Silicate weathering and CO_2 consumption rates: new insights from rivers of the Primorskii Krai (Russia)

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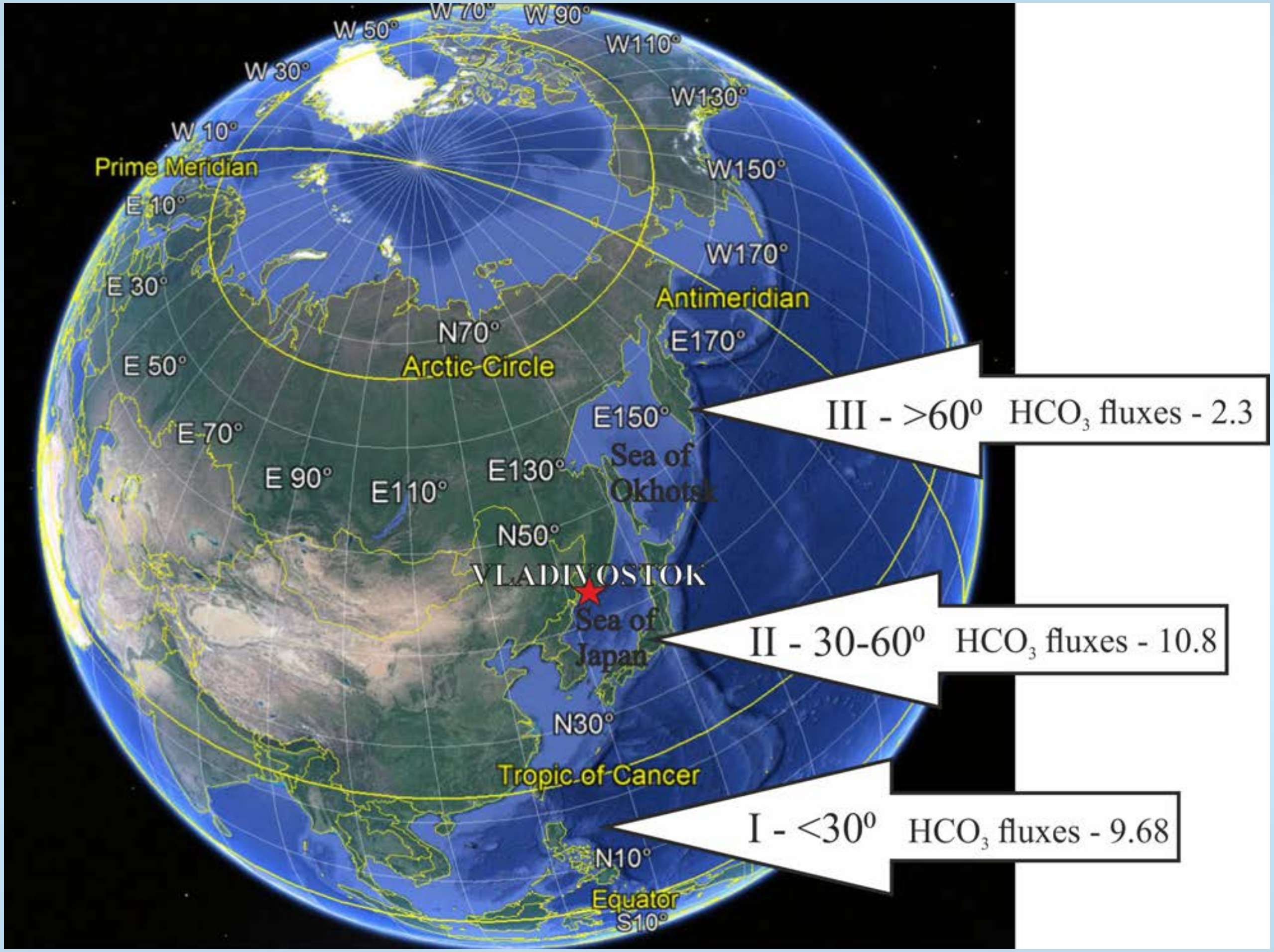
HCO_3^- - fluxes ($Tmol \cdot yr^{-1}$) in the world's top 200 rivers.

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 ($Tmol \cdot yr^{-1}$) in the three latitudinal zones [*W.-J. Cai et al., 2008*]

