



Global Biogeochemical Cycles

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- Major human impacts on the annual global flux of boron
- Atmospheric budget for boron is unbalanced
- Boron isotopes useful for paleoreconstructions at >1 Ma timescales

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Global boron cycle in the Anthropocene

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Abstract This paper presents a revised and updated synthesis of the biogeochemical cycle of boron at the Earth's surface, where the largest fluxes are associated with the injection of sea-salt aerosols to the atmosphere (1.44 Tg B/yr), production and combustion of fossil fuels (1.2 Tg B/yr), atmospheric deposition (3.48 Tg B/yr), the mining of B ores (1.1 Tg B/yr), and the transport of dissolved and suspended matter in rivers (0.80 Tg B/yr). The new estimates show that anthropogenic mobilization of B from the continental crust exceeds the naturally occurring processes, resulting in substantial fluxes to the ocean and the hydrosphere. The anthropogenic component contributes 81% of the flux in rivers. The mean residence time for B in seawater supports the use of $\delta^{11}\text{B}$ in marine carbonates as an index of changes in the pH of seawater over time periods of > 1 Ma.

1. Introduction

Park and Schlesinger [2002] published a synthesis of what is known about the biogeochemical cycle of boron at the Earth's surface. Major imbalances in the flux of boron to/from the atmospheric and marine realms were noted, with a missing source of atmospheric boron dominating their analysis. In the intervening years, a variety of new studies have appeared that make it desirable to update and correct the earlier work and provide a new diagrammatic summary of the global boron cycle.

Boron is an essential trace element for terrestrial and marine organisms, but its role in biochemistry is poorly characterized [Carrano *et al.*, 2009]. Boron limitations for plant development are recognized in agricultural systems, particularly in highly weathered soils. At the same time, elevated boron levels in irrigation water result in plant toxicity and reduction in agriculture production [Nable *et al.*, 1997]. Several studies indicate a limiting role for B in the unmanaged terrestrial [Steidinger, 2015] and marine biospheres [Subba Rao, 1981], but the turnover time of B in both realms should ensure adequate supply [Park and Schlesinger, 2002]. Boron is not considered a major contaminant in drinking water, although the World Health Organization and the European Union recommend an upper limit of 0.5 mg/L [World Health Organization, 1998; Weinthal *et al.*, 2005]. High boron concentrations are sometimes observed in freshwater generated by reverse osmosis (RO) desalination due to the poor rejection of boric acid by the RO membrane [Kloppmann *et al.*, 2008].

During the past decade, studies of boron isotopes (i.e., $\delta^{11}\text{B}$) have improved our understanding of boron sources and transformations in nature. Recognizing various new studies, the objectives of this paper are to (1) revise and confirm estimates of B flux based on updated literature, (2) evaluate the increasing magnitude of anthropogenic effects and fluxes relative to the natural fluxes in the global biogeochemical cycle for B, and (3) evaluate the potential effects of climate change and rising atmospheric pCO_2 on the variations in $\delta^{11}\text{B}$ in marine carbonates. As for the compilation of most global biogeochemical cycles, we focus on the selection of reasonable values often from small data sets and are thus unable to offer formal statistical and uncertainty analysis for many of our flux estimates.

2. Anthropogenic Boron Flux

The natural B cycle exists in a steady state at least over periods >1,000,000 years, whereas the anthropogenic B flux is dynamic and reflects increasing annual utilization of natural resources. The major anthropogenic fluxes stem from coal mining and combustion, oil exploration, and the mining and processing of B ores. The exploitation of these resources has changed significantly during the last three decades and previous estimates of their magnitude did not address these changes.

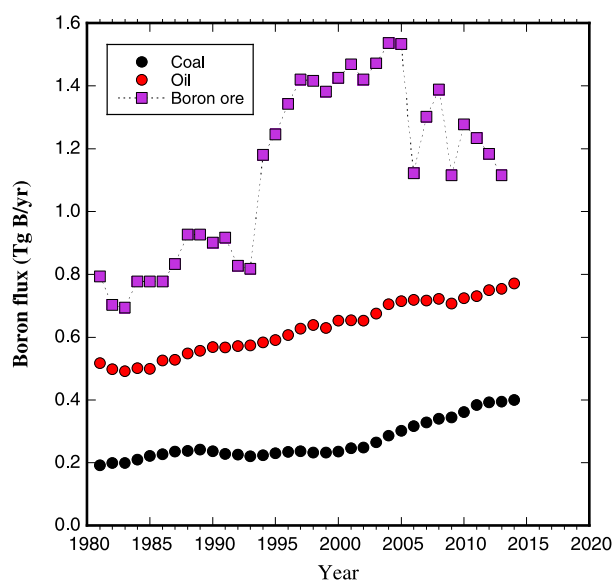


Figure 1. Evaluation of the anthropogenic boron fluxes to its surface geochemical cycle from coal mining, oil extraction, and mining of boron ores. Data for coal and oil production were obtained from the British Petroleum Statistical Review of the World Energy, while data of B ores are from the U.S. Geological Survey [2015]. Fluxes were calculated by integrating annual production rates with B concentrations in coal, oil produced water, and B ores.

