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Rhenium in Indian rivers: Sources, fluxes, and contribution to oceanic budget

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[1] The abundance and distribution of dissolved and particulate Rhenium (Re) has been measured in several rivers draining the Himalaya and Peninsular India, from their origin to outflow into the Bay of Bengal and the Arabian Sea. The large data set resulting from this study on rivers flowing through a variety of lithologies e.g., the crystallines and sediments of the Himalaya, Deccan basalts, Vindhyan sediments and the Indian shield significantly enhances our understanding of the aqueous geochemistry of Re and also constrains its sources to rivers and fluxes to the sea. The concentration of dissolved Re in rivers of the Himalaya and the Peninsular India shows wide range; 1.4 to 72.7 pmol/kg (mean 7.8 pmol/kg) and 0.5 to 122 pmol/kg (mean 15 pmol/kg) respectively. The discharge weighted average annual flux of dissolved Re transported by the rivers from these regions are ∼5800 and ∼15,700 mol/year respectively. The major source of dissolved Re, as determined from inter-element associations, is black shales for the Himalayan rivers and pyrites in basalts for the east flowing Deccan rivers. In addition, there are evidences of considerable anthropogenic supply of Re to some of the rivers that have very high Re concentrations. Estimates of anthropogenic supply based on their Re/K ratios suggest that this source accounts for most of the Re in the Peninsular rivers, particularly the Godavari. The annual flux of anthropogenic Re transported by the Peninsular rivers is ∼14,600 mol, most of which is from the Godavari. This anthropogenic flux accounts for ∼70% of the total Re supply by the Indian rivers to the adjacent seas and 3.4% of the global riverine flux to the oceans. The global average, pre-anthropogenic (natural) concentration of dissolved Re in rivers is estimated to be ∼3 pmol/kg based on Re−K correlation. This value is much lower than the contemporary average determined from the measured concentrations and earlier estimate of natural Re based on Re−SO_4 link.

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1. Introduction

[2] The application of Re as a potential proxy to investigate marine paleo redox conditions [*Morford and Emerson*, 1999; *Jaffe et al.*, 2002; *Morford et al.*, 2007; *Miller et al.*, 2011] and in the development of $^{187}Re-^{187}Os$ pair as a chronometer for dating of ancient organic rich sedimentary rocks such as black shales [*Koide et al.*, 1986; *Ravizza and Turekian*, 1989; *Ravizza and Peucker-Ehrenbrink*, 2003] have motivated detailed investigations on the aqueous geochemistry of Re, particularly its sources to and sinks from the oceans. The abundance and distribution of Re together with other redox sensitive elements (Os, Mo and U) in sediments [*Peucker-Ehrenbrink et al.*, 1995; *Morford and Emerson*, 1999; *McManus et al.*, 2006] have been used to decipher the distribution of oxic and anoxic sinks in both modern and ancient oceans [*Crusius et al.*, 1996]. In oxic waters, Re exists as soluble ReO_4^- which is relatively "un-reactive" and remains in solution [*Anbar et al.*, 1992; *Colodner et al.*, 1993]. In reducing conditions, the oxidation state of Re decreases from $Re^{VII}O_4^-$ to $Re^{IV}(OH)_4$ which in the presence of sulfide promotes the removal of Re to sediments [*Ravizza et al.*, 1991; *Colodner et al.*, 1993, 1995; *Chappaz et al.*, 2008]. As a result, Re abundance in organic rich sediments is orders of magnitude higher than its average crustal value [*Ravizza and Turekian*, 1989; *Ravizza et al.*, 1991; *Peucker-Ehrenbrink et al.*, 1995; *Singh et al.*, 1999]. The weathering of these Re rich organic sediments is a major source of dissolved Re to rivers [*Colodner et al.*, 1993; *Dalai et al.*, 2002; *Jaffe et al.*, 2002] a finding that makes it a useful tracer to estimate black shale weathering in river basins. To fully exploit the potential of Re to investigate the biogeochemical processes in fresh water and marine systems, detailed and systematic knowledge of its sources, sinks and chemical behavior in different aquatic reservoirs is required. The study presented in this paper is a step in this direction, with the aim to characterize the mobility of Re and its aqueous geochemical behavior during weathering of various lithologies present in river basins of India and to determine its fluxes from these tropical rivers. Further, as this study encompasses several rivers draining through basins of different geological settings and climatic conditions, e.g., the Himalaya, Deccan, Vindhyan and the Peninsular shield, it is more likely to yield "representative" flux of Re from the region to the oceans and its impact on the marine Re budget.

[3] In addition to chemical weathering of river basins, another source of Re to rivers and other reservoirs is anthropogenic activities. These activities, particularly mining and use of coal, petroleum and metallic ores and the disposal of wastes from industrial use of Re e.g. aviation, petrochemicals and high temperature catalysis, all add to the natural abundance of Re in rivers thereby enhancing its riverine flux [*Chappaz et al.*, 2008; *Chen et al.*, 2009]. Among the river basins investigated in this study, there are petrochemical industries in the Narmada, Mahi, the Sabarmati [*Rahaman and Singh*, 2010; *Rahaman et al.*, 2011] and the Yamuna basins whereas metal industries such as foundries, metal extraction and catalytic development are present in the basins of the Krishna [*Das et al.*, 2005, 2011], the Godavari [*Gupta*, 2001] and the Yamuna [*Central Pollution Control Board*, 2006]. The study of these rivers therefore provides an opportunity to address the impact of Re contribution to them from anthropogenic sources.

2. Study Area

[4] This work has been carried out on rivers draining the Himalaya (the Ganga, Brahmaputra and their tributaries) and the Indian Peninsula (the Krishna, Godavari, Narmada, Tapi, Mahi, Sabarmati and the Mandovi; Figure 1). The Ganga and the Brahmaputra after draining the central and the eastern Himalaya (Figure 1) enter the plain and drain vast alluvial tracts before flowing into the Bay of Bengal. The catchment of the Peninsular rivers predominantly consists of Deccan traps, parts of older cratons in southern India and alluvial plain. The details of the lithologies drained by these rivers are given in Table 1.

2.1. Geology and Geohydrology of the Himalayan River Basins

[5] The Himalayan sub-basin of the Ganga and its tributaries consists of four major lithological units; the Tethyan Sedimentary Sequences (TSS), Higher Himalaya, Lesser Himalaya and the Siwalik [*Valdiya*, 1980; *Sarin et al.*, 1989]. The TSS mainly consists of carbonates and meta-sediments whereas the HH is composed of crystallines, metamorphosed carbonates and calc-silicates [*Oliver et al.*, 2003]. The dominant lithologies of the Higher Himalayan Crystallines are granites, gneisses and leuco-granites. The lithology of the LH is dominated by crystalline and meta-sedimentary rocks which include limestones, dolomitic carbonates, shales,

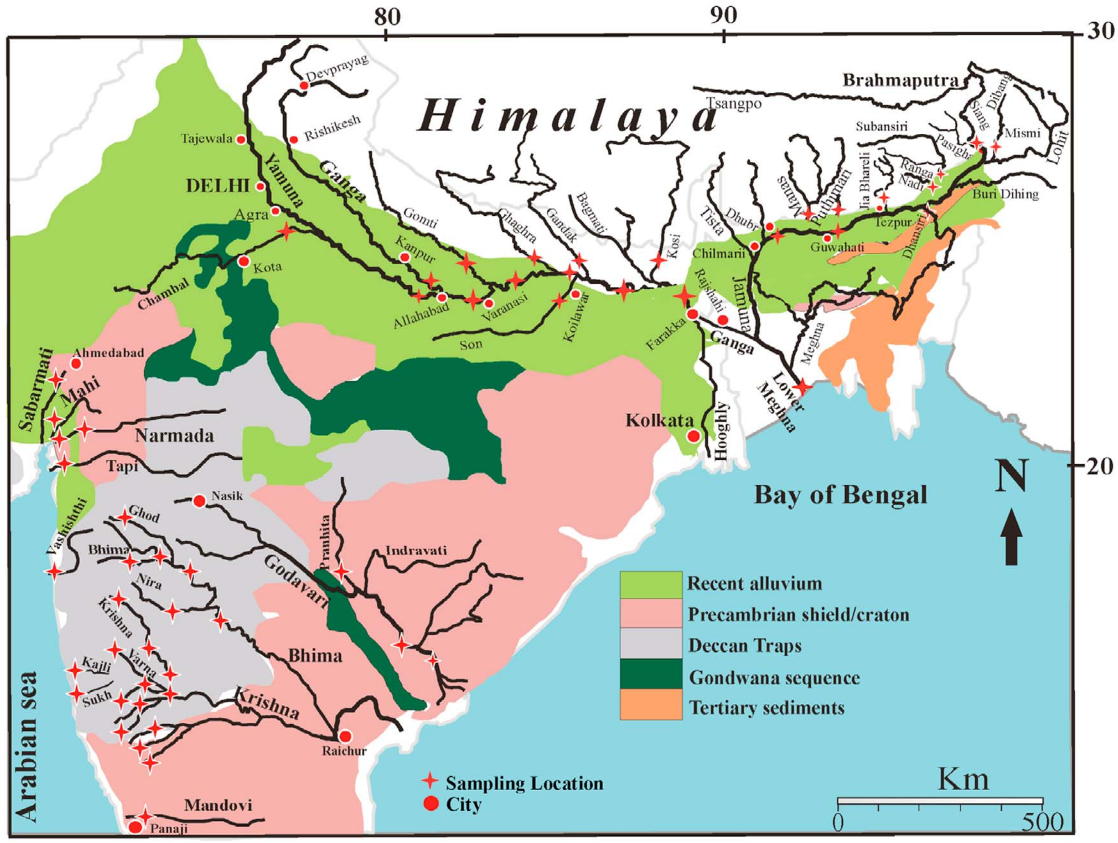

Figure 1. Sampling locations in the Himalayan and the Peninsular Indian rivers. Among the Himalayan rivers, samples are from mainstreams and tributaries of the Ganga-Brahmaputra rivers systems. In case of the Peninsular rivers, except for the Krishna river system samples are mostly from their final out flow.

slates, quartzites, evaporites and calc-silicates. Black shales are one of the minor, but important lithologies of the Himalaya. Their occurrence has been reported from its various regions in the outer Lesser Himalaya. The Siwaliks is the southernmost unit of the Himalaya; it mostly consists of sandstones [*Valdiya*, 1980]. Downstream of the Himalaya, the Ganga flows through the Ganga Plain, made of vast tract of alluvium consisting of clay, sand and gravel [*Sinha et al.*, 2005] brought by the river and its tributaries from the Higher and the Lesser Himalaya [*Singh et al.*, 2008; *Rahaman et al.*, 2009].

