Silicate weathering and CO$_2$ consumption rates: new insights from rivers of the Primorskii Krai (Russia)

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This study examined the chemical composition of mid-latitude river waters in basaltic environments in Primorskii Krai area to characterize the silicate rocks weathering and $CO_2$ consumption rate associated with basalt weathering. The mid-latitude rivers carry a disproportionally high dissolved inorganic carbon flux with a relatively small amount of freshwater discharge.

Average $HCO_3^-$ fluxes (Tmol·yr$^{-1}$) in the three latitudinal zones [W.-J. Cai et al., 2008]
**Geographical setting**

*Razdolnaya R.* originates in northern Manchuria in China, crossing the border of Russia and debouches into Amurskii Bay, the East Sea/Japan Sea. *Partizanskaya R.* originates on the southern spurs of the Sikhote Alin Ridge and debouches into Nakhodka Bay, the East Sea/Japan Sea.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Drainage basin area, km²</strong></td>
<td>16430</td>
<td>4140</td>
</tr>
<tr>
<td><strong>Water discharge, m³/s</strong></td>
<td>3.2 – 403</td>
<td>3.5 – 80</td>
</tr>
<tr>
<td><strong>Average annual water discharge, km³/yr</strong></td>
<td>2.27</td>
<td>1.33</td>
</tr>
<tr>
<td><strong>Average annual runoff, mm/yr</strong></td>
<td>135</td>
<td>320</td>
</tr>
<tr>
<td><strong>Total dissolved solids (TDS), mg/l</strong></td>
<td>65 – 200</td>
<td>68 – 132</td>
</tr>
<tr>
<td><strong>Si concentration, µmol/l</strong></td>
<td>106 – 250</td>
<td>170 – 240</td>
</tr>
</tbody>
</table>
Geological setting

Razdolnaya R. basin: right bank is underlain by volcanic rocks dominated by olivin and alkaline basalts. Basalts layers are interbed with alumosilicates; left bank consists of sedimentary and clayey rocks. Clayey rocks are interbed with tuffs, limestones and coals.

1,2 - alluvial deposit; 3,4 - sedimentary rock; 5 - basalt (Shufan complex); 6 - sedimentary rock; 7 - volcanogenic and terrigenic rock; 8 - sedimentary rock

[A simplified geological map of Razdolnaya R. basin modified from [State Geological Map of the Russian Federation...., 2011].]
Razdolnaya and Partizansksys rivers draining basically silicate rocks. One of the most striking differences between geology of these rivers is the exposure of reef mass of limestones in lower reach of Partizanskaya R. basin.

1 - alluvial deposit; 2 - basalt; 3 - sedimentary rock, tuff; 4,5 - sedimentary and volcanogenic rock; 6 - trachyte/rhyolite; 7 – gneiss; 8 - sedimentary rock; 9 – intrusive (granite, plagiogranite); 10 – Permian limestones

[A simplified geological map of Partizanskaya R. basin modified from [State Geological Map of the Russian Federation....., 2011].]
The lower reaches of Razdolnaya and Partizanskaya rivers were sampled and analyzed for their major elements in 2011-2012 in different flow stages. Major elements ($Cl^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) were analyzed by ion chromatography (LC-20A, Shimadzu). $HCO_3^-$ concentrations were calculated from measured pH and TA.
Relative equivalent concentrations of major ions (% eqv)

% eqv (anions) + % eqv (cations) = 100 %

\[ NICB (\%) = \frac{(TZ^+ - TZ^-)}{TZ^+} \times 100 \text{ is } \pm 5\% \]

\[ TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}; \quad TZ^- = Cl^- + 2SO_4^{2-} + HCO_3^- \]
Molar elemental ratios of Razdolnaya and Partizanskaya rivers

Rock weathering

**Carbonates:** \( \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{HCO}_3^- \)

**Silicates:** \( \text{CaSiO}_3 + 2\text{CO}_2 + 3\text{H}_2\text{O} = 2\text{HCO}_3^- + \text{Ca}^{2+} + \text{H}_4\text{SiO}_4 \)
These diagrams are interpreted as mixing between **carbonate end-member** \((\text{Ca/Na, Mg/Na, HCO}_3/\text{Na} = 60, 30, 120)\) and **silicate end-member** (the least Ca-enriched samples)
Silicate weathering and CO$_2$ consumption rate

I. Inverse method

Well-established inverse method [Gaillardet et al., 1999; Dessert et al., 2003; Han & Huh, 2009] based on mass balance to apportion the river dissolved cations to rain (cyclic salt) and weathering input from evaporite, carbonate and silicate rocks.

1. **Rain contribution:** is calculated using local rain composition at Primorskaya station (43.48N; 132.39E) nearest the study area [monitoring site of the Acid deposition Monitoring network in East Asia (EANET)].

