in *open black triangle*. Physical features discussed in the text are shaded. The *horizontal line* for pH is at 6.33 (the pK_1 for carbonic acid): above the line HCO_3^- is the dominant DIC species, below the line dissolved CO_2 is the dominant DIC species

and sulfate reduction in the wetland. It is unlikely that carbonate minerals will precipitate at either site because the water was undersaturated with respect to calcite and dolomite. Although the two sites differ in physical configuration and the location of maximum flux, in all of the datasets obtained, the majority of the DIC lost was due to CO_2 evasion (Table 4; Fig. 7).

Comparison of CO_2 fluxes

Few studies have reported CO_2 evasion estimates associated with coal mine drainage although related studies have focused on DIC loss in streams receiving mine waters (Atekwana and Fonyuy 2009; Fonyuy and Atekwana 2008a), CO_2 degassing effects as part of mine drainge

Table 4 Calculated fluxes of DIC loss to CO_2 evasion

Site	Date	Discharge			CO_2 evasive flux				
		n	Mean (L/s)	SD (L/s)	% of DIC lost	CO_2 lost (kg-C/day)	CO_2 lost (t-CO_2/year)	By area (kg-C/day-m^2)	By area (t-CO_2/year-m^2)
Iron Falls	5/30/11	2	51.1	0.18	83	249	333	1.97	2.64
Iron Falls	7/27/11	3	51.0	2.00	87	272	364	2.16	2.89
Iron Falls	7/25/12	3	15.3	2.09	66	66.8	89.4	0.53	0.71
LRM	8/6/12	3	3.33	0.58	83	13.3	17.8	0.008	0.10

Fluxes based on DIC loss between sources and export from site. t-CO_2 is metric tons of CO_2. Flux normalized to area based on estimates from aerial photography (126 m^2 for Iron Falls, 1774 m^2 for LRM); the large area for LRM is due to the wetland. Annual evasion in terms of metric tons of CO_2