[6] The Ganga receives water and sediments from its catchments in the Himalaya and the Peninsular India; the dominant source of water being the summer monsoon rainfall in June–September. The Ganga basin encompasses the drainage areas of the Ganga mainstream and its tributaries the Ghaghra, Gandak and the Kosi from the Himalaya, the Yamuna draining both the Himalaya and the Peninsular India, the Son and the Gomti flowing only through the Peninsular India and the Ganga plain (Figure 1 and Table 1). Yamuna is the largest tributary of the Ganga flowing mainly through the Peninsular India and joins the Ganga mainstream at Allahabad. The Chambal, Sind, Betwa and the Ken are the tributaries of the Yamuna, drain the Deccan traps and the Vindhyan sedimentary sequences [*Krishnan*, 1982] (Figure 1 and Table 1). One of the distributaries of the Ganga enters Bangladesh where it merges with the Brahmaputra to form the Padma. The confluence of the Padma with the Upper Meghna forms the Lower Meghna which is a major river with high water discharge that falls into the Bay of Bengal. The other distributary of the Ganga, the Hooghly, after receiving number of rivers from the northeastern edge of the Indian Peninsula debouches into the Bay of Bengal near Kolkata.

[7] The Brahmaputra, originating in the Himalaya-Tibetan region is among the major global rivers. It originates in the Kailash Mountain in Tibet and flows through Tibet, Eastern syntaxis, Mismi Hills, Himalaya and Indo-Burmese Ranges [*Singh et al.*, 2005] before entering the Bay of Bengal. The

Table 1. Lithological and Hydrological Details of Rivers

River	Major Lithologies	Place	Area (10^6 km^2)	Discharge (km^3 yr^{-1})	Runoff (mm yr^{-1})	Reference[a]
		Himalaya Rivers				
Brahmaputra	Igneous rocks, crystalline rocks and carbonates, black shales, quartzite and alluvium.	Bahadurabad	0.636	670	1053	1
Ganga	Granite-gneisses, metamorphosed carbonates, meta-sedimentary rocks, black shales, alluvium	Farraka	0.935	380	410	1
Yamuna	Granite-gneisses, Pre-Cambrian carbonates, black shales, Vindhyan sedimentary sequences, Deccan basalts and alluvium	Allahabad	0.366	93	250	1
Hooghly	Granite-gneisses, carbonates, black shales, meta-sediments, Recent alluvium	Kolkata	0.185	52	657	2
		Peninsular Rivers				
Narmada	Basalts, Vindhyan sediments and alluvium	Bharuch	0.099	47	418	3
Tapi	Basalts and alluvium	Kathor	0.065	18	282	3
Mahi	Shale-gneisses	Kheda	0.035	12	339	3
Sabarmati	Shale-gneisses	Ahmedabad	0.022	4	189	3
Vishwamitri	Trappean, Alluvium	Vadodara	0.003	1	250	4
Krishna	Basalt, Alluvium and Carbonate	Vijyawada	0.026	17.3	463	5
Bhima	Basalt, Alluvium and Carbonate	Raichur	0.033	7.2	463	
Godavari	Basalts, phyllites, schists, Archaean granites-gneisses and alluvium	Rajamundry	0.312	110	409	6
Mandovi	Basalts, granite-gneisses, laterite, alluvium	Goa	0.001	16	1600	7

[a]References are numbered as follows: 1, *Krishnaswami and Singh* [2005]; 2, *Biswas* [1985]; 3, *Madhavan and Subramanian* [2001]; 4, *Raj et al.* [2004]; 5, *Das et al.* [2005]; 6, *Jha et al.* [2009]; 7, *Upadhyay and Gupta* [1995].

dominant lithologies in the drainage basin of the Brahmaputra are the Paleozoic sedimentary sequences of Tibet and the Trans Himalayan Batholith composed of felsic to mafic rocks (Table 1). It flows through highly metamorphosed rocks of the Higher Himalayan Crystallines at the Eastern Syntaxis near Namche Barwa [*Burg et al.*, 1998]. Between Namche Barwa and Pasighat, the river passes through the Abor volcanics and the Miri limestone interbedded with shales and other sedimentary rocks including black shales of the Lesser Himalaya and the Gondwana Group [*Thakur*, 1986]. Downstream of Pasighat, the river flows through the alluvium of the Assam Plain. The Northern tributaries drain the crystalline and meta-sediment lithologies of the Higher Himalaya followed by the sedimentary rocks and crystallines of the Lesser Himalaya and finally the Tertiary sediments of the Siwaliks [*Singh et al.*, 2005]. The eastern tributaries of the Brahmaputra drain the Mishmi hills (Figure 1 and Table 1).

[8] The water discharge and runoff of the Brahmaputra mainstream is given in Table 1. The major contributor to the Brahmaputra discharge is rainfall during the SW monsoon (June to September) and northeast monsoon. In addition there are also contributions from meltwater and to a minor extent from springs and groundwater [*Guan and Chen*, 1981]. The monthly water discharge pattern of the Brahmaputra reflects the influence of monsoon with significant temporal variations [*Singh et al.*, 2005].

2.2. Geology and Geohydrology of the Peninsular River Basins

[9] The major lithologies exposed in the drainage basins of the Peninsular rivers are the Deccan basalts, the Bundelkhand crystallines, the Vindhyan sediments, sedimentary sequences of the Gondwana and Archean shields [*Krishnan*, 1982]. In the Krishna river basin, Deccan basalts are the dominant lithology in the upstream catchments whereas granites, gneisses and sedimentary rocks are predominant in the lower catchments (Table 1). The basin geology of the Godavari consists of Deccan traps, Dharwar craton and Archaean, Precambrian and Gondwana sedimentary sequence and recent alluvial cover [*Biksham and Subramanian*, 1988].

The Narmada drains the Deccan basalts and the Vindhyan. The Tapi drains mostly through the Deccan basalts with part of its downstream drainage in alluvium [*Rahaman and Singh*, 2010]. The Mandovi river flows through the Western Ghats near its origin and the Deccan traps and the Archean shield.

[10] Godavari is the largest river in Peninsular India and the third largest in India. The river originates in the Western Ghats near Nasik and flows east-south before draining into the Bay of Bengal through three main distributaries (Gautami, Vashishtha and Vainatayam; Figure 1). The Krishna is the second largest eastward draining river in Peninsular India; it originates in the Mahadev range of the Western Ghats and its important tributaries are the Bhima, Koyna, Varna, Panchganga, Dudhganga and the Ghataprabha (Figure 1). Bhima is the largest tributary of the Krishna and the Ghod, Mutha, and the Nira being its tributaries [*Das et al.*, 2005]. A number of small/medium west flowing rivers, the Vashishthi, Kajli and the Sukh rise in the Western Ghats and drain mostly Deccan Basalts before falling into the Arabian Sea (Figure 1). The other west flowing rivers are the Narmada, Tapi, Mahi, Sabarmati and the Mandovi (Figure 1). The Narmada, originates from Amarkantak in the Vindhyan Mountains in Madhya Pradesh (MP) whereas the Tapi originates in central India and drains into the Gulf of Cambay. The Sabarmati and the Mahi river basins are composed of lithologies of the Aravalli dominated by alluvium derived from it [*Madhavan and Subramanian*, 2001]. The Mandovi river originates in the Western Ghats and drains into the Arabian Sea [*Upadhyay and Gupta*, 1995]. The drainage areas and runoff of these river basins and the details of lithologies of their basins are given in Table 1.

[11] The dominant source of water to all these rivers is monsoon, however, their water and sediment discharge is moderated through reservoirs/dams built along their course. In addition, the chemistry of these rivers is influenced by the domestic and industrial inputs from various cities located along their banks.

3. Sampling and Analysis

[12] This study forms a part of a major program of the group on chemical weathering in river basins of India [*Dalai et al.*, 2002; *Sarin et al.*, 2002; *Das et al.*, 2005; *Singh et al.*, 2005; *Rai et al.*, 2010; *Rahaman and Singh*, 2010]. Samples for this study are from the archives of earlier collection for chemical and isotopic measurements. These archives are filtered and acidified samples preserved in precleaned bottles. A large number of river water samples were analyzed for Re in this study (Figure 1 and Table 1); in addition a few samples of industrial effluents discharging into some of these rivers were also analyzed to investigate the role of anthropogenic input of Re to the riverine budget.

[13] Samples from the Ganga plain are from the collections made during three field campaigns, May 2004, October 2006 [*Rai et al.*, 2010] and February 2009 (this study). Water and sediment samples from the mainstream and tributaries of the Brahmaputra used in this study were collected by *Singh et al.* [2005] during the field campaigns in October, 1999 and July, 2000. One sample was collected during monsoon 2009 from the Lower Meghna following the confluence of the Ganga and the Brahmaputra rivers to the Bay of Bengal. Most of the samples from the Ganga and the Brahmaputra rivers and their tributaries analyzed in this study were collected during high river stages (July–October).

[14] Among the Peninsular rivers, the Godavari and Krishna and their tributaries were sampled by *Sarin et al.* [2002] and *Das et al.* [2005, 2006] respectively (Table 2). The Krishna and its tributaries were sampled during peak monsoon, August–September 2002. For the Godavari river, three samples collected near its outflow during monsoon, August, 2000 were analyzed. Similarly, samples collected by *Rahaman and Singh* [2010] near the outflow of the Narmada, Tapi, Mahi and the Sabarmati were measured for Re. Most of the archived water samples were filtered at the sampling sites through 0.2 μ nylon filters, except a few samples which were filtered through Millipore cellulose filter (0.45 μ). The filtered samples were acidified to $pH < 2$ with ultra pure nitric acid and stored in precleaned polyethylene bottles. *Rahaman and Singh* [2010] have established that Re abundances in water samples filtered either through 0.2 or 0.45 μ are not discernibly different. In the laboratory a known weight ($\sim$100 g) of filtered and acidified water samples were spiked with a known amount of ^{185}Re tracer. The spiked samples were stored at least for 24 h for sample-spike equilibration and Re was purified following ion exchange procedures [*Rahaman and Singh*, 2010]. The purified Re extract was dissolved in 3 ml 0.5 N HNO_3 and its concentration were determined by measuring its $^{185}Re/^{187}Re$ ratio using ICP-MS (Thermo X-series II). Instrumental mass fractionation correction was made by measuring Re standard of natural composition frequently.