Swaine, 1994; Finkelman, 1999; Williams and Hervig, 2004]. Archival data [U.S. Geological Survey National Coal Resources Data System, 2015] list mean B values of 46 and 47 mg/kg for coals from China ($n=294$) and U.S. ($n=7430$), respectively. A similar average B concentration of 47 mg/kg for international coals was reported by Nalbandian [2012]. Based on the variations of coal production, we estimate that the total B extraction associated with coal mining has increased from between 0.2 and 0.3 Tg B/yr at the end of the twentieth century to 0.4 Tg B/yr during the beginning of the 21st century (Figure 1).

Most of the anthropogenic contribution of B to the atmosphere is derived from the combustion of coal [Park and Schlesinger, 2002]. Fugitive emissions of B from coal combustion are generated by volatilization of boric acid during the combustion and by emission of coal combustion residues (CCRs) as particles. The magnitude of boron emission from coal combustion depends on the global coal production, the B content in coals, boron volatilization to flue gas, the distribution of B between flue gas and CCRs, the fraction of CCRs particles that escape with flue gas, and possible resuspension of disposed CCRs particles from disposal sites. Based on the low ratio of B in ash relative to feeding coal, B is classified as a “Class III element”, which includes highly volatile elements with minimal condensation on ash-residue particles [Meij and Winkel, 2009; Kashiwakura and Takahashi, 2011]. Early studies estimated that 70% of boron present in coal is released to the atmosphere during combustion [Pagenkopf and Connolly, 1982], inferring a B flux to the atmosphere of 0.13 Tg B/yr during early 1980s and increasing to 0.28 Tg B/yr in 2014. This is consistent with the estimate made for the 1980s of 0.15 Tg B/yr by Duce [1996].

In recent years, high-efficiency cold-side electrostatic precipitators (ESPs), fabric filters, and wet flue gas desulfurization (FGD) using the lime/gypsum process, remove about 95% of gaseous boron (50% by ESP and 45% by wet FGD), converting it to CCRs [Meij and Winkel, 2009; Ochoa-González et al., 2011]. In the U.S., most of the coal-fired plants installed these scrubber systems during the 1980s and 1990s. Installation of ESP and FGD systems in major power plants in China has increased from almost zero in early 2000s to about 80% in 2010 [Wang and Hao, 2012]. The dramatic rise in worldwide coal production since the early 2000s is due to the accelerated rate of coal mining in China and India, which infers higher rates of B fugitive emission. The transition to modern coal plants with more efficient removal would restrict this atmospheric emission, although the actual effectiveness is still unknown in countries like India or the industrial sector in China.

2.1. Coal Production

Global coal production has doubled, from 3800 Tg/yr in early 1980s to 8000 Tg/yr in 2014 [U.S. Energy Information Administration, 2015; British Petroleum Statistical Review of the World Energy, 2015]. During the 1980s the production of coal increased from 4000 Tg/yr to 5000 Tg/yr. Production remained steady during the 1990s, but since 2000 the global coal production has increased to about 8000 Tg/yr, indicating that coal production and combustion is a 21st century issue. China extracts 50% of the global total coal production, followed by the USA (12%) and India (10%), while other countries generate less than 5% of the total global production (data from U.S. Geological Survey National Coal Resources Data System [2015] and British Petroleum Statistical Review of the World Energy [2015]). Boron content in coal varies considerably from 10 to 1000 mg/kg [Goodarzi and

The high efficiency of B removal through the ESP and FGD yields high B concentration in CCRs [Pagenkopf and Connolly, 1982]. The ratio between the volume of CCR and the volume of utilized coal is about 0.10 (i.e., coal ash content constitutes ~10% of the total coal volume) [Heidrich *et al.*, 2013]. Upon efficient B removal from coal combustion, all B will be retained on the CCR, which means ~10-fold B enrichment in the residual ash (~500 mg/kg). Thus, the B flux through CCR production will be only slightly less than the total B mobilized in coal mining. In the USA, about half of CCR is used by the cement industry and other beneficial uses [U.S. Environmental Protection Agency, 2015], and the other half is disposed in landfills and surface impoundments. Similarly, a large fraction of CCR in China is used in cement [Heidrich *et al.*, 2013]. Given the high rate of leaching of boron from CCRs, numerous studies have shown high mobilization of B to the hydrological system [e.g., Ruhl *et al.*, 2012, 2014]. Assuming that the management of CCR in the U.S. and China are representative globally, we estimate that half of the CCR flux, or ~0.2 Tg B/yr, is transferred to surface hydrogeochemical cycle. Low $\delta^{11}\text{B}$ characterizes coal and coal ash [Ruhl *et al.*, 2014], so we expect that the B flux from coal combustion and CCRs disposal would be associated with a low $\delta^{11}\text{B}$ input to the hydrosphere and atmosphere.