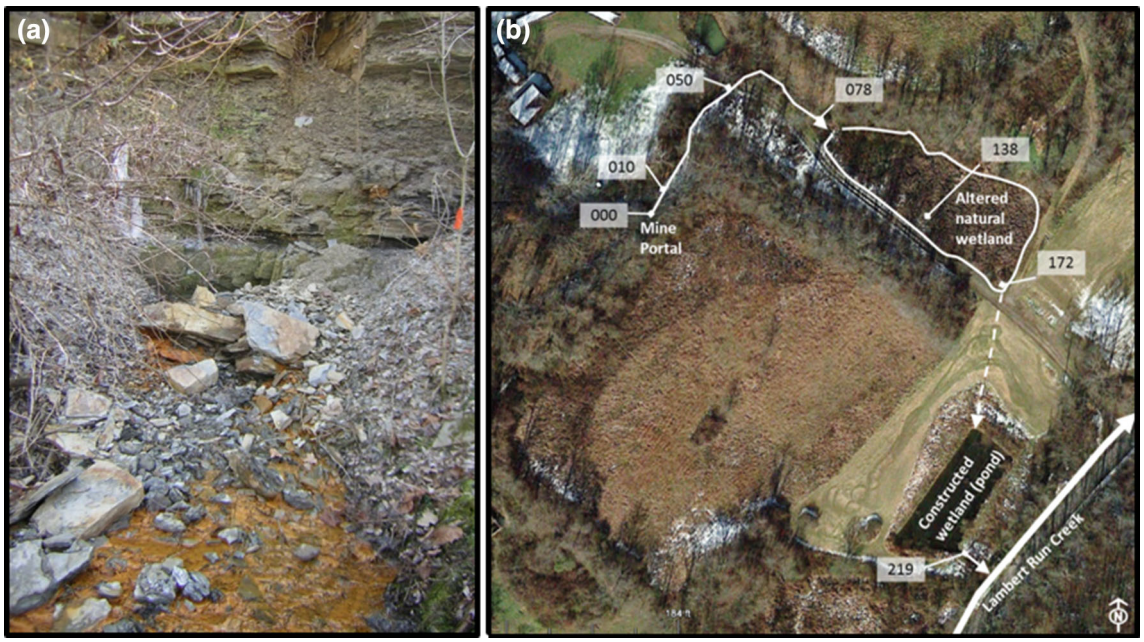

Fig. 5 LRM site. **a** The discharge portal (sample location LRM000); **b** approximate sampling locations on aerial imagery—*location labels* indicate meters from portal. Site location shown on Fig. 2a. Base image from Google Maps

treatment (Cravotta 2007; Geroni et al. 2012; Kirby et al. 2009), and long-term basin-scale estimates on CO_2 released due to mining (Raymond and Oh 2009). Although the goal of those studies was not to calculate the annual CO_2 flux, their data can be used as a comparison with the fluxes calculated in this study.

Fonyuy and Atekwana (2008a) measured 50 to >98 % loss of DIC in streams that received mine drainage. The greatest loss of DIC occurred in streams containing high concentrations of Fe and low concentrations of alkalinity because these parameters controlled the acidity-alkalinity balance, the system's ability to consume generated protons, and ultimately the pH of the water. In both Fonyuy and Atekwana's (2008a) study and the data presented in this study, the pH of the discharge was a principle control on the DIC fate. At pHs below the first pKa for carbonic acid (~6.3), the DIC is predominantly in the dissolved CO_2 species and may either degas or be exported as an aqueous species. Above that pH, dissolved export of HCO_3^- is the dominant fate of the DIC.

The loss of DIC via CO_2 degassing, and the consequent rise in pH, can cause the rate of oxidation of ferrous iron in mine waters to increase. Geroni et al. (2012) compared degassing via mechanical aeration and a cascades for the treatment of net-acid and net-alkalinity mine waters. The flux of CO_2 can be estimated from the discharge and CO_2 concentrations provided in that paper: using the change in dissolved CO_2 for each cascade and an average discharge of 29.5 L/s, a CO_2 flux of 0.0001–0.0002 Mt-CO_2/year can be estimated (Table 5). Geroni et al. caveat their CO_2 concentrations because they are based on colorimetric alkalinity data; however, the estimated fluxes from those

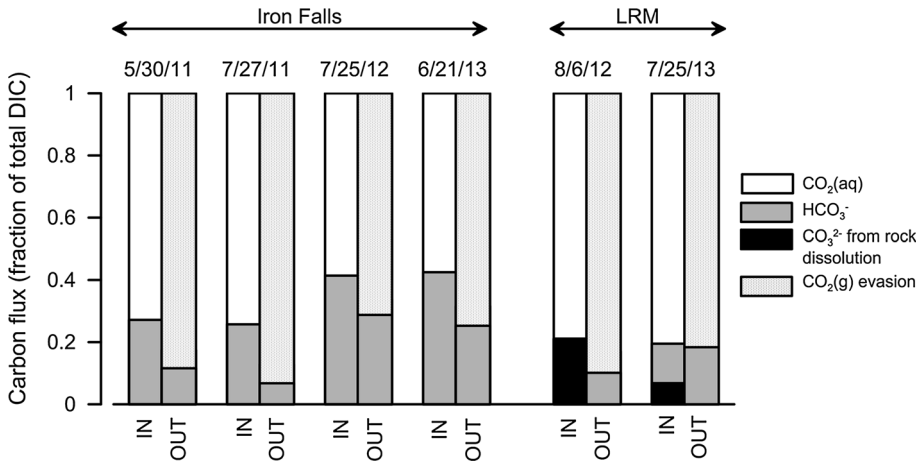

Fig. 6 The balance between input and output of DIC graphed in terms of fraction of the total source mass. The IN includes the source at the portal (DIC_{IN}) and in-stream reactions (DIC_{RX}) as per Eq. (5). Output includes export of dissolved DIC from site and CO_2 evasion. Calculations assume a constant discharge throughout the site