Table 2. Details of the Sampling in the Himalayan and the Peninsular River Basins

Sample Code	River	Place	Location: Lat-Long (°N; °E)	Sampling Period	Reference[a]
		Ganga and Tributaries			
BR 06-12-1	Ganga	Allahabad	25°30.47′; 81°51.76′	20 Oct, 2006	2
BR 06-14-1	Ganga	Varanasi	25°17.83′; 83°00.60′	21 Oct, 2006	2
BR 06-301	Ganga	Patna	25°37.44′; 85°09.21′	16 Oct, 2006	2
BR06-104	Ganga	Rajmahal	25°03.41′; 87°50.23′	15 Oct, 2006	2
BR 06-11-1	Gomti	Ghazipur	25°32.05′; 83°11.91′	19 Oct, 2006	2
GP09-50	Yamuna	Agra	27°15.24′; 78°01.30′	28 Feb, 2009	1
BR-346	Yamuna	Allahabad	25°25.16′; 81°50.19′	14 May, 2004	2
BR 06-13-1	Yamuna	Allahabad	25°25.33′; 81°50.26′	20 Oct, 2006	2
GP09-30	Chambal	Dhaulpur, Kota	26°39.47′; 77°54.25′	27 Feb, 2009	1
BR-201	Son	Koilawar	25°33.81′; 84°47.56′	16 Oct, 2006	2
BR06-901	Ghaghra	Revilganj	25°48.78′; 84°35.81′	18 Oct, 2006	2
BR06-705	Gandak	Hazipur	25°41.33′; 85°11.49′	18 Oct, 2006	2
BR06-501	Kosi	Dhumarighat	25°32.70′; 86°43.14′	18 Oct, 2006	2
		Brahmaputra and Its Tributaries			
BR-59	Siang	Pasighat	95°20.15′; 28°4.67′	28 July, 2000	3
BR-51	Brahmaputra	Guwahati	91°44.22′; 26°11.62′	26 July, 2000	3
BR-73	Brahmaputra	Dhubri	89°59.00′; 76°26′1.12	26 July, 2000	3
BR-10	Dhansiri		93°43.88′; 26°37.87′	24 Oct, 1999	3
BR-12	Buri Dihing		94°53.02′; 27°18.74′	25 Oct, 1999	3
BR-14	Dibang		95°35.15′; 27°47.84′	26 Oct, 1999	3
BR-57	Ranga Nadi		94°3.64′; 27°12.32′	27 July, 2000	3
BR-61	Subansiri		94°15.42′; 27°26.74′	28 July, 2000	3
BR-63	Jia Bhareli		92°52.77′; 26°48.65′	29 July, 2000	3
BR-69	Puthimari		91°39.20′; 26°22.01′	30 July, 2000	3
BR-71	Manas Biki		90°55.17′; 26°29.73′	30 July, 2000	3
LM-1	Low Meghna	Monsoon	–	– Sept, 2009	2
		Peninsular Rivers (East Flowing Rivers)			
KRS-1	Krishna before confluence with Panchganga		16.79°; 74.63°	28 Aug, 2002	4
KRS-2	Krishna after confluence with Panchganga		16.65°; 74.64°	28 Aug, 2002	4
KRS-3	Krishna after confluence with Koyna, near Karad		17.30°; 74.19°	29 Aug, 2002	4
KRS-4	Krishna near Umbraj before confluence with Koyna		17.40°; 74.11°	29 Aug, 2002	4
KRS-5	Krishna after confluence with Varna		16.80°; 74.57°	3 Sept, 2002	4
BHM-3	Bhima after confluence with MTH-1		18.57°; 74.38°	25 Aug, 2002	4
BHM-4	Bhima after confluence with Ghod River		18.40°; 74.57°	26 Aug, 2002	4
NIRA-1	Nira River at Baramati		17.94°; 74.94°	– Sept, 2002	4
KYN-1	Koyna before confluence with Krishna		17.27°; 74.18°	29 Aug, 2002	4
KYN-2	Koyna at origin, near Mahabaleshwar		17.93°; 73.61°	3 Sept, 2002	4
VRN-1	Varna before mixing with Krishna		16.87°; 74.36°	29 Aug, 2002	4
PGN-1	Panchganga before confluence with Krishna		16.69°; 74.60°	28 Aug, 2002	4
GTP-1	Ghataprabha near Adkur village		16.01°; 74.27°	1 Sept, 2002	4
HRN-1	Hiranyakeshi river at Chandkhand-Gadinglaj road		16.36°; 74.35°	31 Aug, 2002	4
TPN-1	Tambrapani at Chandkhand-Belgaum road		15.92°; 74.29°	1 Sept, 2002	4
DDG-1	Dudhganga near Gargoti		16.43°; 74.14°	31 Aug, 2002	4
VDG-1	Vedganga near Gargoti		16.36°; 74.15°	31 Aug, 2002	4
BGW-1	Bhogwati near Amjai village		16.50°; 74.05°	31 Aug, 2002	4
GHOD-2	Ghod before mixing Bhima		19.08°; 73.77°	24 Aug, 2002	4
GD-5/2K/M	Pranhita before mixing Godavari		–	– Aug, 2000	5
GD-9/2K/M	Godavari at Bhadrahalam		–	– Aug, 2000	5
GD-20-99/M	Godavari at Rajhamundry		–	– Aug, 2000	5

Table 2. (continued)

Sample Code	River	Place	Location: Lat-Long (°N; °E)	Sampling Period	Reference[a]
		West Flowing Rivers			
SUKH-1	Sukh	Near Khare patan	16.56°; 73.63°	1 Sept, 2002	4
KJL-1	Kajli	Near Lanjha	16.93°; 73.51°	2 Sept, 2002	4
VAT-1	Vashishthi	Near Chiplun	17.53°; 73.54°	2 Sept, 2002	4
MD-1	Mandovi	Panjim, Goa	15°32.56′ 73°57.69′	25 Oct, 2007	1
TPM-1	Tapi	Surat	21°10.56′ 72°46.74′	19,Sept 2007	1
TPM-14	Tapi	Near Ukai dam	–	19,Sept 2007	1
NE-18	Narmada	Near Bharuch	21°40.51′ 72°57.00′	20 March, 2007	1
NE-21	Narmada	Narmada Dam	21°50.02′ 73°45.34′	20 March, 2007	1
NE-22	Narmada	Narmada Dam	21°51.81′ 73°41.75′	20 March, 2007	1
NEM-1	Narmada	Near Bharuch	21°40.59′ 72°55.58′	17 Sept, 2007	1
NEM-2	Narmada	Near Bharuch	21°39.08′ 72°46.64′	17 Sept, 2007	1
KOH-16	Mahi	Mahi Sagar Bridge	–	27 June, 2008	1
KOH-17	Sabarmati	Vatmann bridge	–	27 June, 2008	1
KOH-13	Vishwamitri	Near Vadodara	–	27 June, 2008	1

[a]Samples are taken from sources numbered as follows: 1, *Rahaman and Singh* [2010]; 2, *Rai et al.* [2010] ; 3, *Singh et al.* [2005] ; 4, *Das et al.* [2005]; 5, this study.

Analytical precession of Re measurements, determined based on several replicate analysis is ∼2% [*Rahaman and Singh*, 2010].

4. Results

4.1. Dissolved Re in the Himalayan Rivers

[15] The dissolved Re concentration in the Ganga mainstream in the Ganga plain during high river stage shows an overall decrease from ∼13 to 6 pmol/kg along its course from Allahabad to Rajmahal (Figure 2). These compare with values of 5.3 pmol/kg for the headwaters of the Ganga at the foothills of the Himalaya near Rishikesh [*Dalai et al.*, 2002] and 9.0 pmol/kg at its outflow at Arichaghat in Bangladesh [*Colodner et al.*, 1993] in samples collected during the same river stage. The concentration of Re among the Ganga tributaries (excluding the Gomti and Yamuna) during high river stage ranges within a factor of ∼2, from ∼4 pmol/kg in the Kosi to ∼9 pmol/kg in the Yamuna (Table 3). The Gomti at Ghazipur has much higher Re, 32.1 pmol/kg a value not unexpected considering that the dense population around the river may be discharging significant quantities of domestic and industrial wastes into the river [*Jain et al.*, 2007; *Rai et al.*, 2010]. The impact of anthropogenic activities in contributing Re to rivers is also evident from its very high concentration, 72.7 pmol/kg in the Yamuna at Agra, a densely populated and industrialized city on its banks. This inference draws support from the observation that Re in the Yamuna at Saharanpur, ∼300 km upstream of Agra is much lower, 7.7 to 15 pmol/kg during different seasons [*Dalai et al.*, 2002]. Measurement of Re in the Yamuna during its low stages (May, 2004) show that it is 40 pmol/kg, about four times higher than the value of 9.2 pmol/kg during its high stage (October, 2006). The lower concentration during high river stage is most likely a result of dilution due to increased water discharge. In addition, the impact of waste disposal in the rivers is expected to be more significant during lean flow periods due to considerably lower water discharge. These results underscore the important role of anthropogenic input in contributing to the spatial and temporal variability of Re in the Yamuna.

[16] Dissolved Re in samples from the Brahmaputra and its tributaries ranges from 1.4 to 6.2 pmol/kg with an average of 3.5 pmol/kg (Table 3). The average Re concentration of the Brahmaputra and its tributaries is lower than that of the Ganga, 18 pmol/kg. This could be because enhanced anthropogenic activities in the Ganga river basin. The highest Re concentration in the Brahmaputra system, 6.2 pmol/kg is observed in the Dibang sample and the lowest value, 1.4 pmol/kg in the Jia Bhareli sample (Table 3). The Dibang flows through the Mishmi Hills composed of calc-alkaline diorite-tonalite-granodiorite complexes and tholeiitic metavolcanic rocks whereas the Jia Bhareli drain through the Lesser Himalayan lithologies mainly consisting of quartzite and schist [*Singh et al.*, 2005]. Therefore, higher Re in metavolcanic rocks compared to quartzite and schist could be responsible for higher