2.2. Petroleum Production

While combustion of petroleum contributes only slightly to the atmospheric budget of B (0.00049 Tg B/yr) [Park and Schlesinger, 2002], oil and gas exploration typically generates a large volume of produced water with high B concentrations (50 to 500 mg/L) and high (>seawater) B/Cl ratios [Warner *et al.*, 2014; Williams *et al.*, 2001; Collins, 1975]. Clark and Veil [2009] estimated that 7 to 10 barrels are produced for every barrel of crude oil onshore, while for production offshore the ratio is much lower. For the U.S., they estimated an average water-to-oil ratio of ~5 for the total production. A global estimate for water-to-oil ratio is lower, with a typical 3:1 ratio [Dal Ferro and Smith, 2007; Ahmadun *et al.*, 2009]. Global oil production has increased steadily from 2.2×10^{10} bbl/yr during early 1980s to 3.4×10^{10} bbl/yr in 2014 [British Petroleum Statistical Review of the World Energy, 2015]. Assuming a global average 3:1 water-to-oil ratio, the change in oil production infers an increase of 1×10^{13} L to 1.5×10^{13} L of produced water during 1980–2014. Assuming B concentration of 50 mg/L in produced water [Collins, 1975], this reflects a large global B flux associated with oil production, from 0.5 Tg B/yr during early 1980s to 0.75 Tg B/yr in 2014 (Figure 1). For comparison, Dal Ferro and Smith [2007] estimated global annual production of produced water of 1.8×10^{13} L (for 2014), which would deliver 0.91 Tg B/yr to the Earth's surface.

This estimate corresponds to conventional oil exploration; however, since 2005 unconventional shale gas and tight sand exploration has increased oil and gas production globally and consequently the volume of produced water [Vengosh *et al.*, 2014]. While new data suggest that the ratio of produced water to oil for onshore unconventional oil exploration is lower (~0.5) than ratios for conventional oil and gas exploration (i.e., 3) [Kondash and Vengosh, 2015], we predict that this large anthropogenic B flux will further increase given the expected global spread of unconventional oil and gas exploration. In the U.S., about 80% of the produced water from onshore oil and gas drilling is disposed by deep well injection, whereas most of the produced water from offshore oil and gas operations is discharged to the ocean (~90% in the U.S. offshore) [Clark and Veil, 2009]. The offshore-produced water contributes about 30% of the total global produced water [Dal Ferro and Smith, 2007], which infers ~0.22 Tg B/yr is discharged to the ocean and a fraction, perhaps 0.1 Tg B/yr (i.e., 20% of the global onshore produced water production), is discharged to the hydrosphere. In some countries, disposal to deep injection wells may not be available due to the lack of geological infrastructure and/or seismicity risks and thus of the B flux to the hydrosphere from onshore oil and gas operations might be larger. Since the range of $\delta^{11}\text{B}$ in produced water (30–50‰) [Warner *et al.*, 2014] spans that of seawater (39‰), we expect negligible changes in seawater composition as a result of discharge. The release of oil and gas to the hydrosphere could change the boron isotope composition of surface water and groundwater in affected areas.

2.3. Mining Boron Ores

A third major anthropogenic B flux derives from mining B ores. U.S. Geological Survey data indicate that production fluctuated from 2.3 Tg B_2O_3 /yr in early 1980s to 4.95 Tg B_2O_3 /yr in 2005. In 2013 it fell to 3.6 Tg B_2O_3 /yr (Figure 1) [U.S. Geological Survey, 2015]. The major boron producers are Turkey (39% of global production), USA (24%), Argentina (14%), and Chile (10%). Boron is used for glass (51%), ceramics (13%), agriculture (14%), detergents (3%), and other users (19%) [Kot, 2015]. The fluctuations of global B ore production are equivalent to 0.7 to 1.5 Tg of B/yr (Figure 1), twice that reported by Park and Schlesinger [2002] and significantly higher than the estimates of Duce [1996]. At current rates of production the lifetime of current

Table 1. Mobilization of B From the Earth's Crust, as Calculated in This Paper

Sources	Boron (Tg B/yr)
<i>Anthropogenic</i>	
Coal mining	0.4
Petroleum extraction and combustion	0.00049
Produced water from oil and gas exploration	0.75
Ore mining	0.7–1.5
Total	2.3
<i>Natural</i>	
Chemical Weathering	0.043
Mechanical Weathering	0.15
Volcanic Emissions	0.02
Total	0.213

known reserves is about 50 years [U.S. Geological Survey, 2015]; boron is one of the elements on the watchlist for scarcity within this century [Henckens *et al.*, 2014].

Most B in glass and ceramics resides in long-life products or landfills. The remaining B, used in detergents, fertilizers, insecticides, fire retardants, and other short-lived products, adds 0.2 to 0.5 Tg B/yr to the surface hydrogeochemical cycle, where much of it is carried to the sea by rivers. Evidence

for increasing anthropogenic contamination from domestic wastewater and agriculture activities in river has been reported for the Seine River in France [Chetelat and Gaillardet, 2005], western coast of India [Singh *et al.*, 2014], the Jordan River [Farber *et al.*, 2004], Taiwan [Liu *et al.*, 2012], and UK [Neal *et al.*, 2010], which consistent with the overall increase of anthropogenic loads of major salts in the world's rivers [Meybeck, 2003, 2005]. The boron isotope composition of boron ores is typically low ($\delta^{11}\text{B} \sim -0\text{‰}$) reflecting the coordination of the borate minerals (i.e., the ratio of trigonal to tetrahedral species) [Oi *et al.*, 1989], and its flux to the hydrosphere is expected to be associated with a low $\delta^{11}\text{B}$ signature. Overall, the total anthropogenic mobilization of B to surface freshwaters from oil production (0.1 Tg B/y), coal combustion residues (0.2 Tg B/y), and B ores (midrange of 0.35 Tg B/y) could approach a total of 0.65 Tg B/y.