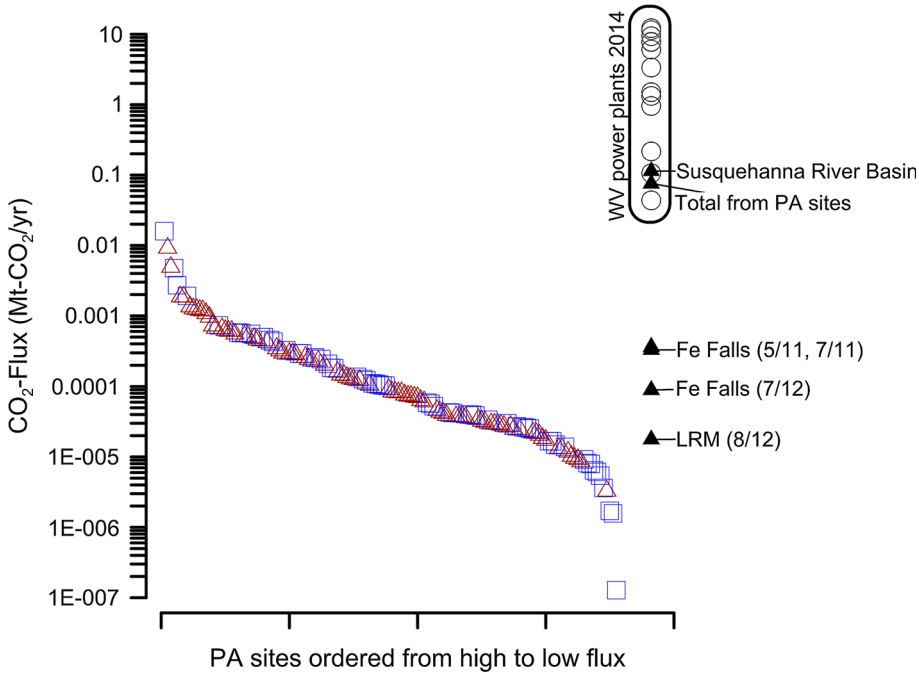

Fig. 7 Comparison of CO_2 fluxes from this study to (1) total flux estimated from 140 sites in Pennsylvania (Cravotta 2008; Kirby and Cravotta 2005); (2) the average annual flux for the Susquehanna River Basin over the past 100 years (Raymond and Oh 2009); and, (3) 2014 fluxes reported for West Virginia power plants (USEPA Air Markets Program Data 2014). The *blue squares* are for the Pennsylvania mine sites with pHs ≥4.5; the *red triangles* are for the mine sites with pHs <4.5. The WV power plant annual data from 2014 are in *gray* and *circled* as a group

data are within the range measured at the Iron Falls and LRM sites in this study (Table 5).

Cravotta (2008) conducted an extensive survey of coal mine water chemistry in Pennsylvania and provided data for 140 samples as supplemental material. In his 2008 analysis of the data, Cravotta focused on trace-element distributions and fluxes; this dataset included pH, alkalinity, and acidity that had previously been evaluated by Kirby and Cravotta (2005). The CO_2 flux was estimated for these data as follows: (1) for sites with pHs >4.5, the dissolved CO_2 concentration was estimated in PhreeqC (Parkhurst and Appelo 1999) using the full site data; and (2) for sites with pHs ≤4.5, the P_{CO2} was assumed to be 10^{-1} atm and the equilibrium dissolved concentration of CO_2 was estimated using a temperature-corrected Henry's Law constant. CO_2 concentrations can be estimated using either alkalinity or DIC data; an assumed concentration was necessary for the low-pH samples because they contain no alkalinity and no DIC data were obtained. The average P_{CO2} calculated for the high-pH samples was 10^{-1} atm.