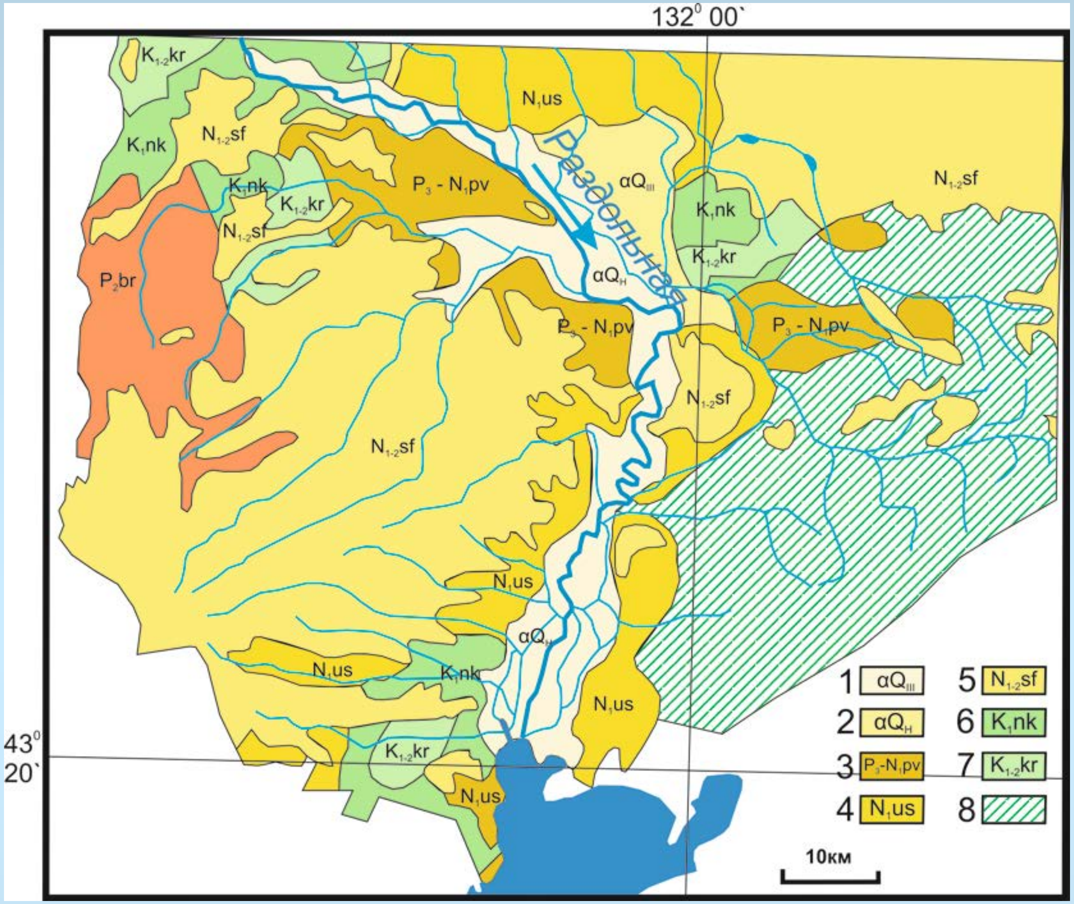
Geographical setting

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.

	Razdolnaya R. (2011)	*Partizanskaya R. (2012)*
Drainage basin area, km^2	**16430**	**4140**
Water discharge, m^3/s	**3.2 – 403**	**3.5 – 80**
Average annual water discharge, km^3/yr	**2.27**	**1.33**
Average annual runoff, mm/yr	**135**	**320**
Total dissolved solids (TDS), mg/l	**65 – 200**	**68 – 132**
Si concentration, µmol/l	**106 – 250**	**170 – 240**