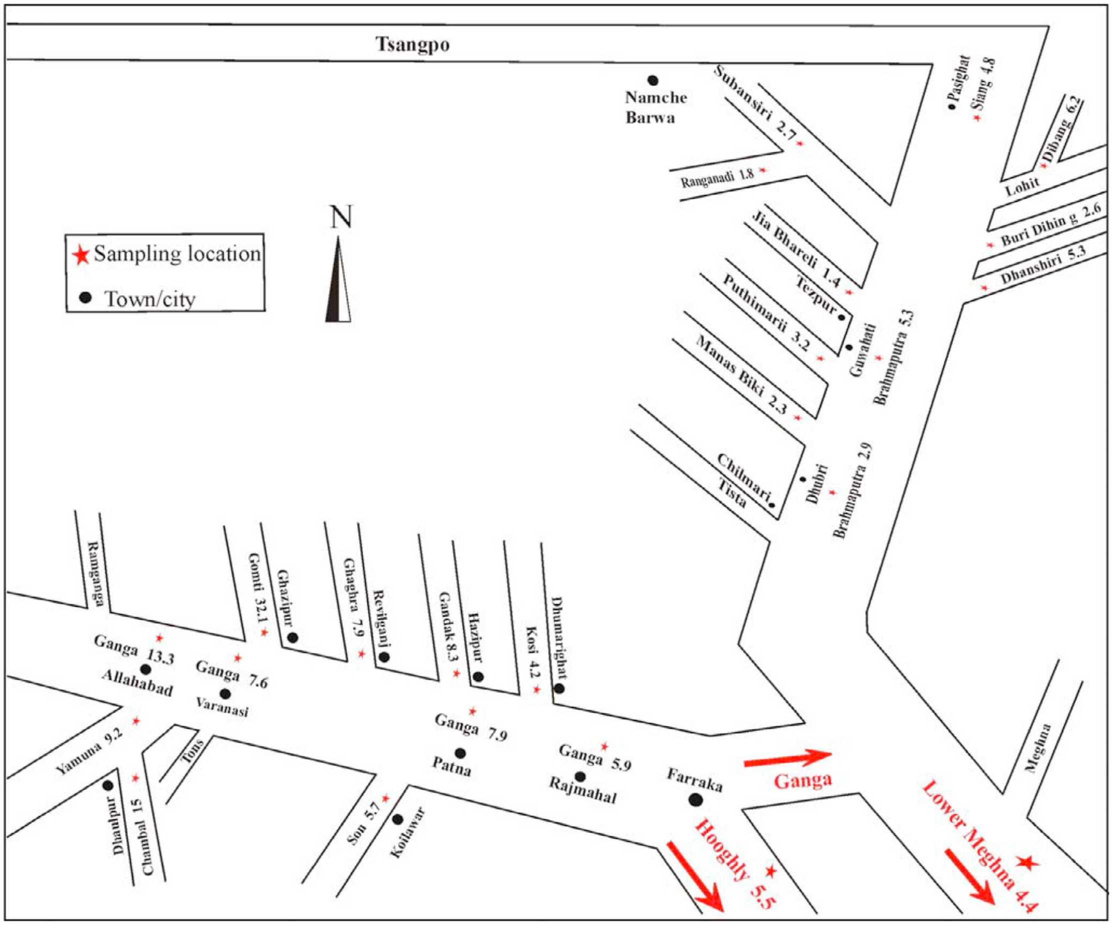

Figure 2. Funnel diagram of the Ganga-Brahmaputra river system. Re concentration measured in mainstream and their tributaries are shown. Re concentration of the individual rivers is expressed in pmol/kg.

Re in the Dibang river. The Re concentration of the Brahmaputra at Dhubri, its outflow from India is ~3 pmol/kg lower than that reported at Arichaghat in Bangladesh, ~6 pmol/kg [*Colodner et al.*, 1993]. Downstream of Arichaghat, the Brahmaputra and the Ganga form the lower Meghna (Figure 2 and Table 3) which has a dissolved Re concentration of 4.4 pmol/kg.

4.2. Dissolved Re in Peninsular Rivers

[17] The concentration of dissolved Re in the Peninsular rivers shows a very wide range varying by more than two orders of magnitude, from 0.5 to 41 pmol/kg and 0.4 to 122 pmol/kg in the west and the east flowing rivers respectively. Re was measured in two samples of the Godavari and one sample of Pranhita, a tributary of the Godavari close to its outflow into the Bay of Bengal; these yield values in the range of 36–122 pmol/kg (Table 3). Among the east flowing rivers, the Ghod and the Godavari have very high Re concentrations 68 and 122 pmol/kg respectively (Table 3). Re in the headwaters of the Krishna and many of its tributaries; the Koyna, Verna, Panchganga, Ghataprabha, Hiranyakeshi, Tambrapani, Dudhganga, Vedganga and the Bhogwati are quite low, ~1 pmol/kg (or lower), exceptions to this being the Bhima and its tributary Nira which have Re concentrations of 4.5 and 8.5 pmol/kg respectively (Table 3). These two tributaries also have high total dissolved solids and sulphate indicating the influence of anthropogenic inputs on their chemistry [*Das et al.*, 2005]. The Narmada, Tapi, Mahi, and the Sabarmati, draining into the Gulf of Cambay have higher Re than the Mandovi and some of the smaller west flowing Peninsular rivers the Sukh, Kajli and Vashishthi (Figure 1 and Table 3). Lower Re in the Mandovi is consistent with the lower rate of chemical weathering in its basin [*Rahaman and Singh*, 2010]. The Re concentration of the Narmada is ~14.5 and 10 pmol/kg during nonmonsoon and monsoon respectively, almost double of that in the Tapi ~6 pmol/kg during monsoon. The Mahi and the

Table 3. Dissolved Re and Major Ions Compositions of the Himalayan and the Peninsular Rivers

Sample Code	River	[Re] (pmol/kg)	Ca (μM)	Mg (μM)	Na (μM)	K (μM)	Cl (μM)	SO_4^{2-} (μM)	$\sum cat^*$ (μM)	Reference[a]
					Ganga and Tributaries					
BR 06-12-1	Ganga	13.3	685	528	829	164	300	238	1906	2
BR 06-14-1	Ganga	7.6	658	415	966	102	447	165	1694	2
BR 06-301	Ganga	7.9	725	376	495	75	164	124	1507	2
BR06-104	Ganga	5.9	709	273	334	75	94	96	1297	2
BR 06-11-1	Gomti	32.1	859	848	1399	130	324	200	2912	2
GP09-50	Yamuna	72.7	1129	1145	6716	413	5375	672	4028	1
BR-346	Yamuna	40.0	794	1104	3575	136	1493	335	4116	2
BR 06-13-1	Yamuna	9.2	673	443	1275	85	696	181	1780	2
GP09-30	Chambal	15.3	655	641	2233	72	885	587	2716	1
BR-201	Son	5.7	537	253	431	43	116	50	1148	2
BR06-901	Ghaghra	7.9	867	384	256	74	43	131	1538	2
BR06-705	Gandak	8.3	712	308	138	82	39	187	1201	2
BR06-501	Kosi	4.2	421	166	173	69	15	67	814	2
					Brahmaputra and Its Tributaries					
BR-59	Siang	4.8	424	99.7	77.6	36.9	17.4	119	621	3
BR-51	Brahmaputra	5.3	475	111	90.3	67.3	20.7	114	723	3
BR-73	Brahmaputra	2.9	396	153	107	49.6	19	73.2	687	3
BR-10	Dhansiri	5.3	230	226	288	63.4	83.1	129	724	3
BR-12	Buri Dihing	2.6	228	293	189	30.7	41.7	85.1	699	3
BR-14	Dibang	6.2	353	49.4	46.5	42.2	13.7	82.4	477	3
BR-57	Ranga Nadi	1.8	126	37.1	105	27.6	10.7	33.8	285	3
BR-61	Subansiri	2.7	303	108	71.2	25.7	8.8	95	499	3
BR-63	Jia Bhareli	1.4	191	59.5	90.3	32	9.8	32.5	363	3
BR-69	Puthimari	3.2	551	219	98.9	36.4	18.5	112	887	3
BR-71	Manas Biki	2.3	416	101	58.5	27.1	10.2	102	592	3
					Peninsular Rivers (East Flowing Rivers)					
KRS-1	Krishna	1.4	454	270	484	20	287	90	941	4
KRS-2	Krishna	1.3	329	206	363	17	262	69	653	4
KRS-3	Krishna	0.7	490	295	410	19	221	46	993	4
KRS-4	Krishna	1.1	645	375	503	22	268	55	1277	4
KRS-5	Krishna	1.6	390	247	468	17	279	86	843	4
BHM-3	Bhima	4.7	768	479	1229	49	627	342	1898	4
BHM-4	Bhima	6.2	822	547	1494	38	779	490	2122	4
NIRA-1	Nira	8.3	672	641	5630	27	1397	1566	5573	4
KYN-1	Koyna	0.5	309	201	276	10	176	18	620	4
KYN-2	Koyna	0.4	81	59	103	5	75	10	173	4
VRN-1	Varna	1.0	297	185	273	31	195	37	591	4
PGN-1	Panchganga	0.9	208	125	239	15	208	40	379	4
GTP-1	Ghataprabha	0.8	74	52	127	6	116	10	143	4
HRN-1	Hiranyakeshi	0.5	71	54	131	5	120	11	141	4
TPN-1	Tambrapani	0.8	107	74	150	9	146	14	194	4
DDG-1	Dudhganga	1.0	289	168	223	10	177	33	513	4
VDG-1	Vedganga	0.8	172	110	178	7	148	13	319	4
BGW-1	Bhogwati	0.9	193	128	192	9	159	17	363	4
GHOD-2	Ghod	68.4	973	1206	3960	65	2333	752	3871	4
GD-5/2K/M	Pranhita	36	470	173	271	43	106	37	851	1
GD-9/2K/M	Godavari	122	756	630	1130	62	332	106	2246	1
GD-20-99/M	Godavari	120	644	470	812	53	275	74	1704	1
					West Flowing Rivers					
SUKH-1	Sukh	1.2	163	130	165	7	102	12	363	4
KJL-1	Kajli	1.1	162	128	168	6	101	11	363	4
VAT-1	Vashishthi	0.5	197	142	176	6	104	12	417	4
MD-1[b]	Mandovi	1.4	144	363	2983	78	3877	181	–	1
TPM-1[b]	Tapi	7.6	685	688	2441	84	2232	189	1666	1
TPM-14[b]	Tapi	4.1	550	345	562	42	204	57	1295	1
NE-18[b]	Narmada	14.8	627	683	2436	124	2112	148	1758	1
NE-21[b]	Narmada	13.9	537	385	479	43	150	42	1294	1

Table 3. (continued)

Sample Code	River	[Re] (pmol/kg)	Ca (μM)	Mg (μM)	Na (μM)	K (μM)	Cl (μM)	SO_4^{2-} (μM)	$\sum cat^*$ (μM)	Reference[a]
NE-22[b]	Narmada	14.7	648	407	522	45	164	44	1458	1
NEM-1[b]	Narmada	10	664	426	777	44	441	83	1470	1
NEM-2[b]	Narmada	11.1	721	533	1675	76	1426	150	1579	1
KOH-16[b]	Mahi	41	321	881	2640	94	1446	188	2490	1
KOH-17[b]	Sabarmati	37	683	673	11128	314	9310	1026	3488	1
KOH-13[b]	Vishwamitri	18							–	1

[a]Major ion data are taken from sources numbered as follows: 1, this study; 2, *Rai et al.* [2010]; 3, *Singh et al.* [2005]; 4, *Das et al.* [2005].
[b]Re data of the Narmada, Tapi, Mahi, Sabarmati, Mandovi and the Vishwamitri are taken from *Rahaman and Singh* [2010].