2.4. Biofuels

Biofuels are another potential source for B atmospheric emission. Biomass fuels provided about 5% of the energy used in the U.S. in 2013, which is composed of wood and wood-derived biomass (45%), liquid biofuels (mainly ethanol; 44%), and municipal wastes (11%) [U.S. Energy Information Administration, 2015]. B is an essential nutrient in plants and animals [Nielsen, 2009], resulting in high concentration in organic matter [Cividini *et al.*, 2010]. In tree foliage B shows a median value of about 20 mg/kg [Stone, 1990]. The global production of liquid biofuel was 105×10^9 L in 2010, which is equivalent to 9.4×10^{11} kg of plant material [U.S. Energy Information Administration on Biofuel, 2015]. Thus, assuming B content in plants of 20 mg/kg, we estimate an atmospheric flux from biofuel of 0.019 Tg B/year. The rapid rise of biofuel production in countries like Brazil and the U.S. is expected to increase the B emission from liquid biofuels in the future. Data on the boron isotope ratios of plants are limited; Rosner *et al.* [2011] have shown a wide $\delta^{11}\text{B}$ range from -30‰ to $+40\text{‰}$ in crops from different countries. Since B is assimilated and transported to plants through passive diffusion of boric acid, it is expected that the $\delta^{11}\text{B}$ of the plant tissue will be identical to that of the water under low and neutral pH but higher than the $\delta^{11}\text{B}$ of soil and irrigation water at high pH, due to the selective transport of $^{11}\text{B}(\text{OH})_3$ to the plants [Dannel *et al.*, 2002]. The wide range of $\delta^{11}\text{B}$ in plants reflects the natural variations of boron isotopes and site specific $\delta^{11}\text{B}$ [Rosner *et al.*, 2011]. Consequently, it is difficult to predict the boron isotopic flux from biofuels.

Overall, the total estimated anthropogenic B fluxes presented here (Table 1) are higher than previous studies. Currently, total anthropogenic removal of B from the Earth's crust (2.3 Tg B/yr) is dominated by the production of B ores (1.1 Tg B/yr), produced water with oil production (0.75 Tg B/yr), and coal mining (0.4 Tg B/yr) (Figure 1). The new, larger estimate for the boron production from ore yields a greater loss of B to rivers, compared to earlier estimates [Lemarchand *et al.*, 2002; Park and Schlesinger, 2002]; the anthropogenic component now accounts for about 80% of the total annual riverflux of B to the sea.

3. Background Geochemical Cycle for Boron

3.1. The Atmosphere

Early studies showed that B/Cl in rainwater is much higher than in seawater [Gast and Thompson, 1959], indicating that boron in the atmosphere is derived from multiple sources including evaporation of boric acid from seawater and sea spray, volcanic emissions, dust, and anthropogenic activities [Fogg and Duce, 1985; Duce, 1996].

Table 2. Boron Concentrations in Rainfall Published Since *Park and Schlesinger* [2002]

	Boron concentration ($\mu\text{g/L}$)	n^a	Reference
<i>Continental Sites</i>			
Katmandu, Nepal	0.1–3.0	9	<i>Rose-Koga et al.</i> [2006]
Quebec, Canada	1.0–2.2	6	<i>Rose-Koga et al.</i> [2006]
Montreal, Canada	0.1–1.6	9	<i>Rose-Koga et al.</i> [2006]
Guiyang City, China	2.1–4.8	15	<i>Zhao and Liu</i> [2010]
Strengbach, France	0.79	50	<i>Cividini et al.</i> [2010]
<i>Maritime Sites</i>			
Etna, Italy	2.0	136	<i>Calabrese et al.</i> [2011]
Brest, Dax, Orléans, Thonon and Avignon, France	6.6–9.0	49	<i>Millot et al.</i> [2010]
Matsuura and Nakanoto, Japan	2.9–3.6 ^b	36	<i>Sakata et al.</i> [2013]
Tokyo Bay, Japan	0.2–3.2	14	<i>Miyata et al.</i> [2000]
Cayenne-Suzini, French Guiana	6.0	12	<i>Chetelat et al.</i> [2005]
San Francisco, California	1.5–1.9	2	<i>Rose-Koga et al.</i> [2006]
Ahmedabad, India	2.0–13.0	11	<i>Singh et al.</i> [2014]

^aNumber of analyzed rainwater samples.
^bTotal suspended particulate in air.

Lewis and Schwartz [2004] estimate the global production of sea salt aerosols at 5000 Tg/yr. Alternatively, *Andreae and Rosenfeld* [2008] estimate the global production of sea salt aerosols at 10,130 Tg/yr (within a range of 3000 to 20,000 Tg/yr) that is close to the value used by *Park and Schlesinger* [2002] (i.e., ~10,000 Tg/year) [Möller, 1990]. The B/TDS ratio in seawater (1.3×10^{-4}) infers a B flux of 1.3 Tg B/yr [Duce, 1996], which is consistent with the estimate of *Park and Schlesinger* [2002] of 1.44 Tg B/yr. As an alternative, using the seawater B/Cl ratio (0.00024) [Lee et al., 2010] and the estimate of 6000 Tg Cl/yr mobilized in sea salt aerosols [Graedel and Keene, 1995] yields a similar B flux of 1.44 Tg B/yr in sea salt.