The CO_2 evasive flux was then estimated by combining the CO_2 data with the discharge and assuming that degassing continued until CO_2 reached equilibrium with atmospheric concentrations. It is recognized that the degassing is unlikely to proceed to this concentration (Cravotta 2008; Geroni et al. 2012), but it provides a consistent endpoint for the calculations. Based on this calculation, the flux from the Pennsylvania mines ranged up to 0.016 Mt-CO_2/year (Fig. 7; Table 5) with a total flux of approximately 0.076 Mt-CO_2/year. Both the largest and

Table 5 Estimates of annual CO_2 fluxes

Data source	CO_2 flux (Mt-CO_2/year)	Location
Point sources		
Geroni et al. (2012)[a]	0.0001–0.0002	5 different aeration-cascade configurations, Strafford UK
Cravotta (2008)[b]		
Mean flux	0.0005	From supplemental data for mine drainage sites in PA
Median flux	0.0001	
Maximum flux	0.016	
All sites combined	0.076	
WV power plants		
Minimum flux	0.047	Data for 14 coal plants in 2014 (USEPA Air Markets Program Data 2014). The three smallest plants by emission are Pleasants Energy, LLC; Ceredo Generating Station; and Big Sandy Peaker Plant
Maximum flux	12.2	
Mean for the three smallest plants	0.12	
This study	0.000002–0.0004	
Regional estimate		
Raymond & Oh (2009)[c]	0.11	Susquehanna River basin

[a] Calculated from reported CO_2 loss and discharge data without correction for temperature or the CO_2-HCO_3 equilibrium

[b] Estimated from pH, alkalinity, discharge and temperature assuming that degassing progresses to atmospheric equilibrium

[c] Calculated from estimated century-long flux: (3.1 tg-C released in the past century)/100.M t-CO_2 is mega metric tons of CO_2

smallest fluxes of CO_2 were obtained from low-pH samples (Fig. 7).

A regional-scale perspective was provided by Raymond and Oh (2009) who estimated the long-term flux of CO_2 due to mining for the entire Susquehanna River basin. By modeling pH and alkalinity data, they estimated that 3.1 Tg of carbon were released to the river due to mining over the past century. The furthest downstream location used in this study was the USGS station on the Susquehanna River at Danville, PA. The drainage area of the river at this location (USGS National Water Information System 2014) covers a land area approximately 25 % of the size of the state of Pennsylvania. On an annual basis, this flux of carbon in this system averages 0.11 Mt-CO_2/year (Table 5). Raymond and Oh (2009) concluded that (1) their flux may be overestimated because they did not include CO_2 drawdown from silicate weathering, and (2) that current fluxes are far less than what was likely during peak periods of mining in the basin.

The fluxes from individual drainage sites cannot be directly compared to the estimates from the Susquehanna River basin, but it is notable that the average flux for the entire basin is only one order of magnitude greater than the C discharged from the single mine with the largest flux (Table 5). Although these two datasets have different sources of data, temporal range, spatial range, and estimation methods, the comparison suggests that carbon release due to mining has a measurable impact but is difficult to accurately estimate.

An additional comparison can be made between the fluxes from the mine waters and regional power plants. The 2014 CO_2 emission data were obtained from the USEPA Air Markets Program Data (USEPA 2014) for power plants located in West Virginia (WV), USA. The John E. Amos plant had the highest annual emissions (12.2 Mt-CO_2/year) which are approximately two orders of magnitude greater than the total emissions estimated from the mine drainage data set from Cravotta (2008). The three smallest WV plants generated between 0.04 and 0.22 Mt-CO_2/year; the estimated annual flux from the Susquehanna River Basin and the total flux from the Cravotta data set fall within this range (Fig. 7).

