Trace metal fluxes to the ocean: The importance of high-standing oceanic islands

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[1] Trace metal analyses of river channel sediments from Taiwan and New Zealand provide new estimates for global budgets of trace metal inputs to the world's ocean. Mean trace metal values from high standing island river sediments are less chemically weathered than observed in sediments collected from large, continental, rivers and more similar to upper continental crust (UCC) values. Our mean values for Cu, Mn, Co and Pb are similar to the UCC; Zn, Ni and Cr are more highly enriched, compared to UCC values. Our new estimates of global trace metal budgets, combining previous estimates with these new data, show that geochemical fluxes of metals into the oceans are lower than previous estimates, ranging from 9% lower for Co to 24% lower for Cu. *INDEX TERMS:* 1065 Geochemistry: Trace elements (3670); 1030 Geochemistry: Geochemical cycles (0330); 4825 Oceanography: Biological and Chemical: Geochemistry; 9355 Information Related to Geographic Region: Pacific Ocean. **Citation:** Carey, A. E., C. A. Nezat, W. B. Lyons, S.-J. Kao, D. M. Hicks, and J. S. Owen, Trace metal fluxes to the ocean: The importance of high-standing oceanic islands, *Geophys. Res. Lett.*, *29*(23), 2099, doi:10.1029/2002GL015690, 2002.

1. Introduction

[2] The average elemental compositions of world river particulate matter are considered to be well-known. Yet this contention is based on the analysis of only ~20% of the global oceanic sedimentary flux. High-standing oceanic islands (HSIs) are those islands which have streams with headwaters lying at elevations of 1,000 m or more above mean sea level and generally correspond to the mountainous islands of Asia and Oceania, particularly between Australia and Asia [*Milliman and Syvitski*, 1992]. These island watersheds, situated close to the ocean, experiencing high intensity rainfall and/or snowmelt events, are important suppliers of sediment to the ocean [*Milliman and Syvitski*, 1992; *Hicks et al.*, 1996; *Restrepo and Kjerfve*, 2000; *Mertes and Warrick*, 2001]. Here we show new trace metal data from sediments from New Zealand and Taiwan rivers whose concentrations and fluxes of metals are less than those measured from large volume, low gradient continental rivers. These islands, representative of high standing islands in the Southwest Pacific Ocean have rivers with short lengths, steep gradients and "flashy" hydrographs which enable them to act as conduits to transport water and sediments quickly from mountains to the ocean. Using these and previously published results from Papua New Guinea, we estimate HSIs' trace metal contribution to the oceans. Inclusion of HSIs' trace metal inputs to the oceans in global budgets greatly alters previous estimates of elemental fluxes and provides a better assessment of the importance of anthropogenic activities in these fluxes.

[3] Rivers are the major sources of dissolved and particulate materials to the oceans, and are thereby the primary contributors to the geochemical composition of both ocean water and marine sediments. With the recent advent of rigorous collection and handling techniques and sophisticated analytical instrumentation, great advances have been made in the quantification of the dissolved riverine fluxes of chemicals. Knowledge of this has also come about because the discharges of the "major" rivers supplying much of the water, and hence the dissolved constituents in the oceans, are relatively well known. Recent sediment flux estimates suggest that rivers draining high-standing oceanic islands in the SW Pacific contribute a very large portion of the total sediment flux to the oceans [*Milliman and Syvitski*, 1992]. Yet few geochemical data exist from these important sediment-producing environments. Much more data exist from large volume Asian rivers, like the Ganges-Brahmaputra system. Although the Ganges-Brahmaputra carries a large sediment load, recent work suggests as much as 30–49% of its annual sediment flux is sequestered in the