Sabarmati rivers have ~40 pmol/kg Re, several times higher than that in the Narmada and the Tapi. *Rahaman and Singh* [2010] had earlier underscored the role of anthropogenic contribution of Re to rivers draining into the Gulf of Cambay through direct discharge of industrial wastewaters into them.

4.3. Particulate Re in the Himalaya and Peninsular River Basins

[18] The abundance of Re in bed loads of the Yamuna collected at Allahabad and the Ganga at Rajmahal are 590 and 774 pg/g respectively (Table 4). *Pierson-Wickmann et al.* [2000] had reported Re concentration of 114 and 779 pg/g in two samples of bulk river bed loads of the Ganga at Rajshahi with an average 456 pg/g. The Re concentration in bulk sediments of the Brahmaputra drainage show a wide range from 30 to 400 pg/g with an average 136 pg/g [*Singh et al.*, 2003]. The limited data available till date seem to indicate that the average concentration of Re in the Ganga basin sediments may be higher than that in the Brahmaputra sediments (Table 4). Re abundance in the Brahmaputra sediments from Guwahati and Dhubri is 67 and 32 pg/g respectively before entering Bangladesh where it increases to 457 pg/g at its final outflow after the confluence of the Tista, whose sediments have a high Re concentration of 1154 pg/g [*Pierson-Wickmann et al.*, 2000]. Re in sediments of the Lower Meghna river is 680 pg/g.

[19] The Re abundance in sediments from the peninsular rivers shows large variability; ranging from

Table 4. Re Abundance in Bed Loads From the Himalaya and the Peninsular Rivers

Sample	River	Place	[Re] (pg/g)	Average [Re] (pg/g)	References
		Himalayan Rivers			
BR-324	Ganga	Rajmahal	353	774	this study
BR06-101	Ganga	Rajmahal	1195		
BGP-5	Ganga	Rajshahi	797	456	*Pierson-Wickmann et al.* [2000]
BGP-6	Ganga	Rajshahi	114		
BR06-13-2	Yamuna	Allahabad		590	This study
BR9	Brahmaputra	Guwahati	60	67	*Singh et al.* [2003]
BR56	Brahmaputra	Guwahati	75		
BR74	Brahmaputra	Dhubri	32	32	*Singh et al.* [2003]
BGP-14	Brahmaputra	Chilmari	161	482	*Pierson-Wickmann et al.* [2000]
BGP-82	Brahmaputra	Chilmari	803		
BGP-34	Meghna	Chor Fasson	680		*Pierson-Wickmann et al.* [2000]
		Peninsular Rivers			
BHM-3	Bhima	–	1570		this study
KIL-1	Kajli	–	3290		this study
KRS-2	Krishna	–	610		this study
VAT-1	Vashishthi	–	870		this study
TP(BS)-1	Tapi	Surat	53	992	*Rahaman and Singh* [2010]
TP(BS)-4	Tapi	Surat	66		
TP(BS)-12	Tapi	Surat	2857		
NE(BS)-1	Narmada	Bharuch	428	456	*Rahaman and Singh* [2010]
NE(BS)-8	Narmada	Bharuch	484		

53 to 3290 pg/g with an average of 1178 pg/g. This value is a factor of ~2 higher than the average Re in Deccan basalts, 595 pg/g [*Allegre et al.*, 1999] the dominant lithology of the Peninsular river basins and several times that in river sediments of the Himalaya (Table 4). In two bed loads samples from the Kajli and the Tapi TP(BS)-12, have very high Re, 3290 and 2857 pg/g respectively. The cause for these high values is unclear, one possibility is the enrichment of platinum group elements including Re in laterites [*Wimpenny et al.*, 2007] that are drained by these rivers. It is however, noted that if these two high Re samples are excluded, the average reduces to 583 pg/g, comparable to that in Deccan basalts.

5. Discussion

5.1. Sources of Rhenium to the Himalayan and the Peninsular Rivers

[20] The sources of dissolved Re to the rivers analyzed can be both natural and anthropogenic; the chemical weathering of major (silicates and carbonates) and minor (black shales, pyrites in basalts) lithologies of the river basins constitute the natural sources. The impact of anthropogenic Re is likely to be relatively more important for rivers draining the Ganga plain and Peninsular basins as these regions are far more populated and industrialized compared to the basins in the Himalaya. *Dalai et al.* [2002] had also made similar observation in the Yamuna river basin. Chemical weathering of different lithologies present in the drainage basin is an important source of Re to rivers. Considering that during their weathering, Re may be released to rivers along with major cations from the parent materials, any link between Re and one or more major cations in rivers can serve as a probe to learn about the behavior of Re during weathering and identify its source(s) to solution. Figure 3 is a scatter plot of Re versus $\sum$cat* (= Na* + K + Ca + Mg), where Na* is Na corrected for cyclic contribution, $Na^* = Na_r - Cl_r$; Na_r being Na measured in rivers, the cyclic Na is assumed to be equal to measured chloride [*Sarin et al.*, 1989]) for the different river systems analyzed in this study. The plot for the Ganga and its tributaries shows an overall significant linear trend ($r = 0.89$, $df = 11$, $p < 0.05$) whereas the correlation is poorer for the Brahmaputra ($r = 0.36$, $df = 9$, $p < 0.05$). Major ion data for the Ganga and the Brahmaputra river sample in Figure 3 are from *Rai et al.* [2010] and *Singh et al.* [2005] respectively. Pooling the data of both the Ganga and the Brahmaputra also yield a good correlation ($r = 0.88$, $df = 22$, $p < 0.05$) indicating that during chemical weathering Re and major cations get released to solution roughly in a constant proportion. This is intriguing as part of Re in some of the Ganga system samples is likely to be from minor phases (black shales) and anthropogenic inputs. The arithmetic average Re/$\sum$cat* molar ratio of the Ganga river system is $(7 \pm 4) \times 10^{-9}$, thus marginally decreases to $(6.2 \pm 2.1) \times 10^{-9}$ if the Yamuna with high Re concentration, 72.7 pmol/kg is excluded from the averaging. These average overlaps with the average ratio for the Brahmaputra $(6.0 \pm 2.8) \times 10^{-9}$. These averages compare with the values 5×10^{-11} [*Dalai et al.*, 2002] in the Himalayan crystalline are two orders of magnitude higher, leading to infer that Re contribution from the Himalaya crystalline is negligible. Re also exhibits significant correlation with $\sum$cat* in both the east ($r = 0.92$, $df = 16$, $p < 0.05$) and the west ($r = 0.89$, $df = 10$, $p < 0.05$) flowing Peninsular rivers (Table 5). The major ion data of the Krishna river system is from *Das et al.* [2005] (Table 3). Re/$\sum$cat* in the west flowing rivers, $(7 \pm 4) \times 10^{-9}$ is higher than that of the east flowing rivers, $(1.5 \pm 1.5) \times 10^{-9}$ excluding the Godavari and the Ghod, a likely cause for this could be potential supply of Re from anthropogenic sources to the west flowing rivers [*Rahaman and Singh*, 2010]. Nevertheless, it is interesting to note that Re/$\sum$cat* for the west flowing rivers and the Himalayan rivers overlap.

[21] Black shales have been inferred to be a significant source of Re to rivers [*Colodner et al.*, 1993; *Dalai et al.*, 2002; *Miller et al.*, 2011]. This conclusion is based mainly on high Re in black shales and the significant $Re-SO_4$ correlation in rivers; the Himalaya rivers analyzed in this study also show a significant linear correlation ($r = 0.91$, $df = 22$, $p < 0.05$; Figure 3), the correlation for the Ganga being better ($r = 0.89$, $df = 13$, $p < 0.05$) than that for the Brahmaputra ($r = 0.63$, $n = 9$, $p < 0.05$). Black shales release Re to dissolved phase during their oxidative weathering [*Ravizza and Turekian*, 1989; *Morford and Emerson*, 1999; *Dalai et al.*, 2002; *Jaffe et al.*, 2002]. Pyrites are often associated with black shales; these produce sulfuric acid during oxidative weathering of black shales which promote the release of both Re and SO_4 to solution. As a result, the concentrations of Re and SO_4 in rivers often show significant positive correlation if their supply is dominated by weathering of black shales [*Dalai et al.*, 2002; *Jaffe et al.*, 2002]. These $Re-SO_4$ correlations in the Ganga and the Brahmaputra therefore, bring out the important role

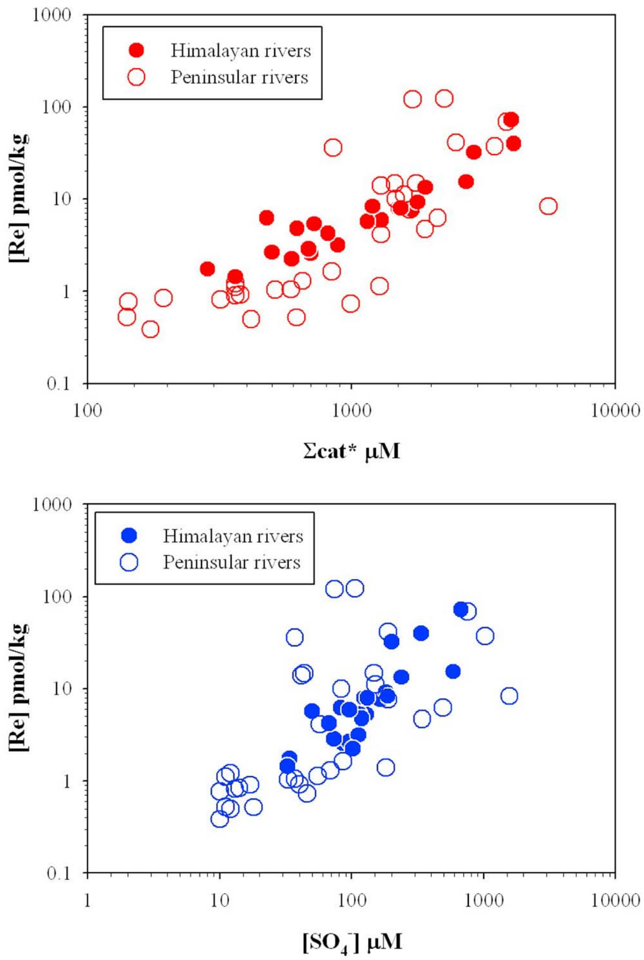

Figure 3. Re versus ∑cat* and Re versus SO_4^- scatter plot of the Himalaya and Peninsular rivers. Re versus ∑cat* shows significant correlation ($r = 0.88$, $df = 22$, $p < 0.05$) in the Himalayan rivers, better than the Peninsular rivers ($r = 0.6$, $df = 28$, $p < 0.05$). Correlation of Re versus SO_4^- in the Himalayan rivers is significant ($r = 0.81$, $df = 22$, $p < 0.05$) whereas it is poor ($r = 0.41$, $df = 28$, $p < 0.05$) in the peninsular river basin. The significant correlation between Re and SO_4 suggest that black shale weathering is a major source of dissolved Re in the Himalayan river basins. However, among the Peninsular rivers, the east flowing rivers shows significant correlation ($r = 0.92$, $df = 16$, $p < 0.05$; not shown). Weathering of pyrite globules present in Deccan basalts could supply both Re and SO_4 leading to their high correlation in the river waters.