Limitations in estimating CO_2 evasion from mine waters

In their review of CO_2 evasion from terrestrial waters, Regnier et al. (2013) stated that the lack of direct CO_2 and DIC data limit the accuracy of flux estimates. In lieu of direct data, alkalinity has commonly been used to estimate the aqueous CO_2 by assuming that the total alkalinity equals the carbonate alkalinity (Cravotta and Trahan 1999; Kharaka et al. 2010; Keating et al. 2010; Raymond and Oh

Table 6 Estimate of flux at Iron Falls based on measured and estimated data

Sample date	Flux based on measured CO_2			Flux based on estimated CO_2			% Difference in flux[f]
	Portal CO_2[a] (mM)	Exit CO_2[a] (mM)	Flux[b] (kg-C/day)	Portal CO_2 (mM)[c]	Exit CO_2 (mM)[d]	Flux[e] (kg-C/day)	
5/30/11	4.14	0.34	249	5.78	0.014	305	23
7/27/11	4.39	0.36	272	5.75	0.015	303	11
7/25/12	3.73	0.31	66.8	7.68	0.016	122	82

[a] Measured CO_2 concentrations from carbonation meter

[b] Calculated from Eq. 5 incorporating carbonate species conversion

[c] C from pH and alkalinity data

[d] Estimated as temperature-corrected equilibrium with atmospheric conditions

[e] Calculated from the difference in portal and exit CO_2 concentrations

[f] The difference in the two fluxes divided by the measured-CO_2 flux

2009). This approach works well in carbonate-dominated waters but in mine waters it can result in a bias in the estimated CO_2 concentration. The presence of colloidal floccs of hydroxides in mine waters can contribute to the total alkalinity (Adams 2012; Vesper and Edenborn 2012) resulting in an overestimate of the CO_2 concentration. Filtering prior to an alkalinity titration may not remove all hydroxide-alkalinity because of the small size of the particles (Waychunas et al. 2005).

An additional limitation in quantifying CO_2 is the chemical disequilibrium of the mine waters after they are discharged from a portal. Once the mine water is exposed to the atmosphere, oxidation occurs concurrent with CO_2 degassing. The significance of these changes is illustrated by the change in field and laboratory measurements reported in the dataset from Pennsylvania (Cravotta 2008). Of the 140 mine-water samples, the pH increased from the field-measured pH to a laboratory-measured pH in 54 % of the samples and decreased in 44 %. The maximum changes in pH were 2.78 and –2.17. If everything else remains constant, a pH change of two units corresponds to a change in the estimated dissolved CO_2 by a factor of 100. The change in alkalinity between field and laboratory measurements has a lesser effect. Alkalinity decreased in 90 % of the samples with detectable concentrations. The greatest change in alkalinity was a sample with 6.2 meq/L in the field that decreased to 1.9 meq/L in the laboratory. The changes in pH and alkalinity were attributed to chemical instability, owing to atmospheric disequilibrium, at the time of collection (Kirby and Cravotta, 2005). Given that the laboratory measurements were made on aged samples, the impacts reported above constitute a worst-case comparison of field and laboratory values but it illustrates the challenges inherent in collecting mine water samples.

Fonyuy and Atekwana (2008b) evaluated post-sampling changes by tracking mine water chemistry in open reactors to determine the rates at which change occurs. They measured pH, alkalinity, DIC, iron, and stable carbon isotopes for 15–88 days after sample collection and found that the mine waters changed significantly more and lost more DIC than did the non-mine control samples. Both of these examples illustrate that even when careful sampling and processing protocols are followed, sample instability can contribute to inaccuracies in CO_2 evasion estimates in mine waters.

To evaluate the error in the calculations, the flux of CO_2 from Iron Falls was recalculated using the same method as used for the Pennsylvania data set: (1) alkalinity was used to estimate the dissolved CO_2 in the water, and (2) the CO_2 degassed until atmospheric equilibrium was obtained. When the flux is estimated using these assumptions, the resulting values are 11–82 % greater than the flux calculated from measured data (Table 6). This comparison suggests that the estimated fluxes from the Pennsylvania data (Fig. 7), which assume the water degasses to atmospheric equilibrium, are likely to be overestimated. However, without measured CO_2 concentrations at these sites, the exact extent of the error is unknown.