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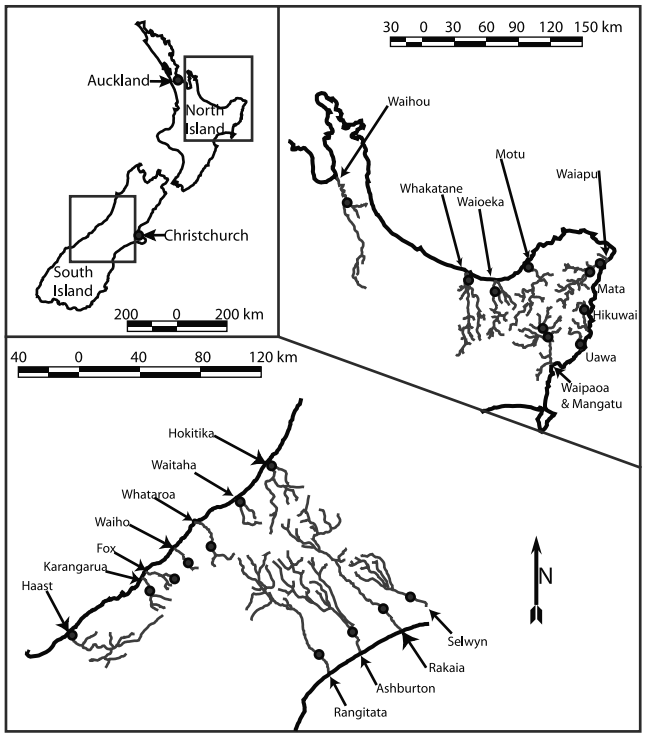

Figure 1. New Zealand sampling locations on North Island—Waipaoa River at Te Karaka gage; Mangatu River at bridge; Hikuwai River at Uawa; Hikuwai River at No. 4 Bridge gage; Mata River just NW of Ruatoria; Waiapu River near Tikitiki; Motu River at SH 35 bridge; Waioeka River at Waioeka; Whakatane River at Whakatane; Waihou River near Paeroa. New Zealand sampling locations on South Island—Hokitika River near Kaniere; Waitaha River in Kakapotahi at SH 6 bridge; Whataroa River in Whataroa at gage; Karangarua River at SH 6 bridge; Waiho River SH 6 bridge at Franz Josef; Fox Glacier stream; Haast River at SH 6 Bridge; Rangitata River at SH 1 bridge; Rakaia River at SH 1 bridge; Ashburton River at SH 1 bridge; Selwyn River.

floodplain [*Goodbred and Kuehl*, 1998; *Islam et al.*, 1999] and thus not delivered to the oceans.

2. Methods

[4] River channel sediment was collected from 21 New Zealand rivers (Figure 1) during two sampling campaigns in 1999 and 2000. The rivers sampled include five of the six highest sediment yielding rivers in New Zealand (i.e., Cropp/Hokitika, Haast, Waiapu, Hikuwai and Waipaoa) [*Hicks and Griffiths*, 1992; *Hicks et al.*, 1996]. Sediments were also collected from six Taiwanese rivers (Figure 2) in a non-typhoon time (in December 2000). In addition, ten suspended load sediments were collected from nine Taiwanese rivers during Typhoons Doug and Tim during 1994. All samples were air-dried under a Class-100 clean hood. The New Zealand samples were analyzed for Cu, Zn, Ni, Mn, Cr, and Co as pressed powders (or as glass disks for Mn) using XRF techniques. The precision of these measurements, determined from triplicate analysis of each sample, ranged from $\leq$1.1% for Mn to $\leq$3.1% for Cr. The Taiwan samples were analyzed by ICP or ICP-MS after *aqua regia* dissolution. The precision of the ICP measurements, as determined from the analysis of duplicate samples, was $\leq$4%.

3. Results and Discussion

[5] Our data from New Zealand and Taiwan, the previously determined global average riverine sediments values [*Poulton and Raiswell*, 2000] and the average value for the upper continental crust [*Taylor and McLennan*, 1985] (UCC) for Cu, Zn, Ni, Mn, Cr, Co, and in some cases, Pb, are tabulated (Table 1). Our data and those available from Papua New Guinea (PNG) [*Alongi et al.*, 1996] were used to calculate mean HSI riverine sediment values for these same metals (Table 1). The HSI elemental means were weighted by the sediment fluxes from these three locations (i.e., New Zealand, Taiwan, and PNG) [*Lyons et al.*, 2002]. We then calculated best estimates for the global riverine sediment concentrations by assuming that the values of *Poulton and Raiswell* [2000] represent 67% of the total