Table 5. Re Versus ∑cats* and Re Versus SO_4 of the Himalaya and Peninsular Rivers

		Re Versus ∑cats*		Re Versus SO_4	
Rivers	Samples (*n*)	Equations	Correlation Coeff. (r)	Equations	Correlation Coeff. (r)
		Himalayan Rivers			
Brahmaputra	11	y = 0.003 x + 1.51	0.36	y = 0.032 x + 0.63	0.63
Ganga	13	y = 0.016 x − 16.08	0.89	y = 0.079 x − 0.068	0.77
Ganga-Brahmaputra (Himalayan river)	24	y = 0.013 x − 7.03	0.88	y = 0.082 x − 2.56	0.81
		Peninsular Rivers			
East flowing rivers[a]	18	y = 0.002 x + 0.28	0.92	y = 0.006 x + 0.95	0.92
West flowing rivers[a]	12	y = 0.013 x − 6.31	0.89	y = 0.030 x + 7.84	0.68
East-west flowing (Peninsular) rivers[a]	30	y = 0.005 x + 0.18	0.60	y = 0.001 x + 4.3	0.41
Considering all rivers	54	y = 0.012 − 1.25	0.52	y = 0.030 x + 9.8	0.26

[a]Excluding Godavari and the Ghod from the Peninsular rivers.

Table 6. Major Elements and Re Abundance in the Lithologies From the Himalaya and Peninsular Rivers

End-Member	Ca (%. wt)	Na (%. wt)	Mg (%. wt)	Re (pg/g)	Ca/Na (μM/μM)	Mg/Na (μM/μM)	Re/Na (pM/μM)
Crystallines[a]	1.04	1.76	0.90	26.00	0.34	0.48	0.00018
Carbonates[a]	24.00	0.03	8.30	52.00	460.00	261.87	0.02141
Black shale[a]	0.67	0.58	1.56	30000.00	0.66	2.55	0.63889
Deccan Basalt[b]	7.29	1.85	1.77	595.00	2.26	0.90	0.00396

[a]*Dalai et al.* [2002].
[b]For Re data *Allegre et al.* [1999] and for major elements *Wimpenny et al.* [2007].

of black shale weathering in contributing to their dissolved Re and to global rivers in general. The extent of Re−SO_4 correlation is likely to be influenced by different factors, that include Re−SO_4 release rates from black shale exposures in their river basin and the supply of Re and/ or SO_4 from sources such as felsic-mafic igneous rocks and evaporite deposits [*Hu et al.*, 1982; *Singh et al.*, 2005] and oxidation of hydrothermal sulfides supplying Re serving as additional sources of SO_4 to the Brahmaputra system with Re/SO_4 ratios significantly different from that in black shales.

[22] The Re versus SO_4 plot of the east and the west flowing Peninsular rivers (excluding the Godavari, Ghod and the Nira) which have high Re/SO_4 due to anthropogenic inputs and solution of alkaline/saline soils [*Das et al.*, 2005] show significant correlation ($r = 0.41$, $df = 28$, $p < 0.05$) (Table 5 and Figure 3). The correlation becomes far more significant when the data set of the east and the west flowing rivers are plotted separately, the east flowing rivers showing better correlation ($r = 0.92$, $n = 17$) than the west flowing rivers ($r = 0.68$, $n = 12$). The poor Re−SO_4 correlation of the pooled data can arise from heterogeneity in the Re/SO_4 ratios of their basins. The average concentration of Re in the headwaters of the Krishna is 1.2 pmol/kg. If all this Re is derived from chemical weathering of basalts, it would require Re to be released from about 0.45 g of basalts to a kg of river water. The solution of 0.45 g of basalts would also release ~8 mg of Na and Mg to solution if Re and these elements weather congruently. The measured Re/Na* and Re/Mg ratios in the Krishna headwaters are 2.8×10^{-9} and 4.7×10^{-9} respectively close to corresponding ratios in Deccan basalts (Table 6). This indicates that dissolved Re in the water can be supported by weathering of Deccan basalts. Further, basalts are known to contain pyrite globules with high Re concentration [*Roy-Barman et al.*, 1998]. Weathering of such pyrite globules if abundant in Deccan basalts could also supply both Re and SO_4 to rivers leading to their correlation in dissolved phase. Sulfur isotopic composition (δ^{34}S) of dissolved SO_4 in Krishna and its tributaries [*Das et al.*, 2011], however, seem to indicate that the role of basalt-sulfides weathering in contributing to the dissolved SO_4 in these rivers is only minor; the δ^{34}S–SO_4 relationship for the Krishna River and its smaller tributaries follow a two end-members mixing pattern i.e., rainwater and an unknown source, most likely pollution.

[23] Attempts to decipher the major lithologies contributing dissolved Re to rivers have been made based on their Re/Na* and Mg/Na* property plot (Figure 4). The plot also includes data on these ratios for potential sources of Re, black shales (BS), carbonates (Carb), crystallines and metasediments (Cryst) in the Himalaya and Deccan basalts (DB). The end-member values plotted in Figure 4 are based on their available data in Table 6. Considering that the end-member values and sample data vary widely, they are plotted on log-log scale (Figure 4). The data of Peninsular rivers show significant scatter in the plot, however, most of them fall in the mixing field between DB-BS and incremental mixing line between BS and 60% of Cryst-Carb end-members. They are also close to the DB end-member. The Re/Na* and Mg/Na* ratios of the Peninsular rivers in Figure 4 seem to support that they are largely controlled by Deccan basalts with minor contribution from black shales. Most of the data of the Ganga and its tributaries are closer to BS indicating black shales to be the main supplier of Re to these rivers with minor contribution from crystallines (Figure 4). The Brahmaputra samples also exhibit a pattern similar to that of the Ganga, underscoring the importance of black shales in supplying dissolved Re. Considering that Ganga data plot within the field of Cyst-BS and 40% of Cryst-Carb end-members, it is difficult to discern the significance of anthropogenic Re supply. In contrast, the data of the mixing diagram that the Himalayan rivers are plotting away from Carb end-member which suggest that carbonates are only minor contributor to their Re budget though they are a major lithology in basin. Further, the Re/Na* of a few of the samples, the Godavari, Nira and the

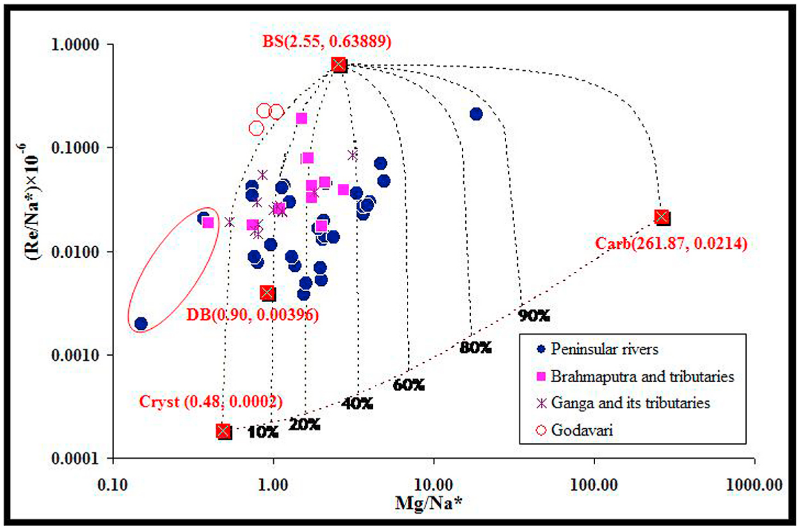

Figure 4. Re/Na* versus Mg/Na* of the Himalayan and the Peninsular rivers are plotted to decipher the major sources of Re. Na* and Mg data are taken from *Rai et al.* [2010], *Singh et al.* [2005], and *Das et al.* [2005]. Most of the points fall within the mixing field defined by the four end-members: crystallines (Cryst), carbonates (Carb), black shales (BS) and Deccan Basalts (DB). The dotted lines represented evolution lines constructed under the assumption that Re/Na* and Mg/Na* are released to waters in the same ratio as their abundances in the four end-members. In this mixing diagram, it is clearly observed that all the Himalayan rivers are falling away from Carb end-member which suggest that though carbonates are major lithologies in the basin, they contribute little to the Re budget of the Himalayan rivers. The Re budget of the Himalayan rivers are mainly governed by black shales and small contribution from the crystallines whereas Re in the Peninsular rivers are largely controlled by Deccan basalts. Few samples of the Godavari, Nira and the Sabarmati encircled in the figure do not fall in the mixing field constructed by four end-members. The higher values of Re/Na* of the Godavari indicate that they are highly influenced by additional sources which contribute disproportionately higher Re over Na to the river water.

Sabarmati plot outside the field of the end-members, suggesting that they are influenced by contribution from additional sources, characterized by Re/Na* ratio higher compared to the four end-members plotted in Figure 4, most likely of anthropogenic origin.

[24] Another important finding of this study is the strong correlation between Re and K ($r = 0.95$, $df = 40$, $p < 0.05$) in the dissolved phase of a group of rivers that include the Ganga, Brahmaputra, Krishna and most of their tributaries and the west and the east flowing minor Deccan rivers (Figure 5). The data of the Ghod, Godavari, Narmada, Mahi, Sabarmati, Yamuna and the Gomti rivers which seem to have been impacted by anthropogenic supply do not follow the linear trend set by the other rivers, therefore, they are not considered in the correlation. The average Re/K molar ratio of rivers $(9.0 \pm 3.2) \times 10^{-8}$ is 1–2 orders of magnitude higher than the average crustal ratio $\sim 3.7 \times 10^{-9}$ and marginally higher than the Himalayan black shales $\sim 5.2 \times 10^{-8}$ [*Singh et al.*, 2003]. This ratio for the Godavari, Ghod and the Mahi is $\sim 1.5 \times 10^{-6}$. The high Re–K correlation (Figure 5) is intriguing and could be a result of release of Re from organic fractions and K by exchange from clay minerals, both of which are often associated with fine grained fraction of black shales. Thus, the chemical weathering of black shales rich in organics and clays with exchangeable cations in their fine fraction could be an important factor contributing to the observed correlation between them (Figure 5). Further, weathering of K rich minerals such as K-feldspars associated with organic rich soils can also release both K and Re to solution [*Hinkley*, 1996] contributing to their correlation. The above arguments though may provide a potential explanation for the K–Re association, it is puzzling that the correlation is valid over sub-continental scale involving a number of rivers draining widely different lithology. More data on Re and K abundances in different fractions of black shales may provide better understanding of the basis of their correlation.