Geological setting

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

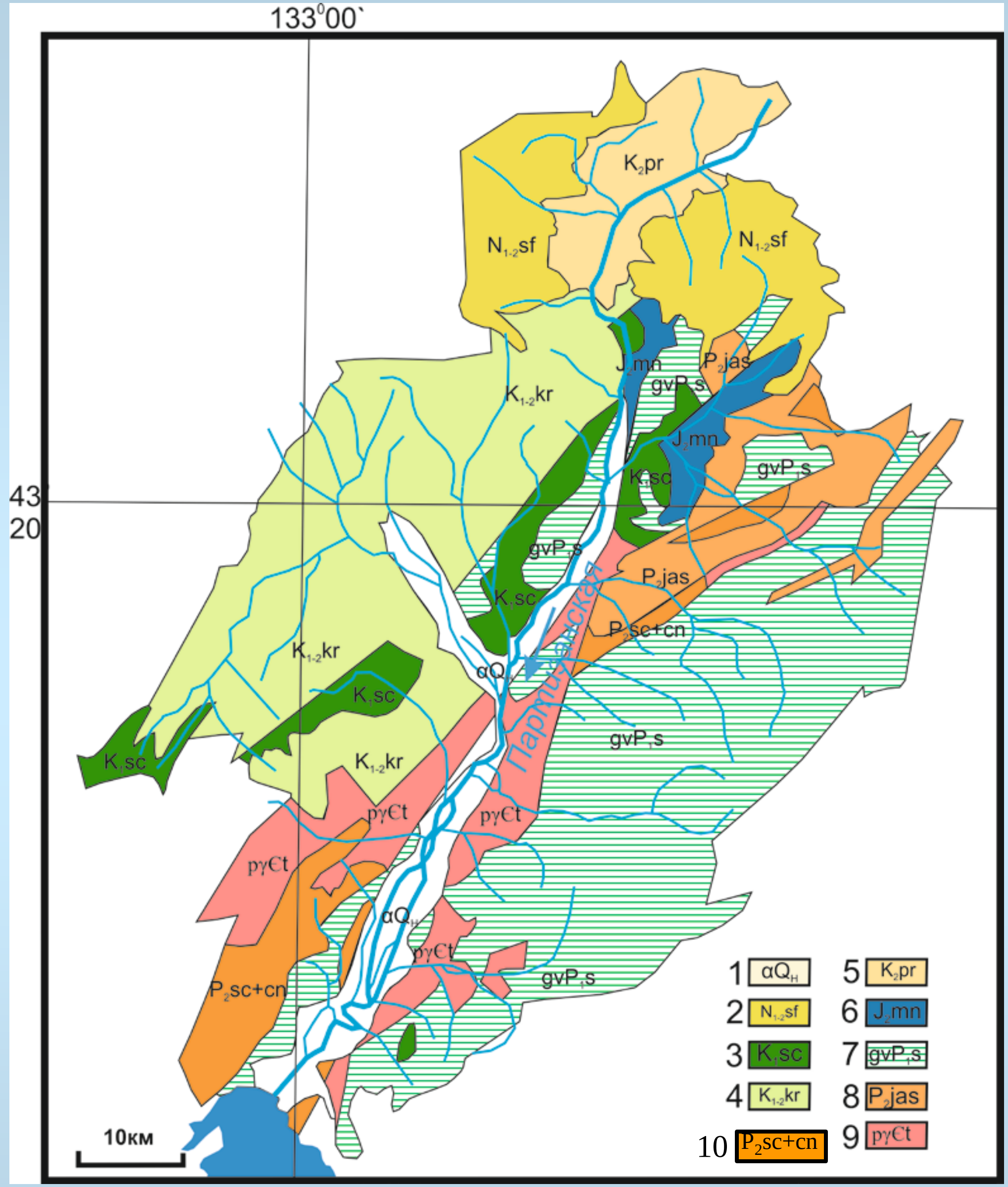


1,2 - alluvial deposit; 3,4 - sedimentary rock; 5 - basalt (Shufan conplex); 6 - sedimentary rock; 7 - volcanogenic and terrigenic rock; 8 - sedimentary rock

[A simplified geological map of Razdolnaya R. basin modified from [*State Geological Map of the Russian Federation…., 2011*].

Geological setting

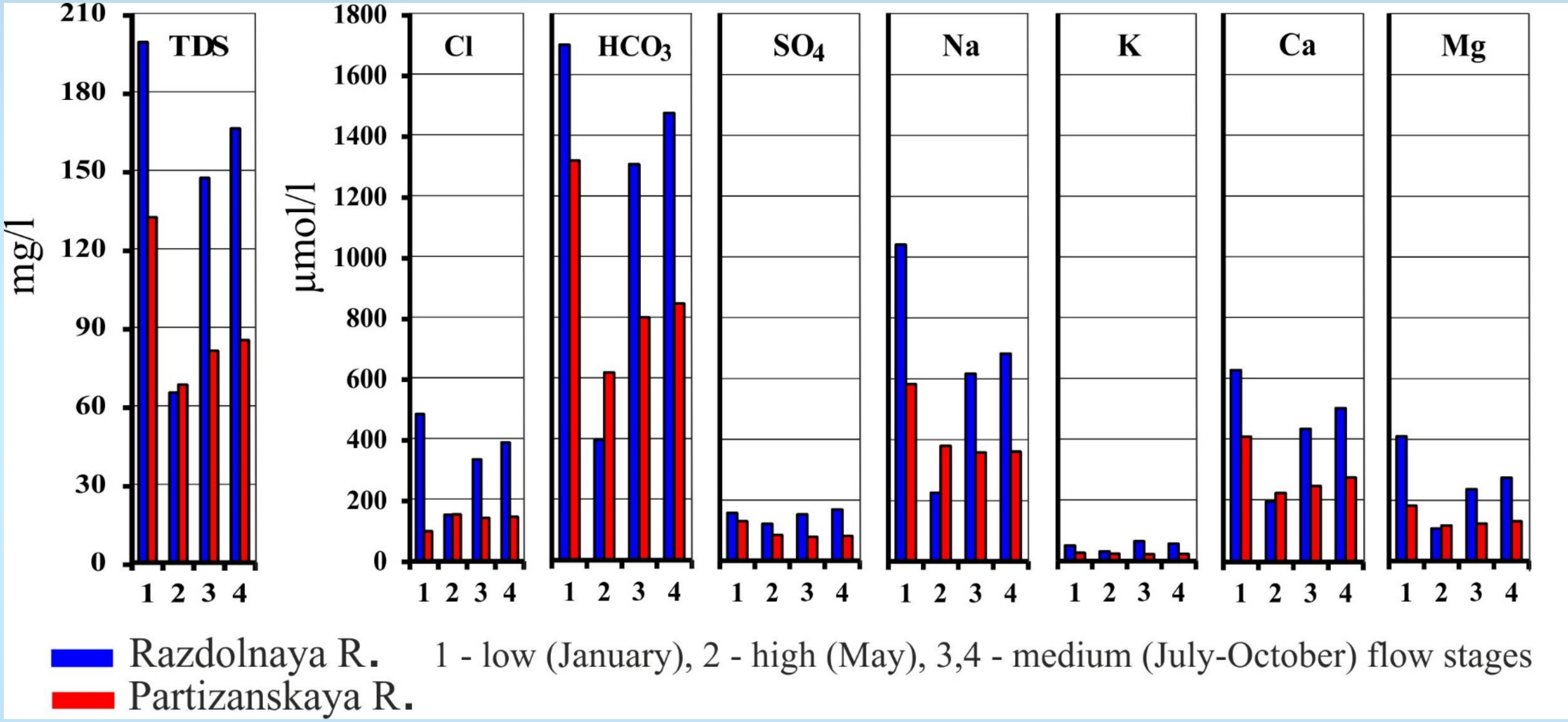
Razdolnaya and Partizansksys rivers draining basically silicate rocks. One of the most striking differences between geology of these rivers is the exposure of reef mass of limestones in lower reach of *Partizanskaya R.* basin.