The high B/Cl ratio particularly in coastal and marine rains infers additional sources of B in rainwater, most likely associated with the evaporation of boric acid from seawater and sea salt aerosols [Duce, 1996; Rose-Koga et al., 2006]. Based on the difference between the isotopic composition of gaseous B ($\delta^{11}\text{B}$ of -12.8‰ to $+5.1\text{‰}$) and rainwater ($+18.9\text{‰}$ to $+34.7\text{‰}$) in the marine environment [Miyata et al., 2000], the high correlation between $\delta^{11}\text{B}$ and $\delta^2\text{H}$ in marine rain water [Rose-Koga et al., 2006], and typically high $\delta^{11}\text{B}$ in marine and coastal rainwater (up to $+45\text{‰}$), Chetelat et al. [2005] hypothesized that boric acid evaporation from sea salt aerosols is associated with water-vapor isotopic fractionation in the order of $\sim 25\text{‰}$, where gaseous B becomes depleted in ^{11}B [Rose-Koga et al., 2006]. Subsequently, condensation of the ^{11}B -depleted gaseous B in raindrops results in a reverse isotopic fractionation that results in ^{11}B -enriched rainwater relative to the gaseous B. Condensation and rainout would cause progressive depletion of ^{11}B from the atmosphere, following a Rayleigh distillation process. This process was suggested to follow the “rainout” process in which ^2H and ^{18}O are progressively depleted in a cloud, and rain water becomes lower in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ relative to the initial stages [Miyata et al., 2000; Rose-Koga et al., 2006]. This new model of B isotope evolution in the atmosphere over the marine environment reflects the importance of the evaporation process, in addition to the sea salt B flux. Duce [1996] estimated that about 70% of the B in sea salt escapes to the gas phase.

The relative proportions of particulate B and gaseous B in the atmosphere reflect the volatilization of boric acid from seawater and particulate B, which is temperature dependent. Anderson et al. [1994] showed that gas/particle ratios were significantly higher in summer, and Duce [1996] suggested that reverse reactions below 20°C cause sea salt to become a sink for volatilized boric acid. Therefore, temperature and geography play a major role on the dynamics of boric acid volatilization from sea salt.

In addition to the large marine B flux, new B isotopic data show that anthropogenic sources affect the B atmospheric budget. Analyses of precipitation over Guiyang, China [Zhao and Liu, 2010], and Paris, France [Chetelat et al., 2009], and aerosols over the coast of Japan [Sakata et al., 2013] have shown a strong anthropogenic contribution with an end-member characterized by low $\delta^{11}\text{B}$ ($<0\text{‰}$) associated with high SO_4/B and NO_3/B ratios, attributed to coal combustion. The coal combustion contribution was shown to affect both the local

atmosphere in urban areas in Guiyang and Paris [Zhao and Liu, 2010; Chetelat et al., 2009] and much wider regional air masses from eastern China flowing to the Japanese coast [Sakata et al., 2013].

The earlier mean value calculated Park and Schlesinger [2002] for the B concentration in the rainfall at coastal and marine sites, 6.6 $\mu\text{g/L}$, is not altered by more recent values (Table 2), so the previous estimate by Park and Schlesinger [2002] for the deposition of B in rain at sea (2.54 Tg B/yr) remains robust. Based on the approach of Graedel and Keene [1995], who showed that sea salt Cl flux to the atmosphere is almost balanced by Cl flux deposition, we suggest that the coastal and marine deposition flux of 2.54 Tg B/yr in wetfall represents the total atmospheric deposition to the seas. In contrast, the estimate of Park and Schlesinger [2002] for the B concentration in continental rainfall (median value 4.35 $\mu\text{g/L}$; $n = 14$) is likely too high given new measurements ($n = 89$) in various locations around the world (Table 2). A concentration of about 2 $\mu\text{g/L}$ seems more reasonable, which lowers the global deposition of B in rainfall over land to 0.22 Tg B/yr, about half of Park and Schlesinger's [2002] earlier value. This revision also lowers previous estimate of the B returned to the land surface in dryfall, which is taken to be equal to the flux in wetfall, as observed for numerous other atmospheric constituents [Schlesinger and Bernhardt, 2013].

Of the amount of Cl added to the atmosphere by sea salt (6000 Tg/yr) only 3% is transported to land in cyclic salts [Graedel and Keene, 1995]—similar to the percentage of S emitted from the surface of the oceans that is transported landward [Schlesinger and Bernhardt, 2013]. Applying 3% landward transport to the global B cycle, we would expect about 0.04 Tg B/yr is transported to land in cyclic salt. In the coastal area of French Guiana, a low $\delta^{11}\text{B}$ content in rainfall ($< +30\text{‰}$) was associated with a high NO_3/B ratio and interpreted as a signature of biomass burning, presumably in Amazonia [Chetelat et al., 2005]. Meville et al. [2010] and Randerson et al. [2012] estimate global emissions of carbon from biomass burning at 2.5×10^{15} g/yr, derived from roughly 5.0×10^{15} g of biomass. About half of biomass burning is natural and half is anthropogenic—for firewood and land clearing [Mouillot et al., 2006]. If we assume an average concentration of 20 mg/kg in plant biomass [Stone, 1990], then 0.10 Tg B/yr is released globally by biomass burning by both natural and anthropogenic sources. The emission of 0.10 Tg B/yr in biomass burning is about one third of the estimate in Park and Schlesinger [2002].

