Anthropogenic alteration of dissolved inorganic carbon fluxes from watersheds

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River Bicarbonate

- Bicarbonate (HCO$_3^-$) is the most abundant anion in water
- It is generated mostly through chemical weathering, which is an atmospheric CO$_2$ sink
- Since riverine anion/cations budget must balance it is linked to major cation cycle (Ca, Mg)
- It provides the majority of buffering capacity to streams/rivers and therefore critical to pH of streams and rivers
- Can counteract local/regional ocean acidification
Chemical Weathering, Atmospheric CO$_2$ and Rivers

Soil Minerals

- CaCO$_3$
- CaAl$_2$Si$_2$O$_8$

Atmospheric CO$_2$

- $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{+2} + 2\text{HCO}_3^-$
- $\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{+2} + 2\text{HCO}_3^-$

Riverine Export to the Ocean
Controls on Contemporary Chemical Weathering

- Climate
- Soil Mineralogy
- Physical Weathering
- Biology
  - Strong linkages back to climate
Fig. 5. Diagram showing for each river of this study, the contribution (as % of concentrations in mg L$^{-1}$ of river water) of the different reservoirs. Rivers are ranked from left to right following the contribution of silicate weathering to total dissolved load. The atmospheric contribution corresponds to bicarbonate ions of atmospheric origin derived from carbonate and silicate weathering. The rain contribution corresponds principally to Na and Cl ions derived from seasalt dissolution.
Controls on Chemical Weathering Rates - Physical Erosion

Chem = 0.39 (Phys)^0.66

Millot et al. 2002
Controls on Chemical Weathering Rates - Climate

Millot et al. 2002

Gislason et al. 2009

Raymond and Oh. 2007
Controls on Chemical Weathering Rates-Biology

• Plants
  – Rates of NPP, root respiration, organic acid exudation, mining minerals, soil development

• Microbes
  – Decomposition rates, soil development

Roelandt et al 2010
Anthropogenic Controls on Contemporary River Carbonate Fluxes

• Direct
  – Land management
    • Alter hydrology
    • Alter soil properties
    • Alter acid/base input
    • Alter species
    • Alter sediment loads

• Indirect
  – Climate change
    • Abiotic
      – Temperature, Precipitation, Redistribution of rainfall patterns (spatial and temporal)
    • Biotic
      – Alter NPP, soil respiration, microbial rates, species changes
Human Influences

• There is attention to the climatic influences on chemical weathering
  – By extension the influences of climate change on weathering
• By comparison there is inadequate attention to the direct impact of humans on river bicarbonate fluxes and chemical weathering.
1980’s Carbon Budget

Sarmiento and Gruber (2002)
Papers on Chemical Weathering

• “Chemical Weathering” 2013 papers
Land Use Studies are few

• “Chemical Weathering” 2013 papers
  – 18 urban
  – 56 agriculture
Land Management
Agricultural Liming

Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin
Khadija Semhi, Philippe Amiotte Suchet, Norbert Clauer, Jean-Luc Probst
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Received 29 January 1999; accepted 22 June 1999
Editorial handling by C. Reimann

Abstract
Knowledge of the impact of N-fertilizers on the weathering-erosion processes of soils in intensively cultivated regions is of prime importance. Nitrification of NH$_4^+$ fertilizers produces HNO$_3$ in the basin of the Garonne river, enhancing soil degradation. Their influence on the weathering rates was determined by calculating the consumption rate of atmospheric/soil CO$_2$ by soil weathering and erosion, and its contribution to the total dissolved riverine HCO$_3^-$. This contribution was found to be less than 50% which corresponds normally to a complete carbonate dissolution by carbonic acid, suggesting that part of the alkalinity in the river waters is due to carbonate dissolution by an acid other than carbonic acid, probably HNO$_3$. © 2000 Elsevier Science Ltd. All rights reserved.

- Argued that nitrification of NH$_4^+$ from fertilizer produces acid that weathers minerals.
- Farmers lime fields in-order to maintain soil pH (counterbalance nitrification)
Agricultural Liming
Oh and Raymond 2005

- Lime application rates in U.S. of 10-30g CaCO₃ m⁻² yr⁻¹

Figure 7. A schematic diagram of the fate of applied CaCO₃.
Agriculture Liming

- Approximately 25% of river bicarbonate in large (5,000-10,000 km²) intensively agriculture watersheds is from liming.