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, plageogranite); 10 – Permian limestones

[A simplified geological map of Partizanskaya R. basin modified from [*State Geological Map of the Russian Federation…., 2011*].

Mean solute concentrations in Razdolnaya R. (2011) and Partizanskaya R. (2012)

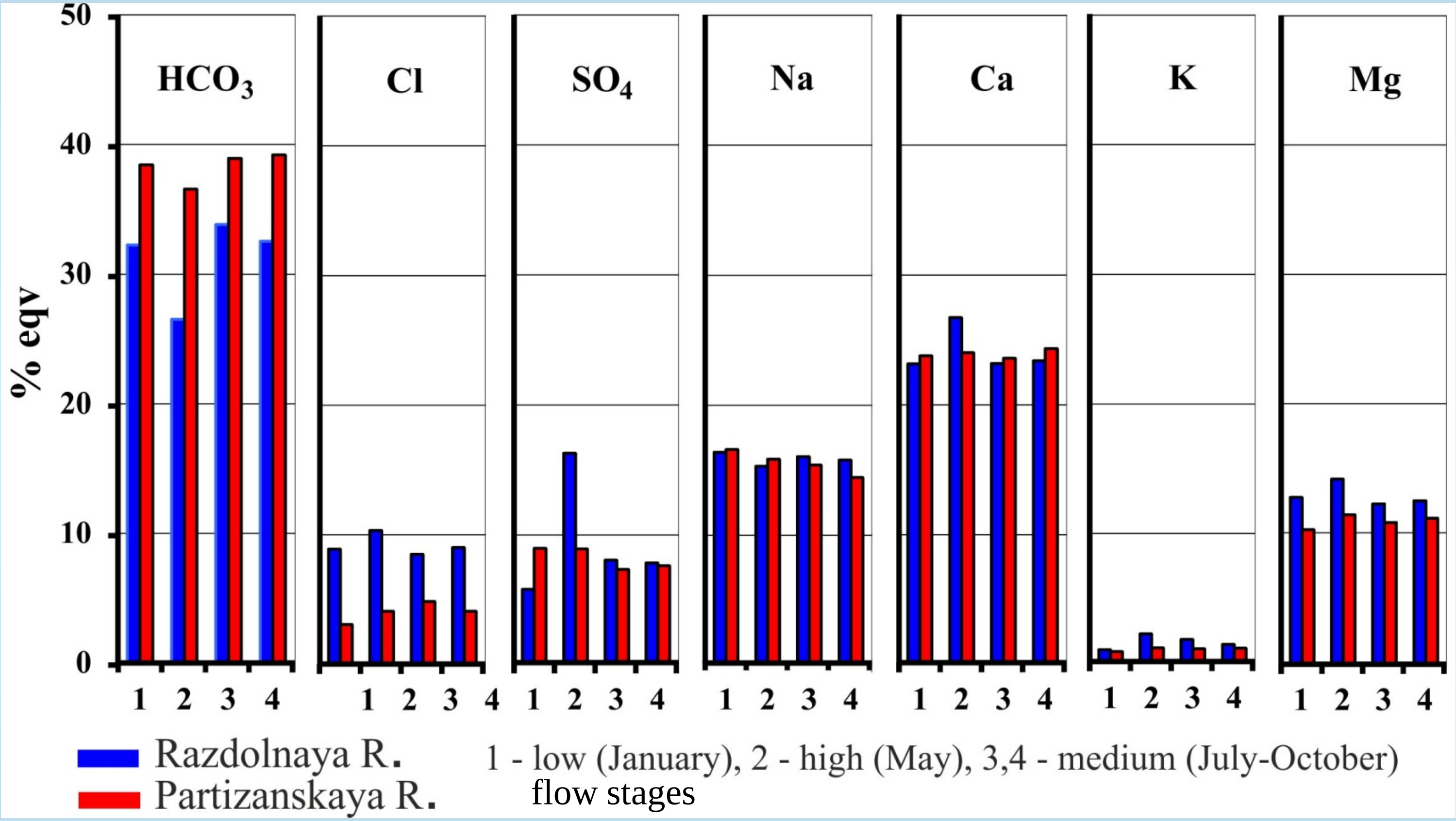


The lower reaches of *Razdolnaya and Partizanskaya rivers* were sampled and analyzed for their major elements in 2011-2012 in different flow stages.

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)