In contrast, CO_2 flux from mine waters may be underestimated when calculations exclude water samples with no detectable alkalinity. For example, the sample taken from the portal at LRM on 8/6/12 had a pH of 3.13 yet contained 3.7 mM DIC in the CO_2 form (Table 2). Fonyuy and Atekwana (2008b) also reported samples that had low pHs (3.72, 3.62) with high concentrations of DIC (17.7, 14.3 mM-C/L).

Assuming an average CO_2 concentration for ground water samples, as we did for the low-pH sample data, adds error to flux estimates. If the same CO_2 concentration assumption is applied to the high-pH sites, the estimated CO_2 flux obtained is approximately 40 % higher than the flux based on the results from PhreeqC. This suggests that assuming a constant CO_2 concentration may cause an overestimate in the total flux values. In contrast, the

exclusion of any low-pH high-DIC samples would result in an underestimation of the total CO_2 flux. If the low-pH samples are excluded from the total estimate, the annual flux for the Cravotta sites decreases from 0.076 Mt-CO_2/year to 0.043 Mt-CO_2/year, a 44 % change.

In addition to needing a more accurate means of determining CO_2flux from mine waters, more data are needed to estimate the percent of the carbon flux coming from geologic storage and evaluating how it changes over time. Sharma et al. (2013) parsed the carbon sources for three waters samples collected from the portal from Iron Falls using a two-endmember carbon-isotope mixing model. The model found that 65–82 % of the carbon being discharged at Iron Falls was from carbonate dissolution while the rest was of atmospheric origin. To obtain a good estimate of the release of geologically-bound carbon due to coal mining, these percentages require refinement. Additional data need to be obtained regarding the distribution of carbon sources vary (1) between sites, (2) in different geochemical settings (e.g., acid vs. alkaline mine waters), (3) with hydraulic conditions (e.g., storm vs. baseflow), (4) seasonally, and (5) over long-term time scales. With the limited amount of directly-measured CO_2 data reported for mine waters, it is not possible to meaningfully assess bias or error at this time.

Conclusions

The Iron Falls and LRM sites discharge mine drainage waters that contain measurable concentrations of CO_2 and DIC. The sites differ in physical layout and availability of in-stream carbon sources, but the evasion of CO_2 to the atmosphere exceeded the downstream export of dissolved DIC at both sites. The magnitude of the CO_2 evasive flux from these sites was comparable to values estimated from literature data for similar sites. These examples illustrate that coal mining can and does contribute to the release of geologically-bound carbon to the surface environment.

Limitations exist in obtaining accurate site-specific or regional estimates of carbon flux due to coal mining. Assumptions regarding the nature of alkalinity and the endpoint of degassing may result in overestimation of the flux while conversely a lack of direct CO_2 measurement in low-pH waters may result in underestimated fluxes. Regnier et al. (2013) concluded that more directly-measured data are necessary to understand CO_2 evasion from surface waters; the data from Iron Falls and LRM suggest this is also true, and perhaps even more so, for mine drainage waters. Furthermore, it is critical that the distribution of carbon sources to the discharge be quantified to a greater spatial and temporal extent. Without additional research on these topics, it may not be possible to determine if current flux measurements overestimate or underestimate the impact of coal mining on terrestrial carbon export.

The preliminary estimates of CO_2 flux from coal mine drainage suggest that these waters may be important to carbon cycling on a regional scale. Although considerable research has been conducted regarding the other environmental legacy of abandoned mine lands, their role in carbon cycling is poorly constrained and a better estimate of the CO_2 flux is necessary to determine the significance of the estimates reported herein.