Figure 9. (a) Potential and estimated export of bicarbonate due to liming from the two most agricultural watersheds (03339000 and 03344000) during 1971–1987, and (b) riverine bicarbonate export as a function of agricultural percentages of the selected 12 watersheds and the entire Ohio River basin.
United States Lime Use and River Bicarbonate

• 30 Tg of CaCO₃ is applied in the United States every year
  – Is equivalent to a maximum of 7.5 potential Tg of HCO₃⁻ per year
• Total Riverine HCO₃⁻ flux from U.S. is 35Tg per year.
  – Max potential liming contribution is ~20%
  – Oh and Raymond conclude ~75% of lime exports as bicarbonate, so potential riverine contribution of ~15%
Granitic Agricultural sites
Brittany France

- Cation losses from ag-end members much higher than other granitic catchments

Pierson-Wickman et al. 2009
Relic Agricultural

Intensifying Weathering and Land Use in Iron Age Central Africa

Germain Bayon,* Bernard Dennielou, Joël Etoubleau, Emmanuel Ponzeverya, Samuel Toucanne, Sylvain Bermell

About 3000 years ago, a major vegetation change occurred in Central Africa, when rainforest trees were abruptly replaced by savannas. Up to this point, the consensus of the scientific community has been that the forest disturbance was caused by climate change. We show here that chemical weathering in Central Africa, reconstructed from geochemical analyses of a marine sediment core, intensified abruptly at the same period, departing substantially from the long-term weathering fluctuations related to the Late Quaternary climate. Evidence that this weathering event was also contemporaneous with the migration of Bantu-speaking farmers across Central Africa suggests that human land-use intensification at that time had already made a major impact on the rainforest.

Intensifying Weathering and Land Use in Iron Age Central Africa
Germain Bayon et al.
Science 335, 1219 (2012);
DOI: 10.1126/science.1215400
Urban/Sub-urban Systems

- Small watersheds in Connecticut
- Different discharge flux relationships
- Slope of urban line ~8x greater than forest and ~2x more than agricultural

Barnes and Raymond 2009
Urban/Suburban Systems

- Annual yields also greater
- Urban: nitrification, high CO$_2$ in lawns, altered hydrology, cement, septics and sewers (import of cations in food/feed)
Atmospheric CO₂ consumption by chemical weathering in North America

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Abstract

Runoff, lithology and land cover were identified as the major predictors of the riverine bicarbonate fluxes and the associated CO₂ consumption. Other influence factors, e.g. temperature, could not be established in the models. Of the distinguished land cover classes, artificial surfaces, dominated by urban areas, increase bicarbonate fluxes most, followed by shrubs, grasslands, managed lands, and forests. The extrapolation results in an average specific bicarbonate flux of 0.3 Mmol km⁻² a⁻¹ by
The role of altered hydrology
Land Management

Changes in climate and land use have a larger direct impact than rising CO₂ on global river runoff trends

• Analysis of sub-watersheds of Mississippi from Raymond et al. 2007
All Sites

A

Discharge at Avg. Precip. (m yr⁻¹)

Δ Discharge (m yr⁻¹)

Δ Precip. (m yr⁻¹)

r²=0.60, p<0.0001
y=1.10x-0.019

Agricultural Sites

B

Discharge at Avg. Precip. (m yr⁻¹)

Δ Discharge (m yr⁻¹)

Δ Precip. (m yr⁻¹)

r²=0.78, p<0.0001
y=1.03x+0.023

C

r²=0.41, p<0.0001
y=0.74x-0.003

D

r²=0.14, p=0.028
y=0.534+0.030
Not only is the amount of water from the Mississippi increasing, but the proportion of water from agricultural land cover is also increasing—changing the chemistry of the River.
Updated Data!!

- Bicarbonate fluxes from the Mississippi have increased by 50% in the last 50 or so years.
- Last 3 years 100%
- Increases are partly due to climate, liming, changes in ag hydrology, potentially more
River Recovery from Acid Mine Drainage.