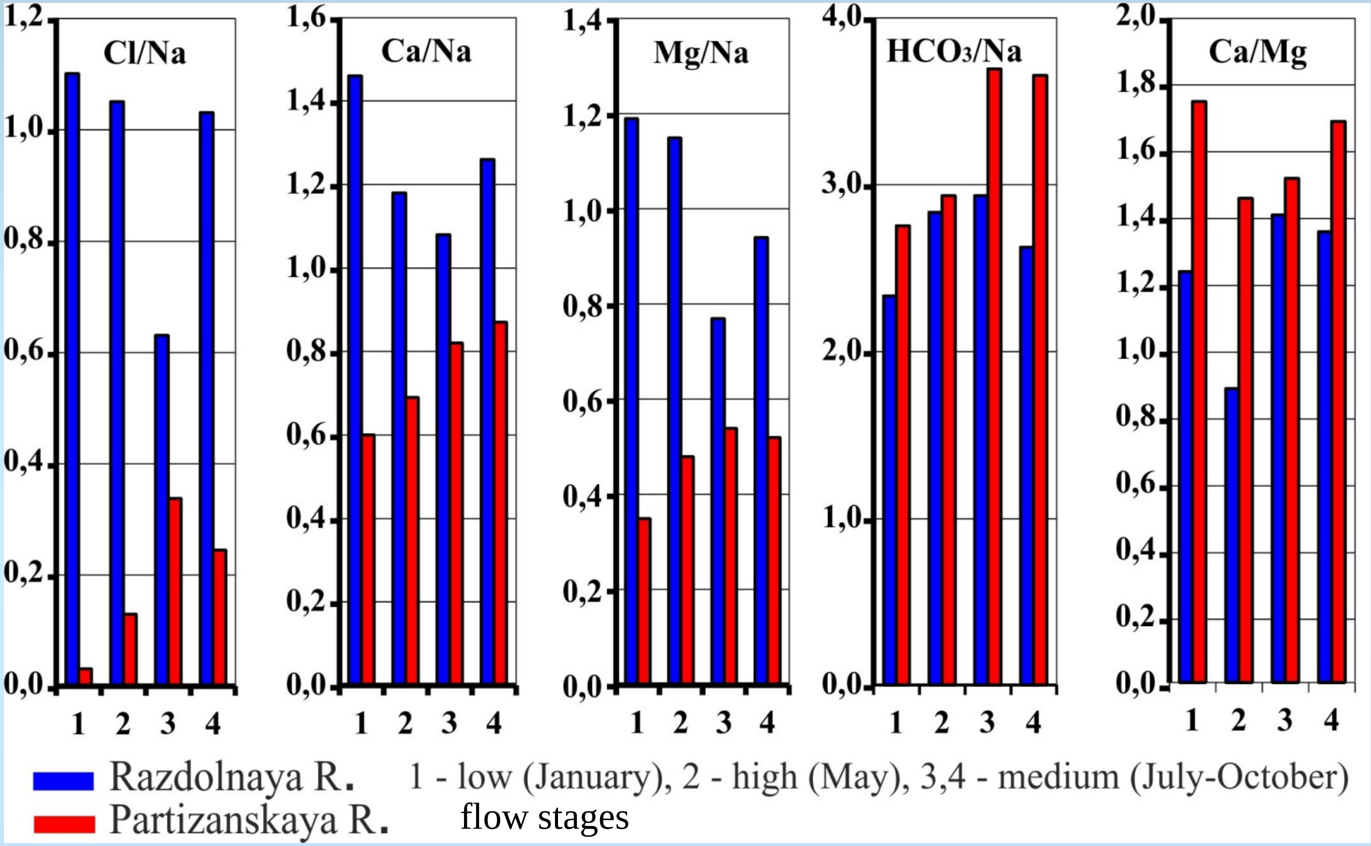
% eqv (anions) + % eqv (cations) = 100 %



NICB (%) = $(TZ^+ - TZ^-)/TZ^+ \times 100$ *is <±5%*

$TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$; $TZ^- = Cl^- + 2SO_4^{2-} + HCO_3^-$