2. **Evaporite weathering input:**

\[
\begin{align*}
\text{Cl}_{\text{evaporite}} &= \text{Cl}_{\text{river}} - \text{Cl}_{\text{atm}} = \text{Na}_{\text{evaporite}} \\
\text{SO}_4_{\text{evaporite}} &= \text{SO}_4_{\text{river}} - \text{SO}_4_{\text{atm}} = \text{Ca}_{\text{evaporite}}
\end{align*}
\]

**X/Cl ratios in local atmospheric precipitations**
3. **Silicate weathering input:**

\[
Na_{sil} = Na_{river} - Na_{atm} - Na_{evaporite}
\]

\[
K_{sil} = K_{river} - K_{atm}
\]

The situation is complicated for Ca and Mg by their dual sources: both carbonate and silicate. Basalt may be the major source of Mg, since carbonates are relatively depleted in Mg:

\[
Mg_{sil} = Mg_{river} - Mg_{atm}
\]

We assume the lowest \(Ca/Mg = 0,9\) (*Razdolnaya R., high flow*) to be the basalt end-member composition:

\[
Ca_{silicate} = 0,9 \times Mg_{silicate}
\]

The Ca/Mg ratio of our basalt end-member is consistent with local rock data of volcanic plateau in northeast Asia (0.88-1.28) [*Chen et al., 2007*].

The remaining Ca after subtracting the rain, evaporite, and silicate components are attributed to carbonate:

\[
Ca_{carbonate} = Ca_{river} - Ca_{atm} - Ca_{evaporite} - Ca_{silicate}
\]
The contribution of the different reservoirs in surface water of Razdolnaya R. and Partizanskaya R.

Silicate contribution to total dissolved cations predominates in all samples reaching above 50%.
Calculation of silicate weathering rate and CO$_2$ consumption rate

1. **Silicate weathering rate (TDS$_{cations}$):**
   \[ TDS_{cations} = \Phi_{Na_{sil}} + \Phi_{K_{sil}} + \Phi_{Mg_{sil}} + \Phi_{Ca_{sil}} \]
   (1.4 and 4.3 tons·km$^{-2}$·yr$^{-1}$ for Razdolnaya and Partizanskaya river basins, respectively)
   \( \Phi_{X_{sil}} \) is the surface specific fluxes derived from silicate weathering of each cation

2. **The CO$_2$ consumption rate (\( \phi_{CO_2} \)):**
   \[ \phi_{CO_2, \text{gyp}} = \phi(Na_{sil} + K_{sil} + 2Mg_{sil} + 2Ca_{sil}) \times \text{Runoff} = Sil_{gyp} \times \text{Runoff} \]
   \( Sil_{gyp} \) (meq/l) is the silicate fraction of total cations assuming all SO$_4$ is from gypsum weathering

   \[ \phi_{CO_2, \text{sulfide}} = \phi(Na_{sil} + K_{sil} + 2Mg_{sil} + 2Ca_{sil} - 2SO_4) \times \text{Runoff} = Sil_{sulfide} \times \text{Runoff} \]
   \( Sil_{sulfide} \) (meq/l) is the silicate fraction of total cations assuming all SO$_4$ is from oxidation of sulfide minerals

   \( \phi_{CO_2, HCO_3^-} \) – convert HCO$_3^-$ concentrations directly to CO$_2$ uptake rates
**CO₂ consumption rate (φCO₂) (10⁴mol·km⁻²·yr⁻¹)**

<table>
<thead>
<tr>
<th>River</th>
<th>Runoff, mm·yr⁻¹</th>
<th>φCO₂, gypsum</th>
<th>φCO₂, sulfide</th>
<th>φCO₂, HCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Razdolnaya</td>
<td>138</td>
<td>7.6</td>
<td>5.9</td>
<td>7.8</td>
</tr>
<tr>
<td>Partizanskaya</td>
<td>320</td>
<td>21.2</td>
<td>18.5</td>
<td>21.9</td>
</tr>
<tr>
<td>Duman</td>
<td>273</td>
<td>14.4-24.0</td>
<td>12.2-22.5</td>
<td>16.3-27.8</td>
</tr>
<tr>
<td>M. Central</td>
<td>478</td>
<td>35.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sao Miguel</td>
<td>734</td>
<td>56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Java</td>
<td>4052</td>
<td>641</td>
<td></td>
<td></td>
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</tbody>
</table>

**In summary:**

- (φCO₂) of Razdolnaya and Partizanskaya river basins are on the lower end of worldwide rivers draining basaltic watersheds. Basalts play a major role in the carbon cycle. Many basaltic areas are located near the sea, so that only small rivers flow through these formations. As a rule small rivers are not taken into account in global budgets of weathering fluxes. However, even if individual river fluxes of dissolved material to the ocean are negligible compared to those of large rivers, these fluxes accumulated over the world-wide surface of volcanic provinces are not negligible.
THANKS FOR YOUR ATTENTION !!!

Спасибо за внимание!!!