Other sources of atmospheric B include the mobilization of soil dusts (1600 Tg/yr) [Andreae and Rosenfeld, 2008]. The B content of the Earth's continental crust is given as 11 mg/kg [Wedepohl, 1995; cf. Leeman and Sisson, 1996], but the mean content of B in soils of the U.S. and global soils is higher—33 and 40 mg/kg, respectively [Shacklette and Boerngen, 1984; Kot, 2015]. Assuming the average content in soils is about 30 mg/kg, the mobilization of soil dusts corresponds to a B flux of 0.053 Tg B/yr. Estimates of the other, small sources of B in the atmosphere (plant aerosols, fugitive industrial emissions, and volcanoes) have not changed from the earlier estimates of Park and Schlesinger [2002], although it is worth noting that the flux from volcanoes (0.02 Tg B/yr calculated therein) is much smaller than proposed by Fogg and Duce [1985].

Boron has a short atmospheric lifetime, but the sum of estimated sources of B to the atmosphere does not equal the estimates of deposition; the imbalance in the budget of boron noted by Park and Schlesinger [2002] persists in this treatment.

3.2. The Oceans

Lemarchand et al. [2002] report a global river flux to the oceans of 0.38 Tg B/yr in dissolved form. This is similar to the flux reported by Bertine and Goldberg [1971] (0.36 Tg B/yr) derived from Turekian [1969]. A new estimate for the global transport of suspended sediments in rivers, 12,600 Tg/yr [Syvitski et al., 2005], multiplied by 30 mg/kg, the average concentration of B in soil, gives similar value of B transport in this pathway of 0.42 Tg B/yr. Thus, the total (dissolved plus suspended sediments) river transport, 0.80 Tg B/yr, slightly above the range (0.53–0.63 Tg B/yr) given in Park and Schlesinger [2002]. These estimates of the flux in B in rivers are compatible with earlier estimates of the B derived naturally from chemical weathering (0.043 Tg B/yr) and mechanical weathering (0.15 Tg B/yr), which remain unchanged from Park and Schlesinger [2002]. The excess dissolved B in rivers appears to be derived from atmospheric deposition and from direct and fugitive anthropogenic emissions to the land surface. Thus, our estimate of the anthropogenic mobilization of B to rivers (0.65 Tg B/yr) dominates (81%) the current global transport of B in rivers (0.80 Tg B/yr).

The recent estimate by Kwon et al. [2014] of submarine groundwater discharge to the oceans, $120 \times 10^3 \text{ km}^3/\text{yr}$, is about 3 times larger than the riverine flux and greater than the amount of precipitation that falls on land

[Trenberth *et al.*, 2007]. Most of the submarine groundwater discharge is likely to be cyclic, and the net flux of water in this pathway is not likely to be greater than $2 \times 10^3 \text{ km}^3/\text{yr}$ [Trenberth *et al.*, 2007]. Assuming B concentration of 0.1 mg/L in coastal groundwater [Vengosh *et al.*, 1999, 2002], submarine discharge would yield an annual transport from land to sea of 0.2 Tg B/yr

Boron is also derived from the high-temperature flux from primary and off-axis hydrothermal vents in the oceans. For these, Elderfield and Schultz [1996] indicate flux of 0.011 to 0.045 Tg B/yr and 0.019 to 0.19 Tg B/yr, respectively. The sum of the midpoint of these ranges suggests a global flux of 0.13 Tg B/yr from hydrothermal vents, slightly larger than the value used earlier (0.08 Tg B/yr) [Park and Schlesinger, 2002]. An additional source that was not included in previous estimates is the backflux of B from active mud volcanism, which occurs in marine subduction zones at plate boundaries [Komf and Deyhle, 2002; Komf, 2002]. Mud volcanism facilitates expulsion of fluids, and given the high concentrations of B in pore fluids and authigenic minerals generated in mud volcanoes, this mechanism may yield an important B flux to the ocean [Komf and Deyhle, 2002]. While the actual magnitude of this backflux has not been quantified, Komf and Deyhle [2002] have argued that mud volcanism has a similar magnitude to the high-temperature flux.

There seems to be no good reason to alter the conclusion that the oceans are a net sink of 0.5 Tg B/yr as gaseous boron (as boric acid), given that the measured gaseous concentrations of B in the marine atmosphere are in excess of the equilibrium with seawater predicted by Henry's Law (19 ng B/m^3) [Nishimura and Tanaka, 1972]. In addition to deposition from the atmosphere, the oceans receive B via the dissolved and suspended load of rivers (0.80 Tg B/yr) and via the submarine discharge of groundwater (0.2 Tg B/yr). We earlier showed an additional anthropogenic inflow to the ocean by discharge of produced water from offshore oil operations of $\sim 0.2 \text{ Tg B/yr}$, which is of similar magnitude to the natural occurring fluxes. Thus, the sum of all inputs to the oceans is about 4.2 Tg B/yr, with 72% derived from atmospheric deposition on the ocean surface.