Molar elemental ratios of Razdolnaya and Partizanskaya rivers

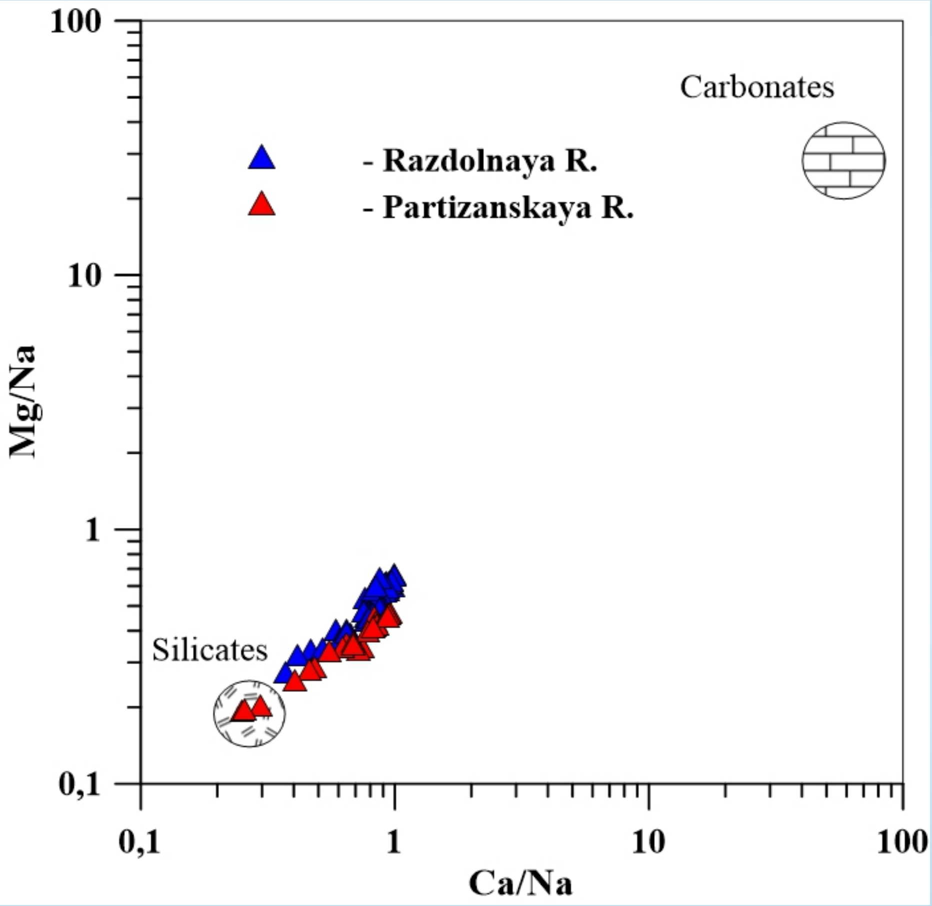


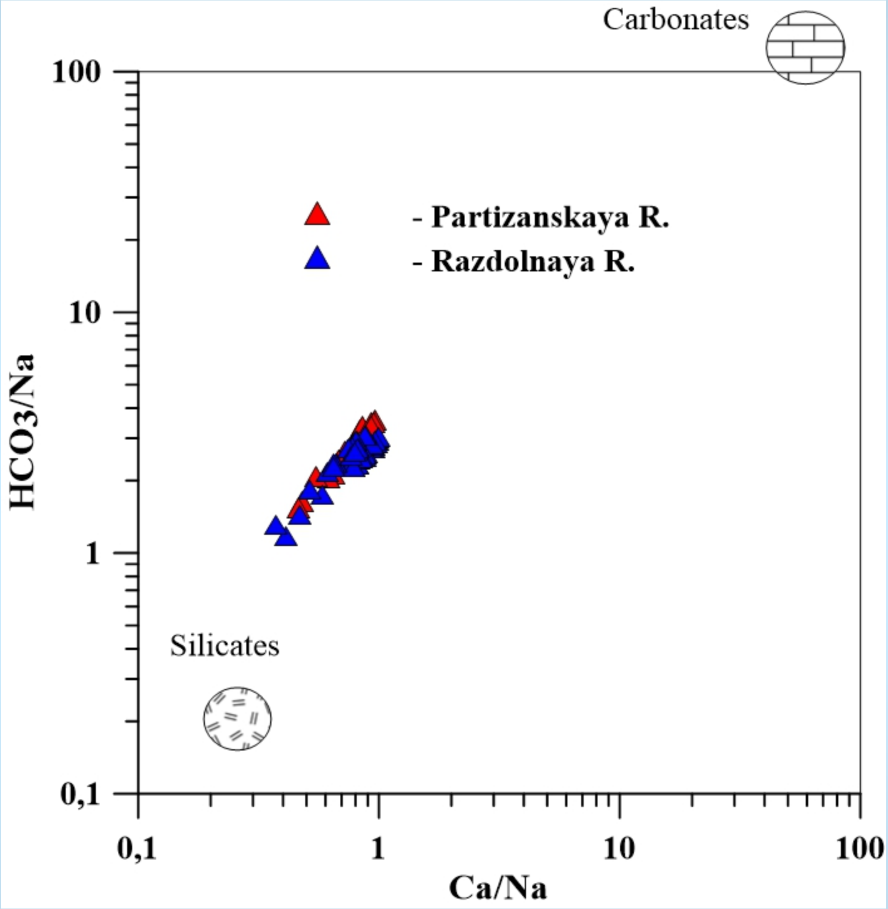
Rock weathering

Carbonates: $CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$

Silicates: $CaSiO_3 + 2CO_2 + 3H_2O = 2HCO_3^- + Ca^{2+} + H_4SiO_4$

Ca/Na vs. Mg/Na and Ca/Na vs. HCO_3/Na diagrams for Razdolnaya R. and Partizanskaya R.



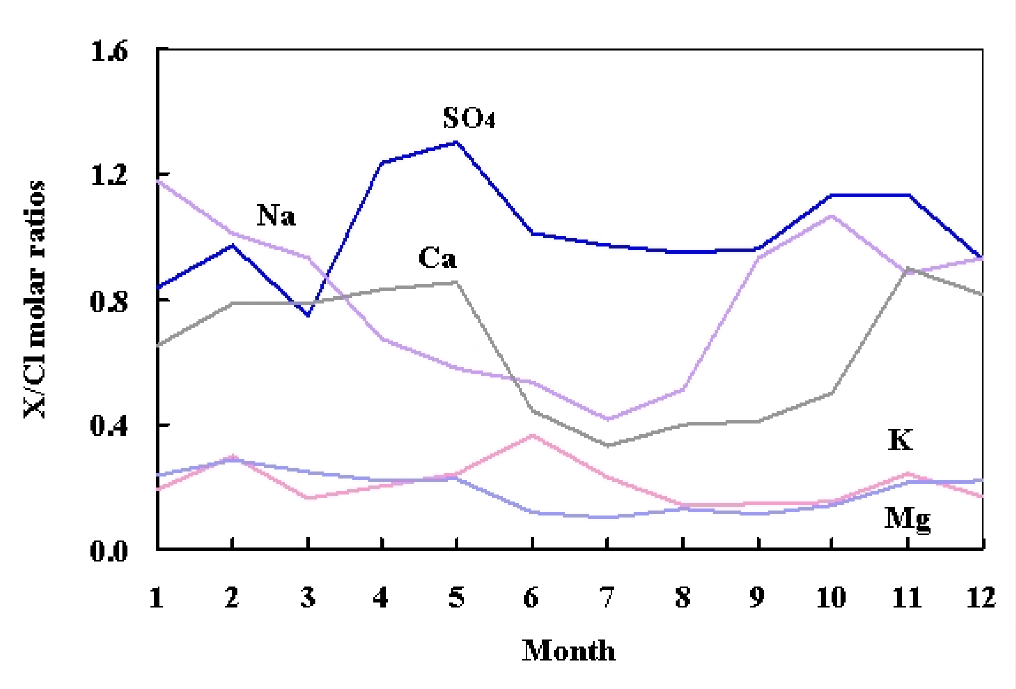


These diagrams are interpreted as mixing between *carbonate end-member* (*Ca/Na, Mg/Na, HCO_3/Na = 60, 30, 120*) and *silicate end-member* (the least Ca-enriched samples)

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)*].



