The release of dissolved inorganic carbon (DIC) and CO₂ from coal mine drainages

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First. The conclusion.



Data from 190 sites in PA and WV (2010 to 2024)

https://share.america.gov/english-idiom-canary-coal-mine/

We've known about gasses in mines for a long time....



so why are we interested in this?



https://share.america.gov/english-idiom-canary-coal-mine/

Carbon & fossil fuels: in the simplest reaction



$CH_2O + O_2 = CO_2 + H_2O + energy$

Photosynthesis



https://share.america.gov/english-idiom-canary-coal-mine/

Carbon & fossil fuels: in the simplest reaction



$CH_2O + O_2 = CO_2 + H_2O + energy$

Combustion of fossil fuels, compost, lunch...





 $FeS_2 \dots \rightarrow H_2SO_4 \dots$







 $FeS_2 \dots \rightarrow H_2SO_4 \dots$

 $CaCO_3 + H_2SO_4 \rightarrow$







Dissolved Inorganic Carbon (DIC)











Why might we care about this CO₂ gas?

Most limestone dissolves because of carbonic acid:

$$CaCO_{3} + H_{2}CO_{3}^{*} = Ca^{+2} + 2HCO_{3}^{-}$$
Young carbon
Old carbon



Why might we care about this CO₂ gas?

But when sulfuric acid is the driver, only old carbon is involved.

$$CaCO_{3} + H_{2}SO_{4} = Ca^{+2} + H_{2}CO_{3} + SO_{4}^{-2}$$
Young carbon
Voung carbon
Old carbon



But... how we estimate CO₂ in mine waters doesn't always work.

- Assumes that alkalinity is carbonate
- Samples must have measurable alkalinity
- DIC analyzers do not keep gas in
- Titrations can be challenging in chemically unstable waters

 $P_{\text{CO2}} = \frac{a_{\text{H}} a_{\text{HCO3}}}{(K_1 K_{\text{CO2}})}$





Anton Paar CarboQC Carbonation meter

- Built for the soda & brewing industries
- CO₂ and DIC measured in field or in lab





Vesper DJ, Edenborn HM (2012) Determination of free CO₂ in emergent groundwaters using a commercial beverage carbonation meter. J Hydro 438–439(0):148-155. https://doi.org/10.1016/j.jhydrol.2012.03.015

West Virginia University.

Back to the data.. Is this a lot?







Compare with karst & mineral springs



Compare with karst & mineral springs



Old Sweet Spring, Monroe County, WV



WestVirginiaUniversity.

CO₂ can be present over a wide range of pH values





The species of DIC depends on the pH

$$DIC = CO_2 + HCO_3 + CO_3^{-2}$$





At low pHs, no alkalinity exists, so P_{CO2} can't be estimated from the bicarbonate. But there can still be CO_2 present.





Is this important in the grander scheme of things?

<u>**CO**</u>₂ evasion – how much do mines contribute? And does that matter on a regional or global scale?



Our CO₂ numbers v. terrestrial freshwaters?

Raymond *et al. (2013) Nature* **503:** 355-359 doi:10.1038/nature12760

Global carbon dioxide emissions from inland waters





Our CO₂ numbers v. terrestrial freshwaters?



WestVirginiaUniversity.

Is CMD important to CO₂ evasion? – *we don't even know if we are underestimating or overestimating the issue*.

- Number of mine discharges –chemistry & flow
- Low pH waters underrepresented in most datasets
- Non-point sources
- Degassing in mine or pipelines prior to discharge
- Seasonal & storm variability
- Do we degas to atmospheric levels



Is this important in the grander scheme of things?

 CO₂ evasion – how much do mines contribute? And does that matter on a regional or global scale?

- BUT... can we utilize the CO₂ for treatment?
 - Can we alter treatment systems to cut back on CO₂ evasion... dissolving more limestone... and even gain alkalinity?



Dr. Bob Hedin

Top 3 take-away points

- Many mine waters have high concentrations of DIC which either degases (low pH) or is exported offsite as dissolved alkalinity
- CMD may be important in understanding terrestrial water CO₂ evasion (but we don't know for sure)
- Maybe the CO₂ can be harnessed in the CMD treatment process



The bigger picture – beyond mine waters



https://wnpa.org/the-history-of-carlsbadcaverns-national-park/



https://www.researchgate.net/publication/27953251 2_Climate_Diagnostics_of_Future_Water_Resources_i n_BC_Watersheds/figures?lo=1



The bigger picture – beyond mine waters

1986.. Romania



Isolated for > 5 million years

Has more than 33 endemic species





Thanks for listening.



Frasassi Cave Italy

https://www.hoteltermedifrasassi.it/en/discover-the-frasassi-caves.php