Boron is lost from the oceans in a variety of pathways, of which incorporation in carbonates is the best known and the basis for the use of $\delta^{11}\text{B}$ as an indicator of past changes in the pH of seawater [Vengosh *et al.*, 1991; Hemming and Hanson, 1992]. Numerous attempts have made to calibrate and evaluate the magnitude of the selective ^{10}B incorporation into biogenic skeletons and its dependence on boron speciation and thus pH [Spivack *et al.*, 1993; Lemarchand *et al.*, 2000; Sanyal *et al.*, 2000; Hönisch *et al.*, 2007, 2009; Hemming and Hönisch, 2007; Kubota *et al.*, 2015]. While the boron isotope ratios of corals correspond to an apparent boron species fractionation magnitude of $\sim 20\%$ determined earlier by Kakihana *et al.* [1977], the boron isotopic ratios of benthic foraminifera are consistent with a higher fractionation factor of 26–27% [Hönisch *et al.*, 2008; Rae *et al.*, 2011], which is consistent with direct isotopic measurement of boron species through separation by RO membranes [Nir *et al.*, 2015]. Planktonic foraminifera have intermediate isotopic values [Sanyal *et al.*, 1995; Henehan *et al.*, 2013]. With the new calibrated isotopic fractionation factor of 26% between trigonal and tetrahedral B [Nir *et al.*, 2015], the magnitude of the selective ^{10}B removal via both carbonate precipitation and adsorption to terrigenous sediments is larger than previous estimate of $\sim 20\%$ [Kakihana *et al.*, 1977], requiring an adjustment to previous paleo-pH reconstructions [Nir *et al.*, 2015].

Overall, Simon *et al.* [2006] suggest a flux of 0.06 Tg B/yr into marine carbonates, slightly larger than the value of Park and Schlesinger [2002] of 0.04 Tg B/yr. The largest sedimentary flux of B (0.18 Tg/yr) derives from deposition and adsorption of B in terrigenous sediments. Various other sedimentary fluxes are each small, and the total sedimentary flux is $< 0.3 \text{ Tg B/yr}$ [Park and Schlesinger, 2002]. Independently, Plank [2014] has estimated flux of B in subducted sediment and its pore waters at 0.088 Tg B/yr, a value we should expect to be less than the gross sedimentary flux as a result of fluids expelled during subduction [You *et al.*, 1993; Komf and Deyhle, 2002]. Other sinks for B in the oceans include, low-temperature hydrothermal circulation, which has been estimated by a variety of workers, yielding a range of 0.08 to 0.27 Tg B/yr [Park and Schlesinger, 2002]. We would expect that the low-temperature flux should be slightly less than the high-temperature flux, due to the net uptake of B during serpentinization [Seyfried *et al.*, 1984; Vils *et al.*, 2008].

Considering the mass balance of boron isotopes; the oceans are fed by rivers ($+10\%$ $\delta^{11}\text{B}$) [Lemarchand *et al.*, 2002] and high-temperature hydrothermal flux ($+33\%$) [Spivack and Edmond, 1987], both of which are lower in $\delta^{11}\text{B}$ with respect to seawater ($+39.6\%$) [Foster *et al.*, 2010]. Deposition of 0.36 to 0.47 Tg B/yr in pelagic sediments, which range from -6.6 to $+4.8\%$ in $\delta^{11}\text{B}$ [Ishikawa and Nakamura, 1993], would selectively remove ^{10}B to the solid phase and maintain steady state B and $\delta^{11}\text{B}$ in seawater. This deposition is only slightly greater than the sum of the various sedimentary processes (0.28 Tg B/yr, above) that remove B from the oceans.