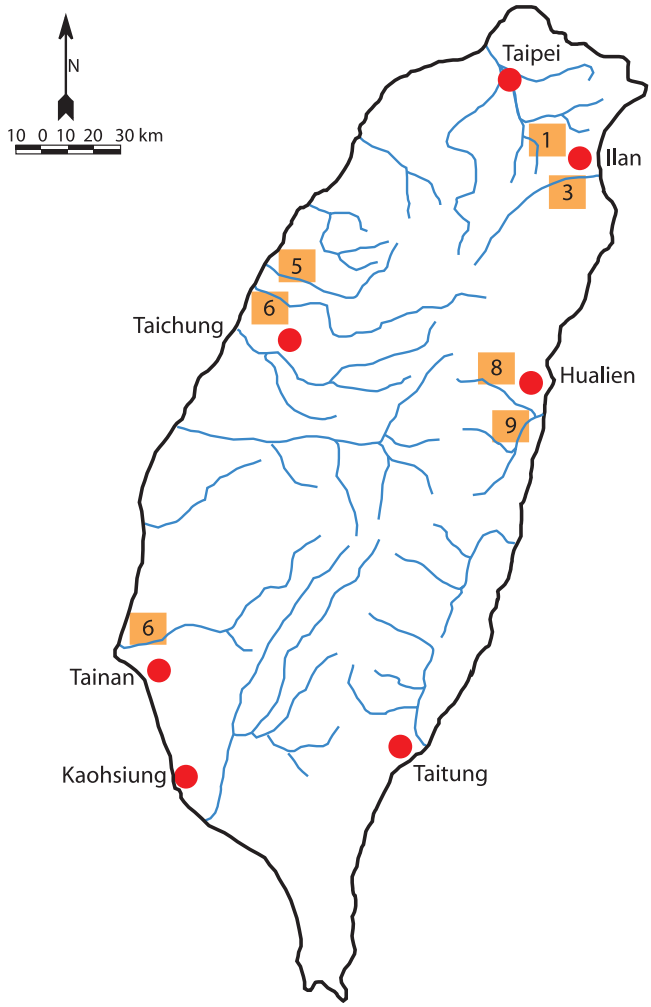

Figure 2. Taiwan sampling locations. 1. Fu-shan experimental watershed #2, 3. Lanyang Hsi, 5. Daan Hsi, 6. Daja Hsi, 8. Hualien Hsi, 9. Shenmiku Hsi (tributary to Hualien Hsi).

flux to the oceans and our HSI values represent the other 33% of the flux (Table 1).

[6] The individual HSI values and our newly calculated global mean values are much closer to UCC values [*Taylor and McLennan*, 1985] than those reported previously [*Poulton and Raiswell*, 2000]. The HSI means for Cu, Mn, Co and Pb are similar to the UCC, while Zn, Ni and Cr are more highly enriched, compared to the UCC values. The metal concentrations of the mean HSI, close to those of the UCC, indicate that these HSI sediments are less chemically weathered than are the sediments from larger river basins. In large river basins, where large volume sediment storage occurs, the soils and sediments have long residence times within the watershed [*Gaillardet et al.*, 1999]. HSI watersheds have very steep slopes and short lengths, enabling rapid transport of sediments to the ocean [*Milliman and Syvitski*, 1992]. In addition, HSI watersheds are dominated by frequent mass-wasting events which add large sediment volumes to the streams [*Hovius et al.*, 1997, 2000]. The observed enrichments of Ni and Cr in HSI sediments implies natural preconcentration into weathering residues during the early stages of the weathering process [*Dupré et al.*, 1996]. The typhoon suspended sediments from Taiwan are enriched in all metals but Cr when compared to the riverine sediments collected at non-typhoon times. This enrichment indicates a larger input of highly weathered regolith during intense discharge events accompanying typhoons. Clearly the HSI values are much different than the previously tabulated "average" global riverine sediment concentrations [*Poulton and Raiswell*, 2000].

[7] Our new global values determined using both the non-HSI [*Poulton and Raiswell*, 2000] and our HSI data are lower than previously reported for the non-HSIs alone. Hence the geochemical flux of particulate metals into the oceans must also be lower. Recent results from 12 Chinese rivers also support our conclusions [*Chen et al.*, 2000]. Mean river sediment concentrations for Cμ, Zn and Pb from those Chinese river systems are 28, 140 and 37 μg g^{-1}, respectively. Although higher than our HSI values, they are also lower than the global averages previously determined [*Poulton and Raiswell*, 2000]. Because as much as 75% of the sediment entering the oceans comes from these HSIs and Asia [*Milliman and Syvitski*, 1992; *Lyons et al.*, 2002], the oceanic particulate flux must be dominated by these sources.