Acknowledgments Thanks to Harry Edenborn for help throughout the project; Jill Riddell for help in collecting field data; to the J.F. Allen Memorial Muzzleloader Range for allowing access to the LRM site; and to John Eleyette of the Guardians of the West Fork for providing background information and facilitating access at the LRM site; and to useful suggestions made by Dr. Charles Cravotta and an anonymous reviewer. This work was performed as part of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), a collaborative initiative of the NETL, under the RES contract DE-FE0004000.

References

Adams JP (2012) The geochemistry and CO_2 flux of two mine discharges, Allegheny County Pennsylvania. Masters thesis, West Virginia University

Allison JD, Brown DS, Novo-Gradac K (1991) MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems

Anton Paar GmbH (2010) Instruction manual for CarboQC lab and at-line beverage carbonation meter. Document number: C26IB02I. Anton Paar, Graz, Austria, pp 67

Atekwana EA, Fonyuy EW (2009) Dissolved inorganic carbon concentrations and stable carbon isotope ratios in streams polluted by variable amounts of acid mine drainage. J Hydro 372:136–148

Buchanan TJ, Somers WP (1969) Discharge measurements at gaging stations. In: US Geological Survey Techniques of Water-Resources Investigations. Washington, DC

Butman D, Raymond PA (2011) Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geosci 4:839–842

Calmels D, Gaillardet J, Brenot A, France-Lanord C (2007) Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: climatic perspectives. Geology 35:1003–1006

Capo RC, Winters WR, Weaver TJ, Stafford SL, Hedin RS, Stewart BW (2000) Hydrogeologic and geochemical evolution of deep mine discharges, Irwin Syncline, Pennsylvania. In: Proceedings of the 21st West Virginia Surface Mine Task Force Symposium, Morgantown, WV, April 3–4 2000, pp 144–153

Cravotta CA III (2007) Passive aerobic treatment of net-alkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA. Min Water Environ 26:128–149

Cravotta CA III (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA: 1. Constituent quantities and correlations. Appl Geochem 23:166–202

Cravotta CA III, Trahan MK (1999) Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. Appl Geochem 14:581–606

Fonyuy EW, Atekwana EA (2008a) Effects of acid mine drainage on dissolved inorganic carbon and stable carbon isotopes in receiving streams. Appl Geochem 23:743–764

Fonyuy EW, Atekwana EA (2008b) Dissolved inorganic carbon evolution and stable carbon isotope fractionation in acid mine drainage contaminated streams: insights from a laboratory study. Appl Geochem 23:2634–2648

Geroni JN, Cravotta CA III, Sapsford DJ (2012) Evolution of the chemistry of Fe bearing waters during CO_2 degassing. Appl Geochem 27:2335–2347

Hennen RV (1912) Doddridge and Harrison Counties. WV Geological Survey, Wheeling

Hercod DJ, Brady PV, Gregory RT (1998) Catchment-scale coupling between pyrite oxidation and calcite weathering. Chem Geol 151:259–276

Keating EH, Fessenden J, Kanjorski N, Koning DJ, Pawar R (2010) The impact of CO_2on shallow groundwater chemistry: observations at a natural analog site and implications for carbon sequestration. Environ Earth Sci 60:521–536

Kharaka Y, Thordsen J, Kakouros E, Ambats G, Herkelrath W, Beers S, Birkholzer J, Apps J, Spycher N, Zheng L, Trautz R, Rauch H, Gullickson K (2010) Changes in the chemistry of shallow groundwater related to the 2008 injection of CO_2 at the ZERT field site, Bozeman, Montana. Environ Earth Sci 60:273–284

Kirby CS, Cravotta CA III (2005) Net alkalinity and net acidity 2: practical considerations. Appl Geochem 20:1941–1964

Kirby CS, Dennis A, Kahler A (2009) Aeration to degas CO_2, increase pH, and increase iron oxidation rates for efficient treatment of net alkaline mine drainage. Appl Geochem 24:1175–1184

Lerman A, Wu L (2006) CO_2 and sulfuric acid controls of weathering and river water composition. J Geochem Explor 88:427–430

