

Neutralization of acid mine drainage by carbonate alkalinity is a significant CO₂ emission source for mining of sulfide-rich metal ores

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The transition to net-zero greenhouse gas emissions requires a significant increase in metal mining. Comprehensive understanding of mining industry carbon footprints is therefore essential for guiding pathways towards net-zero [1]. The neutralization of acid mine drainage (AMD) by carbonate alkalinity is a poorly constrained indirect source of mining industry CO₂ emissions [1]. Here we quantify the magnitude of this CO₂ emission source from metal mining activities within the Odiel and Tinto river catchments (Spain). These rivers are among the most heavily impacted by AMD worldwide, characterized by low pH (2 to 4) and high concentrations of dissolved 'acidic' metals (Al, Fe and Mn) [2, 3, 4]. Both rivers drain into the Ria de Huelva estuary, where their acidity is neutralized by seawater-derived carbonate alkalinity (HCO₃⁻, CO₃²⁻) leading to CO₂ emissions (eqn. 1).



Field data and laboratory experiments are used to constrain the consumption of seawater-derived alkalinity per volume of AMD-impacted river water discharge into the estuary. The resulting CO₂ emissions are then estimated using the ratio of total alkalinity to carbonate alkalinity (HCO₃⁻ and CO₃²⁻) calculated for local seawater.

The results show that the magnitude of seawater alkalinity consumed (hence CO₂ emitted) in the estuary is proportional to the riverine input flux of acidic species (H⁺, Al³⁺, Fe³⁺, Fe²⁺, Mn²⁺). River-derived acidity is dominated by acidic metals (Al, Fe and Mn; 83 to 97%) with only minor contributions from free H⁺ ions. Literature timeseries data of riverine dissolved Al, Fe and Mn fluxes into this estuary [2, 3, 4] are used to estimate annual CO₂ emissions of 20 to 90 Gg/yr. These CO₂ emissions are estimated to be ca. 20-1400% the size of conventional carbon footprints for the mining activities in these catchments, highlighting the importance of this poorly considered emission source.

[1] Azadi et al. (2020), *Nature Geoscience* 13, 100-104

[2] Olias et al. (2006), *Applied Geochemistry* 21, 1733-1749

[3] Galván et al. (2016), *Journal of Hydrology* 540, 196-206