5.2. Sources of Anthropogenic Rhenium

[25] In recent decades, anthropogenic activities have significantly influenced the exogenic cycle of Re by modifying its abundance and distribution in

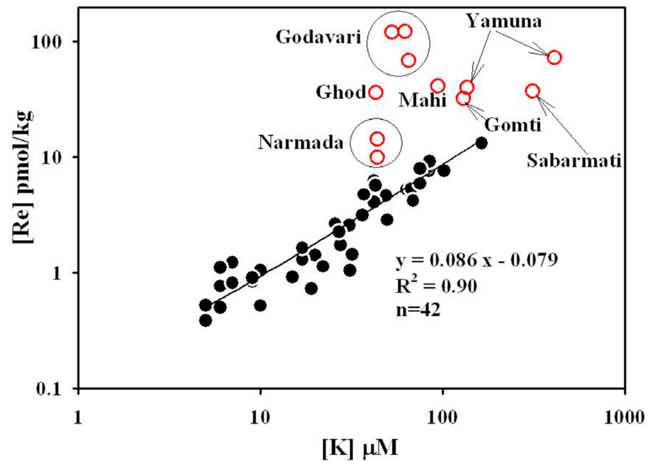

Figure 5. Re versus K scatter plot of all the Himalayan and the Peninsular rivers. Excluding the river having higher Re, most of the data shows significant correlation (r = 0.95, df = 40, $p < 0.05$). Such correlation could be resulting either from weathering of black shales in the river basin or K-Feldspar in organic rich mature soils. Higher Re/K ratio of some of the samples with their deviation from the linear correlation indicate contribution of Re from anthropogenic sources.

rivers, coastal oceans and enclosed basins. The high concentrations of dissolved Re in the Mississippi, Rhine, Yangtze and the Danube [*Walker and Peucker-Ehrenbrink*, 2004] and in the rivers flowing into the Black Sea [*Colodner et al.*, 1995] have been attributed to anthropogenic impact. A potential source of anthropogenic Re to the Black Sea is coal combustion [*Colodner et al.*, 1995]. Similarly, *Chappaz et al.* [2008] have shown that Re/Al molar ratio in lake sediments deposited during the twentieth century are significantly higher than that of pre-industrial times; a result attributed to atmospheric deposition of anthropogenic Re derived from coal burning and nearby smelter emissions. Re occurs in nature as an accessory or trace constituent in sulphide ores such as molybdenites in Cu-Mo porphyries [*Berzina et al.*, 2005; *Grabezhev*, 2007]. The exploitation of theses ores during the past century is one of the anthropogenic sources of Re. Similarly, the ever increasing use of fossil fuels containing significant concentrations of chalcophile elements including platinum group metals and the use of Re in various industries that include fuel processing, catalysis and aviation all serve as anthropogenic sources of Re to the environment [*Bertine and Goldberg*, 1971; *Chang*, 1998; *Selby et al.*, 2007].

[26] Among the rivers analyzed in this study, there are indications based on chemical (Na, Cl and SO_4) and isotopic composition (δ^{34}S) that some of the tributaries of the Krishna and the Bhima draining the Deccan basalts may have been impacted by anthropogenic inputs [*Das et al.*, 2005, 2011]. In the Godavari basin coal mining is an ongoing process as its basin has large areas of coal deposits of the Gondwana sequence [*Sarin et al.*, 2002]. In addition, mining of limestone, slates, manganese and iron ores is also occurring in the basin [*Gupta*, 2001], all of which contribute Re to the Godavari river. Recently, *Rahaman and Singh* [2010] have reported that the Gulf of Cambay receives substantial amount of anthropogenic Re through the Narmada and Tapi. The disposal of wastes from coal combustion and fossil fuel burning in thermal power plants, smelters and other industries such as oil refinery and pharmaceuticals situated along the bank of the Narmada, Mahi and the Sabarmati rivers are the potential sources of anthropogenic Re to these rivers [*Rahaman and Singh*, 2010]. Similarly, the high concentration of Re in the Yamuna river at Agra could also be due to supply of anthropogenic Re through effluents of petroleum refinery situated at Mathura, tens of kms upstream and metal foundries and plating industries situated on its banks at Delhi and Haryana [*Central Pollution Control Board*, 2006].

5.3. Rhenium Fluxes From the Himalayan and the Peninsular Indian Rivers

[27] The annual flux of Re transported through the major river systems of the Himalaya and Peninsular India have been estimated based on their Re concentration measured at their outflow and available data on their water discharge (Table 7). Considering that the dissolved Re concentrations of rivers are measured during their high stages, the estimated

Table 7. Re Flux Based on the Re Concentration and Water Flux at the Final Outflow

River	Place	Season and Year	Water Flux (km^3/year)	[Re] (pmol/kg)	Total Re Flux (mol)	References[a]
		Ganga and Its Tributaries				
Ganga	Rishikesh	Tail-end of monsoon, 1999	24	5.3	127	3
Yamuna	Allahabad	Tail-end of monsoon, 2006	93	9.2	856	1
Chambal	Kota	Nonmonsoon, 2009	4.8	15	72	1
Son	Koilawar	Tail-end of monsoon, 2006	31.8	5.7	181	1
Gomti	Ghazipur	Tail-end of monsoon, 2006	7.4	32.1	238	1
Ghaghara	Revilganj	Tail-end of monsoon, 2006	94.4	7.9	746	1
Gandak	Hazipur	Tail-end of monsoon, 2006	52.2	8.3	433	1
Kosi	Dhumarighat	Tail-end of monsoon, 2006	62	4.2	260	1
Ganga	Rajmahal	Tail-end of monsoon, 2006	380	5.9	2242	1
Ganga		Monsoon, 2007	493	4.4	1923	5
Ganga		Nonmonsoon, 1983	–	9.1	–	4
Hooghly	Kolkata	Nonmonsoon, 2006	52	5	270	2
		Tributaries of Brahmaputra				
Siang		Monsoon, 1999	200	4.8	952	1
Dibang		Monsoon, 1999	60	6.2	373	1
Buri Dihing		Monsoon, 1999	14	2.6	36	1
Ranga Nadi		Monsoon, 1999	5.8	1.8	102	1
Dhansiri		Monsoon, 1999	20	5.3	105	1
Jia Bhareli		Monsoon, 1999	26	1.4	37	1
Puthimari		Monsoon, 1999	4.4	3.2	13	1
Manas Biki		Monsoon, 1999	32	2.3	72	1
Subansiri		Monsoon, 1999	54	2.7	144	1
Brahmaputra	Dhubri	Monsoon, 2000	670	2.9	1943	1
Brahmaputra		Nonmonsoon, 1983	–	9.1	–	4
Brahmaputra		Monsoon, 2007	510	3.9	2244	5
Lower Meghna		Monsoon, 2009	1269	4.4	5584	1
(combined flow of Ganga-Brahmaputra -Meghna)		Nonmonsoon, 2006	–	1.4	–	
		Peninsular Rivers				
Narmada	Bharuch	Monsoon, 2007	47	10	470	2
Tapi	Surat	Monsoon, 2007	19	4	76	2
Mahi	Dhuvaran	Monsoon, 2007	12	41	488	2
Sabarmati	Ahmedabad	Monsoon, 2007	4	37	152	2
Mandovi	Goa	Monsoon, 2007	16	1	22	2
Vishwamitri	Vadodara	Monsoon, 2007	1	18	18	2
Krishna	Alamatti	Monsoon, 2001	17	2	28	1
Bhima	Takli	Monsoon, 2001	7	6	45	1
Godavari	Rajamundry	Monsoon, 1999	119	120	14280	1

[a]References are numbered as follows: 1, this study; 2, *Rahaman and Singh* [2010]; 3, *Dalai et al.* [2002]; 4, *Colodner et al.* [1993]; 5, *Miller et al.* [2011].

fluxes are very likely to be representative of their annual flux. Further, the impact of anthropogenic supply of Re to the rivers during high stages is likely to be minimum [*Rai et al.*, 2010]. An interesting observation of this study is that some of the small rivers draining the plain, because of their relatively high Re concentration, contribute significantly to the Re budget of the major Himalayan and the Peninsular river systems. The Re supply from the Yamuna determined based on its concentration of 9.2 pmol/kg during monsoon at Allahabad before the confluence with the Ganga is ~850 mol/year. The dissolved Re flux transported by the Ganga at Rajmahal is ~2200 mol/year based on the measured Re at Rajmahal and water discharge of the Ganga before its bifurcation (Table 7 and Figure 2). The sum of Re fluxes from tributaries and mainstream Ganga is ~2700 mol/year, ~20% higher than the estimate based on the Re concentration and water discharge at Farraka. Such difference have also been reported for major elements [*Rai et al.*, 2010] and is attribute to interannual variation in water discharge of various rivers. The release rate of Re from individual river basins

Table 8. Re Release Rate in the River Basins of India

Rivers	Area (10^3 km^2)	Total Re Flux (mol/year) Dissolved	Total Re Flux (mol/year) Particulate	Re Release Rate ($mmol/km^2/year$) Dissolved	Re Release Rate ($mmol/km^2/year$) Particulate
Rivers Linked to the Bay of Bengal (BOB)					
Hooghly	185	270		1.5	
Ganga at Rajmahal	935	2242	2152	2.4	2.3
Ganga[a]	1033	1923	–	1.9	
Brahmaputra at Arichaghat	636	3377	1320	5.3	2.1
Brahmaputra[a]	595	2244	–	3.8	
Lower Meghna	1571	5584		3.6	
Godavari at Rajmundry	312	14280		45.8	
Rivers Draining Into the Arabian Sea					
Narmada at Bharuch	98	678	66.2	6.9	0.7
Tapi at Surat	65	76	62.5	1.2	1
Mahi at Dhuvaran	35	488		13.9	
Sabarmati at Vatmann Bridge	21	152		7.2	
Mandovi at Goa	10	22		2.2	
Vishwamitri	3	18		6.0	
Krishna	36	28	6.5	0.8	0.2
Bhima	34	45		1.3	

[a]Data from *Miller et al.* [2011].

