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Comparison of Methods for Estimating Carbon Evasion and Export Associated with a Coal Mine Discharge

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Introduction

The evasion of CO_2 from terrestrial waters plays a role in the global cycling of carbon but there are few datasets that have an accurate accounting of the flux. It has been shown that discharges from coal mines can have elevated concentrations of CO_2 due to sulfuric acid-driven dissolution of carbonate rock.

In this study we compared three methods for calculating the export dissolved inorganic carbon (DIC) and the evaluation of CO_2 from an abandoned-mine discharge in West Virginia. In general, the methods based on direct measurement of DIC and CO_2 were within an order-of-magnitude of the diffusive-flux model.

Surveying the stream channel at the LRM site. Looking upstream toward the portal.

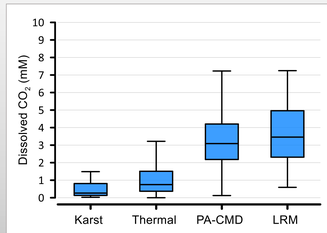
DIC and CO_2 in Coal Mine Drainage

In mine waters, pyrite (FeS_2) oxidizes and releases sulfuric acid (H_2SO_4). If the acid reacts with limestone ($CaCO_3$), it produces DIC in the form of CO_2 gas (Eq. 1) or bicarbonate (HCO_3^-; Eq. 2)

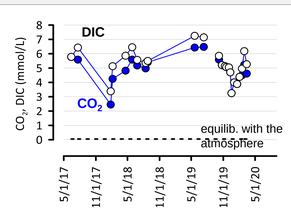
$$Eq.1.\ H_2SO_4 + 2CaCO_3 \rightarrow 2CO_2\,(gas) + 2H_2O + 2Ca^{+2} + SO_4^{-2}$$ dominates at pH < 6.3

$$Eq.2.\ H_2SO_4 + 2CaCO_3 \rightarrow 2HCO_3^- + 2Ca^{+2} + SO_4^{-2}$$ dominates at pH > 6.3

The DIC is the sum of the carbonate species (CO_2 + HCO_3^- + CO_3^{-2}); the dominant species is controlled by the pH of the system.



Dissolved CO_2 concentrations in different water types. Data from Mass and Wicks 2017 (typical karst, thermal), Cravotta 2008 (PA-coal mine drainage), and this study (LRM). The data clearly show that mine waters can have elevated concentrations of CO_2.



CO_2 and DIC concentrations at the source portal at the Lamberts Run site (LRM). Although CO_2 concentrations change over time they are not solely linked to discharge. The pH is the primary control on the relative concentrations of DIC and CO_2. DIC in the CO_2 form is lost as gas to the atmosphere while DIC in the HCO_3 form is exported offsite in the dissolved form.

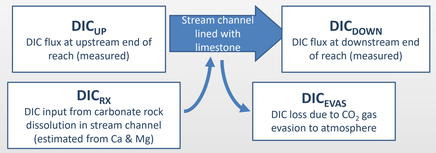
Methods for measuring CO_2 evasion and export from mine drainage

Flux was estimated using three methods:

Method #1, Source Flux is calculated from the discharge and the concentrations at the portal. CO_2 and DIC concentrations are measured directly in the field following procedures developed by Vesper and Edenborn (2012, 2015).

Source Flux (mass/time) = CO_2 concentration (mass/vol) x discharge (volume/time)

Method #2. Stream Flux is calculated over a stream reach and considers both upstream and downstream chemistries. This is based on the mass balance of DIC between two points in the stream.



Mass balance for DIC: $DIC_{UP} + DIC_{RX} = DIC_{DOWN} + DIC_{EVAS}$

Method #3. The diffusive flux model estimates rates evasion based on transport of CO_2 through the water column following the approach used by Maas and Wicks (2016). In this method, the flux is calculated as follows:

$$F_{CO2} = k\,K_O(P_{CO2w} - P_{CO2a})$$

Where k is the gas transfer velocity of CO_2 in cm h^{-1}, Ko is the solubility constant of CO_2 in water in mol m^{-3} atm^{-1}; P_{CO2} is the partial pressure of CO_2 in water (P_{CO2w}) and air (P_{CO2a}) in atm.

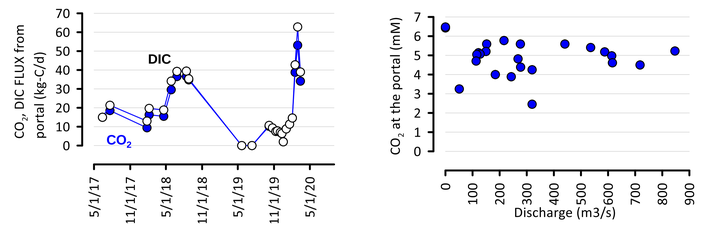
Ko is calculated based on temperature and salinity. The value for k is calculated as

$$k = C(Sc/600)^{-0.5}$$

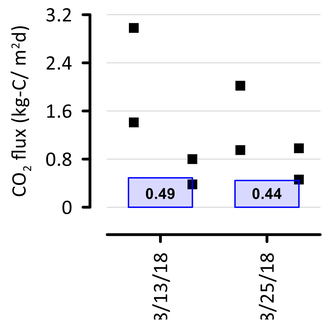
Where C is a constant (1.91 for wind speeds less than 3 m/s. Sc is the Schmidt number which is a function of temperature. The Schmidt number depends on the viscosity, diffusivity and density of the solution along the boundary layer.

Comparison: Methods #2 and #3 can be compared against each other by normalizing the method #2 flux by the area of the stream surface between the upstream and downstream locations used for the mass balance. To estimate this area the stream reach was surveyed and the stream width measured at 1 meter intervals.

Comparison of values obtained for CO_2 loss from mine discharge at LRM



The flux of CO_2 and DIC from the portal at LRM (left). Discharge and concentrations do not vary with each other (right) and therefore the temporal patterns of flux differ from those of concentration.



Methods #2 (mass balance, blue bar chart) and #3 (diffusion model, squares) were compared for two datasets collected in August 2018. Method #2 flux is calculated over the entire 0-40 m stream reach based on measured values of CO_2 and DIC. The black squares provide the high and low flux estimates obtained from the diffusion model – calculated for both the upstream and downstream end of the reach.

The Method #3 diffusion model generates higher CO_2 fluxes than those based on the mass flux from the detailed measured concentrations.

Method	Advantages	Limitations
Method 1. Source Flux	Single point measurement	Direct measurement of CO_2 is most accurate at low-pH and high-CO_2 waters; does not account for degassing at the surface
Method 2. Stream Flux	Mass balance can be used to identify shifts in chemical species and types of DIC loss	CO_2 and DIC concentration vary with stream reach, depth and cross-section. Need to know the area of the reach.
Method 3. Diffusion model	No direct measurements of CO_2 or DIC are needed; can be broadly applied	Does not account for changes over distance or final equilibrium CO_2

Summary

- CO_2 is high in coal mine water relative to other natural waters
- CO_2 concentrations change over time
- CO_2 evasion and flux can be calculated using different means but with some limitations
- Direct measurements of CO_2 are critical for low-pH high-pH waters; Although CO_2 can be estimated from the DIC and pH, high-CO_2 water typically lose mass due to degassing prior to analysis.
- Limestone used to remediation the mine water can dissolve and release DIC into the system

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