- Recovery of rivers from Acid Mine Drainage
- Greater than a doubling of alkalinity yields for Susquehanna (discharge of ~35 km$^3$ yr$^{-1}$)
  - ~2.5 to 6 g C m$^{-2}$ yr$^{-1}$

Raymond and Oh (2009)
Alterations in Climate

• Watershed can respond to both temperature and precipitation
  – Which one dominates will probably be dependent on the current state of ecosystem
  – Abiotic and Biotic responses

Gislason et al. 2009

Raymond and Oh. 2007
Modeling the Climate Response
Mackenzie River

- 50% Increase
- 40% due to climate
  - Temperature and water throughput
- 60% vegetation responses to climate
  - CO₂ Fertilization

Figure 3 | Atmospheric CO₂ consumption by weathering in the Mackenzie watershed, at 355 ppmv (reference simulation) and 560 ppmv (2 x CO₂ simulation), calculated by the B-WITCH model. Total carbonate and total silicate consumption.

High sensitivity of the continental-weathering carbon dioxide sink to future climate change

E. Beaulieu¹, Y. Goddéris¹*, Y. Donnadieu², D. Labat¹ and C. Roelandt¹,⁴
Impact of Biological Process on River Carbonate Fluxes

• This has long been the holy grail of chemical weathering research
• Hope in new integrating high resolution monitoring programs
Young Woman’s Creek PA
90% Forested

<table>
<thead>
<tr>
<th>Year Day</th>
<th>Temperature (°C)</th>
<th>Flux at Avg Flow (mg CaCO₃ m⁻² d⁻¹)</th>
<th>NDVI (%)</th>
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Graph showing temperature, flux at average flow, and NDVI data over the year.
Piceance Creek, CO
40% Evergreen, 40% Scrub/Shrub

![Graph showing temperature, flux avg flow, and NDVI values over a year.](image-url)
How big is the Anthropogenic Signal?

Direct

• All signs seem to point to land use change/management increasing river carbonate fluxes
  – Probably continue to accelerate as we need to grow more food
  – Changing to cropland generally increases discharge
• Mississippi fluxes have gone up ~50% (100% in past 3 years)
• Changjiang (Yangtze) River: 15-20% of fluxes anthropogenic (Chetelat et al. 2008)
• Anthropogenic yields of 1-2 g C m$^{-2}$ yr$^{-1}$ on urban and agricultural land cover seem reasonable.
  – Global land cover anthropogenic flux of 0.04-0.08 Pg C.
    • 10-20% of Global DIC flux
How big is the Anthropogenic Signal? In-Direct- Temperature: Northern Latitudes

• Growing body of evidence that northern latitudes will have positive response to increase in temperature/climate change
  – Beauliu et al. Mackenzie River. ~1.75 g C m^{-2} yr^{-1}
  – Gislason et al. Iceland. ~1 g C m^{-2} yr^{-1} per degree C
  – Striegl et al. Yukon River.
  – Tank et al. in press
  • Larger fluxes from Arctic watersheds with discontinuous permafrost than permafrost
In-Direct Precipitation

• Studies now argue that DIC export from watersheds is “chemostatic”
  – Concentrations vary by a factor of 2-3 in face of orders of magnitude change in discharge
• By extension it is argued that water fluxes are a primary determinant of anion/cation fluxes
  – The response to increased precipitation will be larger fluxes of cation/anions to the ocean
How big is the Anthropogenic Signal? In-Direct- Precipitation

- Global Climate Sensitivity of \(~0.03\ \text{g C m}^{-2} \\text{yr}^{-1}\) per cm precip year
- Current global average river fluxes = 2.75 g C m\(^{-2}\) yr\(^{-1}\)
- Suggests 1-1.5% increase for every cm increase

Raymond et al. in prep
Anthropogenic Alteration of Riverine Carbonate Fluxes

Conclusion

• Direct: All signs seem to point towards an increase in flux
  – Probably a significant part of current record is already anthropogenic signal
  – The increase in flux could easily be on the order of $\sim 1 \text{ g C m}^{-2} \text{ yr}^{-1}$
    - Average global flux is currently $\sim 2.75 \text{ g C m}^{-2} \text{ yr}^{-1}$

• InDirect
  – High latitude temperature sensitivity
  – Global Precipitation Sensitivity
Thank You

• Funding Sources: NSF, NASA
Chemical Weathering and Paleo-CO$_2$

Berner 1997