has been determined based on their area, annual particulate and dissolved Re fluxes (Table 7). The rates for dissolved and particulate Re from the Ganga basin and for dissolved Re from the Yamuna are quite similar, 2.3 $mmol/km^2/year$ (Table 7). The particulate Re release rate is based on suspended sediment flux of 520 million tonnes/year at Rajmahal [*Milliman and Meade*, 1983]. Similar calculations for the Brahmaputra basin yield values of 5.3 and 2.1 $mmol/km^2/year$ for dissolved and particulate Re respectively based on suspended sediment flux of 540 million tonnes/year with Re concentration of 457 pg/g at Chilmari (Table 5). These preliminary estimates seem to indicate that the release rates of dissolved and particulate Re from both the Brahmaputra and the Ganga basins are roughly similar, given the uncertainties associated with various parameters in the calculation. The Ganga and the Brahmaputra merge in Bangladesh to form the Lower Meghna which supplies ~5580 mol/year of dissolved Re to the Bay of Bengal. This flux coupled with that transported by the Hooghly corresponds to a total dissolved Re flux of ~5850 mol/year and release rate of ~3.6 $mmol/km^2/year$ for the entire Ganga-Brahmaputra basin (Table 8). The dissolved Re flux of the Ganga-Brahmaputra-Hooghly system is only about one third of that supplied by the Peninsular rivers, ~15,740 mol/year though their water flux is several times higher. Among all the Indian rivers, the Godavari supplies the maximum dissolved Re, ~14,280 mol/year, ~3.3% of the global river supply. The highest Re release rate among all the river basins of India is also observed for the Godavari, 47.6 $mmol/km^2/year$ (Table 8), a rate is difficult to be supported by chemical weathering of rocks in its basin, underscoring the importance of anthropogenic Re supply to this river. Currently, the Himalaya and Peninsular rivers together supply 21600 mol Re annually, ~5% of its global riverine supply to the oceans. The Re release rate among the global rivers [*Miller et al.*, 2011] vary from 0.45 $mmol/km^2/year$ for the Orange river to 116 $mmol/km^2/year$ for the Fly river. The discharge weighted average Re release rate of the global rivers (based on the available data for rivers comprising 37% global discharge [*Miller et al.*, 2011]) is ~5 $mmol/km^2/year$.

5.4. Natural and Anthropogenic Re in the Indian Rivers

[28] As modern riverine supply of Re become higher than the pre-anthropogenic activities, it is unlikely that modern seawater is at steady state for Re input. To understand its magnitude and response of such perturbation in the oceans, it is important to apportion natural and anthropogenic supply. Recently, *Miller et al.* [2011] obtained pre-anthropogenic world river Re concentrations ranging from 6.5 to 11.9 pmol/kg based on the relationship observed between Re-SO_4 using both anthropogenic SO_4 estimates [*Berner*, 1971; *Berner and Berner*, 1987] as well as pristine river SO_4 concentrations [*Meybeck and Helmer*,

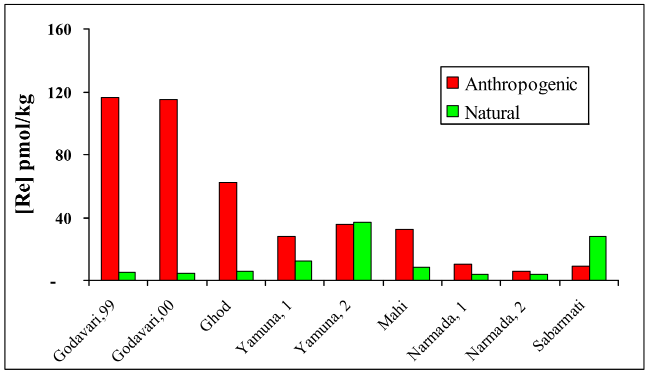

Figure 6. Based on the linear relationship of the Re versus K, anthropogenic and natural Re have been calculated. In some of the rivers, the anthropogenic contribution is too high.

1989] (SO_4 81.5 μmol kg^{-1}). The estimates of Re concentration of the pre-anthropogenic and post-anthropogenic river are 11.2 and 16.5 pmol/kg respectively [*Miller et al.*, 2011]. It is important to mention that correlation ($r^2 = 0.46$, n = 53) between the Re-SO_4 of the Indian rivers is far lower compared to that of the compilation of the World Rivers ($r^2 = 0.72$) reported by *Miller et al.* [2011]. The large number of data set of Re in Indian rivers draining through variety of rock types suggest that calculation of natural and anthropogenic Re based on the extrapolation of Re-SO_4 of the global river may not be valid for Indian river basins. It becomes, therefore, imperative to explore new proxy to decipher natural and anthropogenic sources of Re in the Indian river basins. In this study, significant correlation has been observed between Re versus K (r = 0.95, df = 40, $p < 0.05$) which has been discussed in the earlier section. In the Re versus K plot, some of the rivers having higher Re concentration such as the Ghod, Mahi, Sabarmati, Godavari and the Yamuna do not fall in the linear trend set by other rivers (Figure 5). The rivers deviated from the linear trend with higher Re/K ratio indicate significant amount of Re contributed by the anthropogenic sources. As Re and K both come from weathering of rocks in the drainage basin, therefore, we can infer that Re versus K correlation can be used to delineate natural and anthropogenic Re. The natural Re of the rivers impacted by anthropogenic activities can be calculated based on the equation of the correlation between Re versus K observed for the pristine rivers. The natural Re concentration in the polluted rivers calculated based on their dissolved K and the relation of Re and K in pristine rivers (Figure 5) are several times lower than their measured Re values (Figure 6) in many rivers. This clearly suggests supply of anthropogenic Re dominated over the natural supply particularly in the Godavari, Ghod, Narmada, Sabarmati and the Mahi river basins; ∼95% of the total Re supplied by these rivers is contributed by the anthropogenic sources. Among all the Indian rivers studied here, the Godavari supplies the highest Re to the ocean ∼14,280 mol/year. However, it is noteworthy that out of such higher Re flux, the natural Re is only 550 moles and the rest ∼13,700 moles Re is of anthropogenic in nature. The magnitude of anthropogenic Re supplied by the Godavari river is significantly higher compared to the total natural Re supply by the Himalayan and the Peninsular rivers. Approximately ∼70% of the total Re supply to the Bay of Bengal and the Arabian Sea is anthropogenic. This value is biased toward the anthropogenic Re of the Godavari river. However, knowledge of the sources of the anthropogenic Re in the Godavari river requires systematic study of Re in this basin.

5.5. Natural Re in Global Rivers

[29] *Miller et al.* [2011] estimated pre-anthropogenic (natural) global riverine average of Re concentration ∼11.2 pmol/kg based on the observed relation between Re and SO_4 concentration in the global rivers comprising 37% of the global water discharge and flux of anthropogenic SO_4. The relationship observed between Re and K concentrations in the Indian rivers in this study is extended to the available data of the global rivers [*Miller et al.*, 2011] to estimate the natural Re. Considering only river data from *Miller et al.* [2011], it is amazing that even for the global rivers the correlation between dissolved Re and K concentration is significant (r = 0.70, df = 121, $p < 0.05$) (Figure 7) establishing the global nature of this relation. Following the similar approach

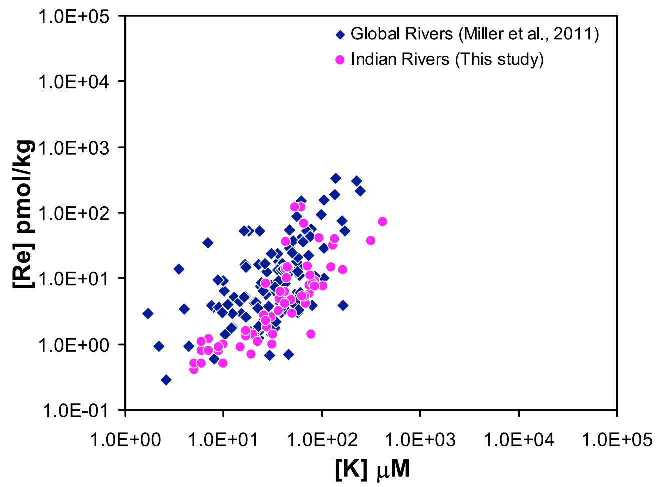

Figure 7. Re versus K relationship in global rivers shows strong correlation (r^2 = 0.496, n = 123) [*Miller et al.*, 2011]. This relation has been used to estimate the natural Re in the global rivers. See the text for details.

as in section 5.3, the natural (pre-anthropogenic) Re concentrations of various global rivers [*Miller et al.*, 2011] are estimated. The natural Re concentrations in these rivers [*Miller et al.*, 2011, Table A.6B] vary from ~0.1 to ~21 pmol/kg. Discharge weighted natural Re concentration of the global rivers is ~3 pmol/kg based on rivers comprising 37% of the global discharge [*Miller et al.*, 2011, Table 1A]. This estimate based on Re-K relation is much lower compared to that based on Re-SO_4 relation [*Miller et al.*, 2011]. The cause for difference in natural Re based on the two approaches is not clear at this moment. It could arise due to the fact that pristine rivers taken for Re-K relationship are not properly considered or flux of anthropogenic SO_4 is underestimated.

6. Conclusions

[30] In this study, a comprehensive study of dissolved Re have been carried out in major rivers from the Himalaya and Peninsular India. The Re versus ∑cat* shows positive linear correlation in the Himalayan rivers whereas the Peninsular rivers do not show significant correlation. Re versus SO_4 plot shows significant correlation in the Himalayan and the Deccan rivers indicating their common sources such as black shales and pyrites hosted in black shales and basalts. Re/Na* and Mg/Na* plot indicates that basalts are the dominant supplier of Re to the Peninsular rivers except for few rivers impacted by anthropogenic activities. In case of the Himalayan rivers, black shales is the dominant supplier of Re whereas other lithologies such as crystallines and carbonates contribute little Re to these rivers. The dissolved and particulate Re release rates have been estimated based on dissolved and particulate Re fluxes at their final outflow of the rivers. This estimate suggests that dissolved Re supply is higher than the particulate Re. The dissolved Re release rate in the Ganga-Brahmaputra basin is 3.7 mmol/km^2/year·

[31] The Peninsular rivers Godavari, Ghod, Nira, Narmada, Mahi and the Sabarmati have disproportionately higher Re over ∑cat*, K and SO_4 indicating substantial Re of anthropogenic origin in these rivers. Based on the Re versus K correlation, natural and anthropogenic Re supply by the Himalayan and the Peninsular rivers have been estimated assuming chemical weathering of rocks is the only source of K. This estimate suggests that approximately ~70% of the total Re supplied to the Bay of Bengal and the Arabian Sea is anthropogenic. Re versus K relationship is valid for the global rivers. Based on this relation, the discharge weighted natural Re in global rivers is estimated to be ~3 pmol/kg, much lower compared to earlier estimate.

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