Table 1. Riverine Sediment Elemental Geochemistry

	Cu[a]	Zn	Ni	Mn	Cr	Co	Pb
New Zealand rivers (n = 21)	17	70	26	366[b]	68	8[b]	21[b]
Taiwan rivers (n = 6)	21	74	31	424	63	9	20
Taiwan rivers during typhoons (n = 10)	28	117	39	620	26	15	35
Fly River[c] (n = 4)	33	108	34	721	83	20	13
HSI Average	30	101	33	645	75	17	16
Upper Continental Crust[d]	25	71	20	600	35	10	20
Global Average[e]	110	217	77	922	116	23	–
Our Global Average	84	179	62	831	102	21	–

[a]All concentrations in μg λ g^{-1}.
[b]n = 4.
[c]*Alongi et al.* [1996].
[d]*Taylor and McLennan* [1985].
[e]*Poulton and Raiswell* [2000].

Table 2. Riverine Particulate Dissolved and Total Fluxes to the Oceans

	Annual fluxes[a]					
	Cr	Mn	Co	Ni	Cu	Zn
Particulate	2.04	16.62	0.42	1.24	1.68	3.58
Dissolved[b]	0.04	0.32	0.004	0.02	0.06	0.02
Total	2.08	16.94	0.424	1.26	1.74	3.60
Theoretical[b]	1.85	2.65	0.21	1.32	0.79	2.38
Flux ratio (unitless) Total/Theoretical	1.10	0.62	1.92	0.95	2.15	1.49

[a]All fluxes in 10^9 kg·yr^{-1}.
[b]*Poulton and Raiswell* [2000].

[8] Riverine dissolved fluxes of all these metals are less than 3% of the total riverine flux [*Poulton and Raiswell*, 2000]. This is due, in part, because most metals are strongly particle reactive [*Pilson*, 1998] and relatively insoluble in water with oxic conditions of circa neutral pH. With our newly calculated global mean values for riverine sediments and the total sediment flux to the ocean [*Milliman and Syvitski*, 1992], the particulate metal fluxes to the oceans can be determined (Table 2). The riverine dissolved fluxes from *Poulton and Raiswell* [2000] have been included so that total metal fluxes to the ocean are also shown (Table 2). These new fluxes are indeed lower than previously determined, ranging from 9% lower (for Co) to 24% lower (for Cu).

[9] *Poulton and Raiswell* [2000] calculated a flux ratio to compare their empirically determined metal fluxes to theoretically determined fluxes based on world average soil chemistry [*Martin and Meybeck*, 1979]. Their theoretical flux is calculated from the average content of an element in average world soil and the world average discharge of particulate matter to the oceans. In a like manner, we have performed an exercise using both our new data from the HSIs and *Poulton and Raiswell*'s [2000] theoretical loads (Table 2). All our newly calculated flux ratios are less than those previously calculated [*Poulton and Raiswell*, 2000]. Given the constraints inherent in the calculations, the new flux ratios we report for Cr and Ni are essentially unity, and suggest that these fluxes are little affected by anthropogenic perturbations. Our Co and Cu empirical fluxes are approximately twice the theoretical fluxes and higher than anticipated, as observed by others [*Poulton and Raiswell*, 2000]. However our new data show that when the sediment flux from HSIs is considered, the Co and Cu fluxes are lower than previously thought. The Ni and Cr empirically determined input is essentially equal to the theoretical. Previous mismatches in Cu, Zn and Pb mass balances have been attributed to increased input of these metals from various anthropogenic activities [*Li*, 1981] or, as suggested by *Poulton and Raiswell* [2000], to differential weathering or geochemical fractionation selectively affecting these metals, especially Cu. Our new calculation of global fluxes implies that the anthropogenic flux of these metals, especially of Cu, maybe ~25% lower than previously determined.

4. Conclusions

[10] The role of HSIs as sources of sediment to the world's ocean is now acknowledged [*Milliman and Syvitski*, 1992]. HSIs may contribute as much as 33% of the

total sediment which enters the world's oceans annually [*Milliman and Syvitski*, 1992; *Lyons et al.*, 2002], leaving little doubt that HSIs are important sediment and particulate organic carbon sources to the oceans [*Lyons et al.*, 2002]. This must be the case for other particle-reactive substances, yet these important sediment-supplying landscapes have not been considered in previous elemental particulate mass balances [*Poulton and Raiswell*, 2000; *Martin and Whitfield*, 1983; *Drever et al.*, 1988]. The role of HSIs in geochemical budgets of particulate materials clearly requires that additional data from other HSIs such as Indonesia and the Philippines be obtained in order to assess more accurately the overall flux of chemicals associated with sediments into the world's ocean and to support the conclusions presented herein. Recent isotopic measurements also support our conclusion that input from HSIs could have great importance to ocean chemistry [*Martin et al.*, 2000].

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