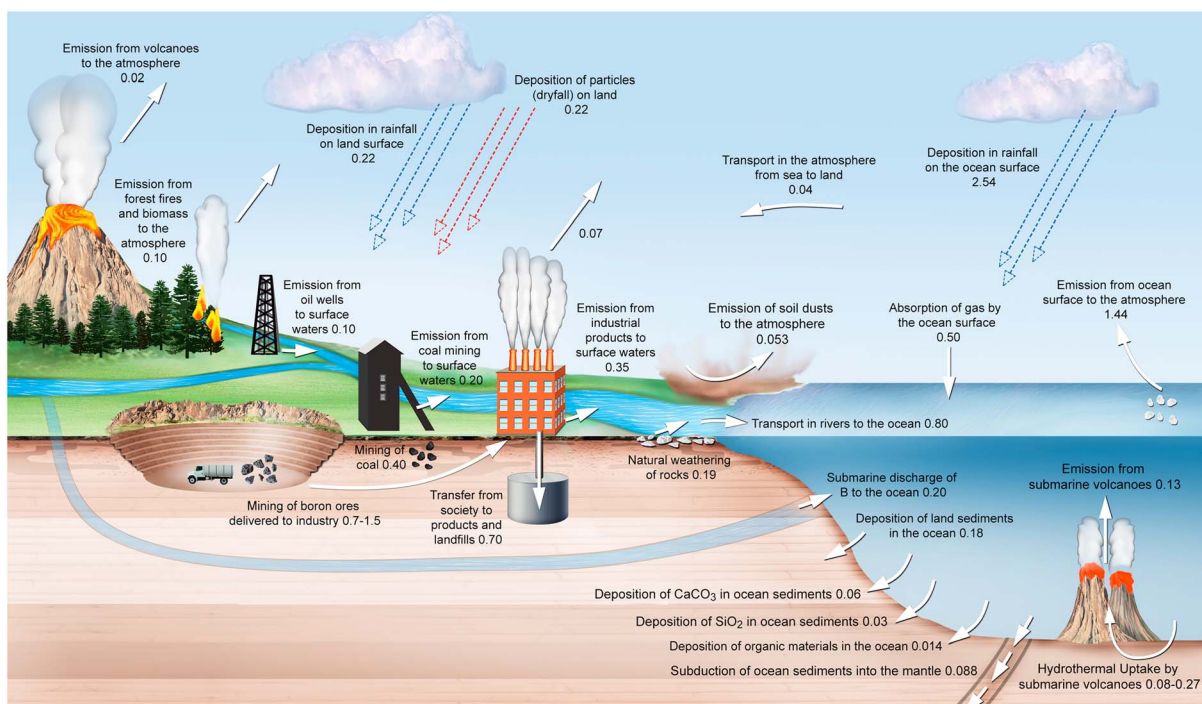


Figure 2. The global boron cycle, as revised and updated from *Park and Schlesinger* [2002], emphasizing the major flux between reservoirs and omitting the internal biological circulation in terrestrial and marine ecosystems. All flux values are given in Tg B/yr ($= 10^{12}$ g B/yr).

About 4.3 Tg B/yr circulates through the marine biosphere [*Park and Schlesinger, 2002*], and 6.2×10^6 Tg B are held as dissolved forms of B in seawater. The estimated inputs of B to the oceans exceed the total of estimated losses (Figure 2), and the imbalance is exacerbated by the recent anthropogenic additions to the B carried in rivers. The sum of all inputs to the ocean (4.2 Tg B/yr) yields a mean residence time of 1.5 Ma for B in ocean water. The residence time increases to 7.1 Ma if we ignore the large flux of B to the atmosphere, most of which is redeposited on the ocean surface. As first noted by *Lemarchand et al.* [2000], these residence times would suggest caution when using the $\delta^{11}\text{B}$ content of marine carbonates to reconstruct ocean pH at < 1 Ma intervals [e.g., *Sanyal et al., 1995*], although greater success may be expected over longer periods of time.

3.3. The Terrestrial Biosphere

About 2.2 Tg B/yr circulates in the terrestrial biosphere, as determined by its net primary production and the average B concentration in plant tissues [*Stone, 1990; Schlesinger and Bernhardt, 2013*]. The land portion of the global boron cycle is reasonably well balanced, as is the balance in the atmosphere over land. Each year, about 0.28 Tg B enters the atmosphere over land and about 0.44 Tg B/yr is deposited on the land surface. Each year, 2.5 Tg B is mobilized from the Earth's crust (92% by human activities), 0.70 Tg B is retained in products and landfills, and 0.80 Tg B/yr moves to the sea in rivers. As shown earlier, increasing exploitation of coal, oil, and B ores as well of development of biofuels could change these cycles.

4. Conclusions and Future Trends

This paper shows that the increasing human activities, particularly through exploration of fossil fuels and boron ores, have increased the anthropogenic B fluxes to the hydrosphere and atmosphere. The magnitude of the anthropogenic flux (total 2.3 Tg B/yr) is comparable and even exceeding major natural B flux. For example, the total anthropogenic flux is more than half of the total B input to the ocean (4.2 Tg B/yr).

While global warming would increase the terrestrial flux to the ocean due to intensification of weathering process and river flow, it is not expected to change the B budget due to the long residence time of B in the ocean. Together with natural decadal variability in seawater pH [*Wei et al., 2015*], the rise of pCO_2 in the atmosphere and the induced ocean acidification caused by absorption of anthropogenic CO_2 into the ocean

[Hönisch *et al.*, 2012] is expected to change the boron speciation and the boron isotope ratio of carbonates. A study of *Porites* corals in areas of subtropical gyres, where surface seawater is close to equilibrium with atmospheric $p\text{CO}_2$, has shown a slight parallel decrease in pH (8.2 to 8.1) and $\delta^{11}\text{B}$ in corals age dated from 1900 to 2000 [Kubota *et al.*, 2015]. Likewise, a reconstruction of seasonal variability and anthropogenic change in seawater pH and temperature from a long-lived coralline alga has shown a decline in the $\delta^{11}\text{B}$ during the twentieth century [Fietzke *et al.*, 2015]. A similar pattern was observed $\delta^{11}\text{B}$ in a planktonic foraminifera (*G. sacculifer*) from Ocean Drilling Program (ODP) site 668B in the eastern equatorial Atlantic during the glacial and interglacial cycles of the Pleistocene. The $\delta^{11}\text{B}$ variations were in synchrony with atmospheric $p\text{CO}_2$ variations recorded in the Vostok ice core and showed a decrease of $\delta^{11}\text{B}$ during interglacial periods with maximum atmospheric $p\text{CO}_2$ [Hönisch and Hemming, 2005]. Similar results were found in reconstruction of $\delta^{11}\text{B}$ using a different planktonic foraminifera (*G. ruber*) from ODP site 999A and GeoB1532-1 as compared CO_2 concentrations from ice cores during the last 30,000 years [Henehan *et al.*, 2013]. The rise of atmospheric CO_2 from the last glacial period (~200 ppm) to preindustrial modern time (280 ppm) was associated with a decrease in $\delta^{11}\text{B}$ from 21.3‰ to 20.7‰ [Henehan *et al.*, 2013]. Consequently, future climate change and ocean acidification are expected to shift the distribution of boron species in the ocean and decrease the $\delta^{11}\text{B}$ of coprecipitated carbonate skeletons under lower pH conditions.

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