X/Cl ratios in local atmospheric precipitations

2. *Evaporite weathering input*:

$Cl_{evaporite} = Cl_{river} – Cl_{atm} = Na_{evaporite}$

$SO_{4,\ evaporite} = SO_{4,\ river} – SO_{4,atm} = Ca_{evaporite}$

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:

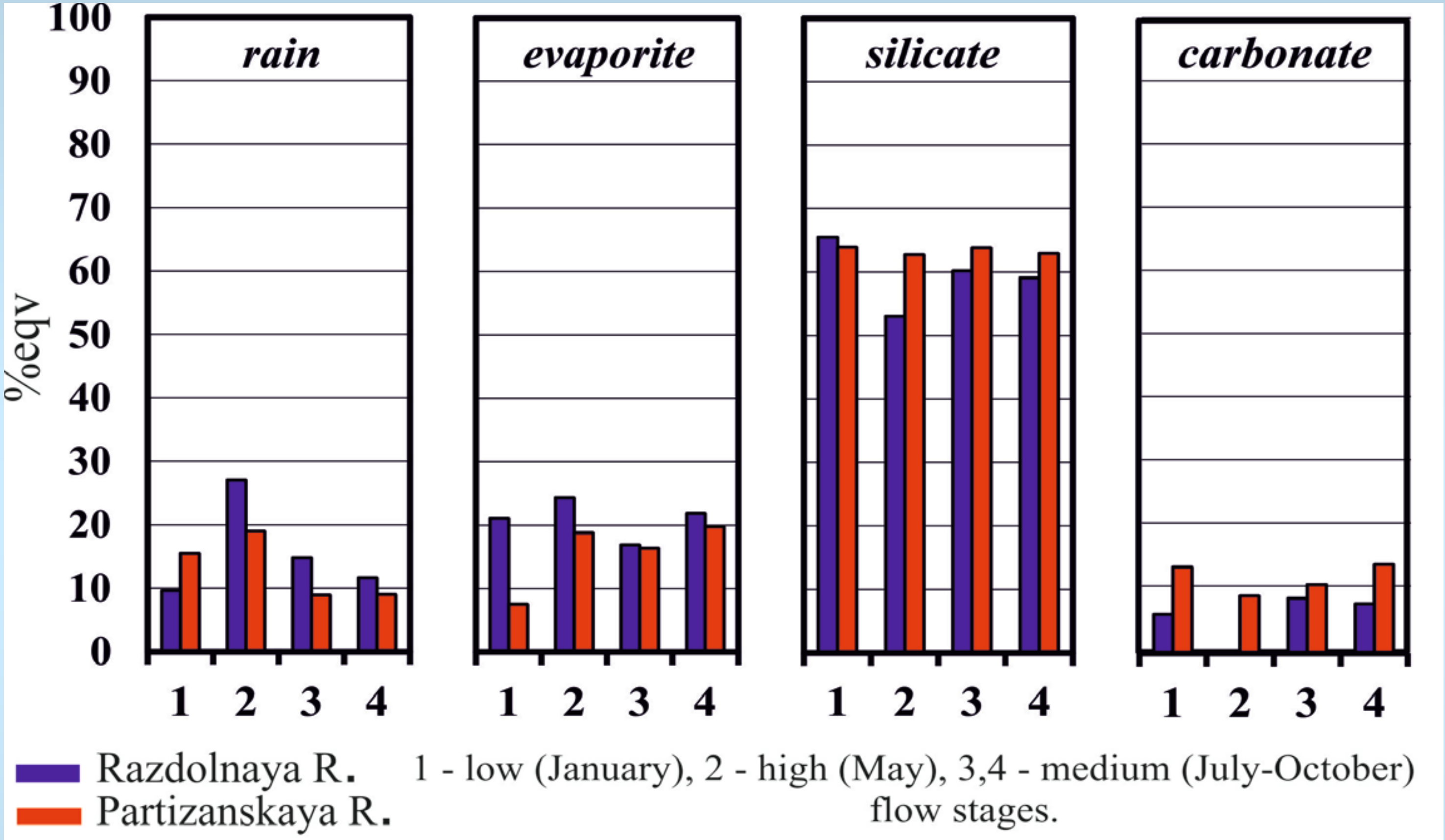
$$Ca_{silicate} = 0{,}9 \times Mg_{silicate}$$

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 subsracting 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)

ΦX_{sil} is the surface specific fluxes derived from silicate weathering of each cation

2. ***The CO_2 consumption rate*** (φCO_2):

$$\varphi CO_{2,\,gyp} = \varphi(Na_{sil} + K_{sil} + 2Mg_{sil} + 2Ca_{sil}) \times Runoff = \mathbf{Sil_{gip}} \times Runoff$$