Lorah MM, Herman JS (1988) The chemical evolution of a travertine-depositing stream: geochemical processes and mass transfer reactions. Water Resour Res 24:1541–1552

Millot R, Jé Gaillardet, Dupré B, Allègre CJ (2003) Northern latitude chemical weathering rates: clues from the Mackenzie River Basin, Canada. Geochim Cosmochim Acta 67:1305–1329

Palmer AN (2007) Cave Geology. Cave Books, Dayton

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, US Geological Survey Water Resources Investigation Report 99-4259

Pullman-Swindell (1977) Irwin Syncline Basin Mine Drainage Pollution Abatement Project, Operation Scarlift. Prepared for the PA Department of Environmental Resources, Pittsburgh

Raymond PA, Oh N-H (2009) Long term changes of chemical weathering products in rivers heavily impacted from acid mine drainage: insights on the impact of coal mining on regional and global carbon and sulfur budgets. Earth Planet Sci Lett 284:50–56

Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, Laruelle GG, Lauerwald R, Luyssaert S, Andersson AJ, Arndt S, Arnosti C, Borges AV, Dale AW, Gallego-Sala A, Godderis Y, Goossens N, Hartmann J, Heinze C, Ilyina T, Joos F, LaRowe DE, Leifeld J, Meysman FJR, Munhoven G, Raymond PA, Spahni R, Suntharalingam P, Thullner M (2013) Anthropogenic perturbation of the carbon fluxes from land to ocean. Nature Geosci 6:597–607

Rice KC, Herman JS (2012) Acidification of Earth: an assessment across mechanisms and scales. Appl Geochem 27:1–14

Sharma S, Sack A, Adams JP, Vesper DJ, Capo RC, Hartsock A, Edenborn HM (2013) Isotopic evidence of enhanced carbonate dissolution at a coal mine drainage site in Allegheny County, Pennsylvania, USA. Appl Geochem 29:32–42

Skousen J, Simmons J, McDonald L, Ziemkiewicz P (2002) Acid-base accounting to predict post-mining drainage quality on surface mines. J Environ Qual 31:2034–2044

Stookey LL (1970) Ferrozine - A new spectrophotometric reagent for iron. Anal Chem 42(7):779–781

Stumm W, Morgan JJ (1996) Aquatic chemistry, chemical equilibria and rates in natural waters, 3rd edn. John Wiley & Sons, New York

Telmer K, Veizer J (1999) Carbon fluxes, pCO2 and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives. Chem Geol 159:61–86

USEPA Air Markets Program Data (2014) http://www.epa.gov/ampd. Accessed 10 Sept 2015

USGS National Water Information System (2014) USGS 01540500 Susquehanna River at Danville, PA. http://waterdata.usgs.gov/nwis/uv/?site_no=01540500&agency_cd=USGS

Vesper DJ, Edenborn HM (2012) Determination of free CO_2 in emergent groundwaters using a commercial beverage carbonation meter. J Hydro 438–439:148–155

Vesper DJ, Edenborn HM, Billings AA, Moore JE (2015) A field-based method for determination of dissolved inorganic carbon in water based on CO_2 and carbonate equilibria. Water Air Soil Pollut 226:28

Waychunas GA, Kim CS, Banfield JF (2005) Nanoparticulate iron oxide minerals in soils and sediments: unique properties and contaminant scavenging mechanisms. J Nanopart Res 7:409–433

Webb JA, Sasowsky ID (1994) The interaction of acid mine drainage with a carbonate terrane: evidence from the Obey River, north-central Tennessee. J Hydro 161:327–346

Younger PL, Banwart SA, Hedin RS (2002) Mine water hydrology, pollution, remediation. Kluwer Academic Publishers, Dordrecht

Zhang DD, Zhang Y, Zhu A, Cheng X (2001) Physical mechanisms of river waterfall tufa (travertine) formation. J Sed Res 71:205–216