Sil_{gyp} *(meq/l)* is the silicate fraction of total cations assuming all SO_4 is from gypsum weathering

$$\varphi CO_{2,\,sulfide} = \varphi(Na_{sil} + K_{sil} + 2Mg_{sil} + 2Ca_{sil} - 2SO_4) \times Runoff = \mathbf{Sil_{sulfide}} \times Runoff$$

$Sil_{sulfide}$ *(meq/l)* is the silicate fraction of total cations assuming all SO_4 is from oxidation of sulfide minerals

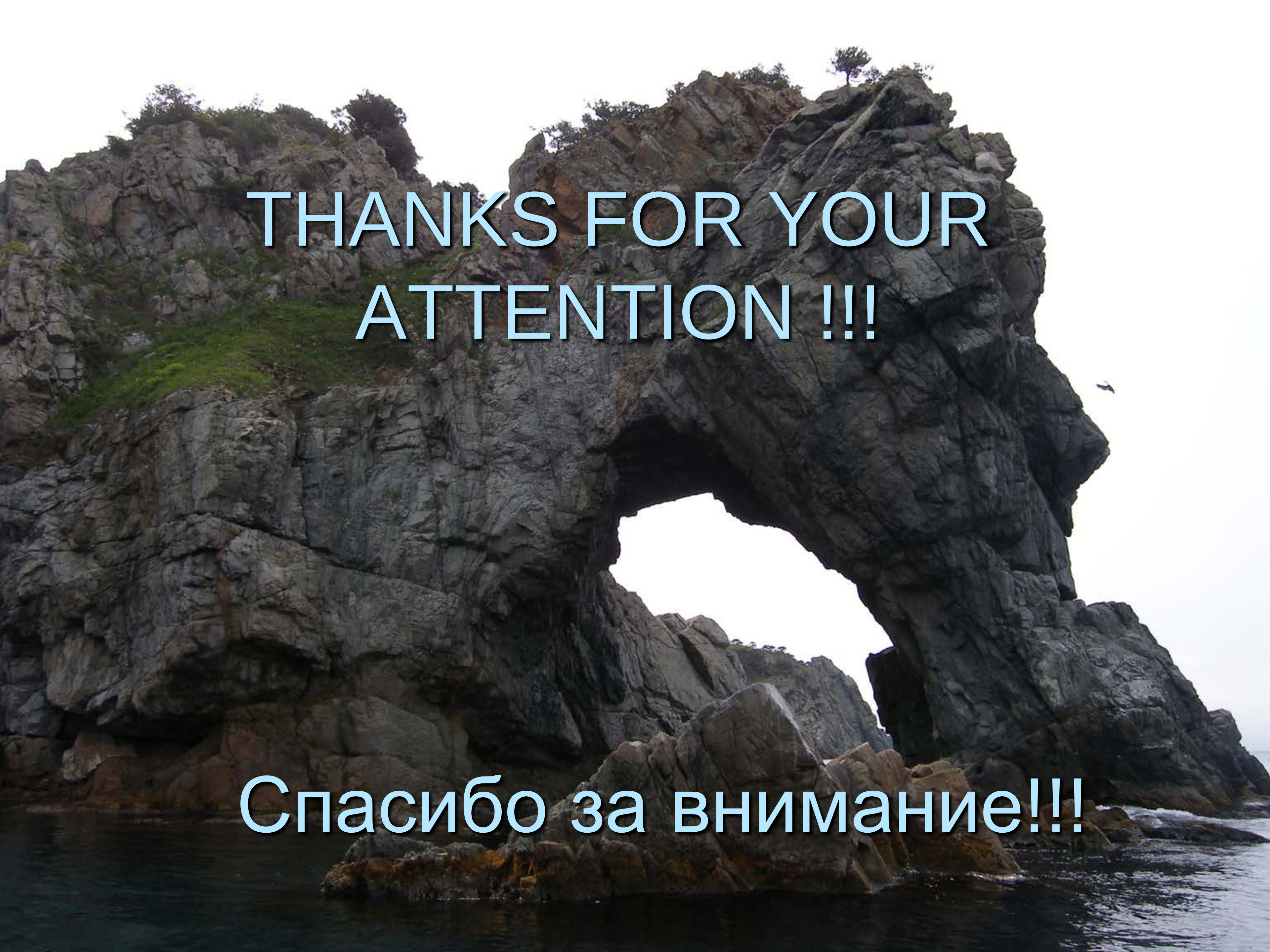
$\boldsymbol{\varphi CO_{2,\,HCO3}}$ – convert HCO_3^- concentrations directly to CO_2 uptake rates

CO_2 consumption rate (φCO_2) *($10^4 mol \cdot km^{-2} \cdot yr^{-1}$)*

River	Runoff, $mm \cdot yr^{-1}$	$\varphi CO_{2,\ gyp}$	$\varphi CO_{2,\ sulfide}$	$\varphi CO_{2,\ HCO3}$
Razdolnaya	138	7.6	5.9	7.8
Partizanskaya	320	21.2	18.5	21.9
Duman	273	14.4-24.0	12.2-22.5	16.3-27.8
M. Central	478	35.0		
Sao Miguel	734	56		
Java	4052	641		

In summary:

- (φCO_2) 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!!!