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Statistical evaluation of stream sediment geochemistry in interpreting the river catchment of high-grade metamorphic terrains

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ABSTRACT

Stream sediment geochemistry is extensively used in mineral exploration and environmental studies. However, quantitative assessments of the effectiveness of stream sediment geochemistry for describing upstream lithologies are rare, especially in high-grade metamorphic terrains. This study statistically evaluates whether stream sediment geochemistry can aid in recognizing variations in upstream geology in several high-grade metamorphic lithotectonic units having different metamorphic and tectonic histories, including the Highland Complex, Vijayan Complex, Wanni Complex, and Kadugannawa Complex of Sri Lanka. For this study, concentrations of 21 elements were measured in 2080 stream sediment samples collected from the Walawe River, Maha Oya, Gala Oya basins located on above lithotectonic units and Uma Oya, Belihul Oya, Badulu Oya basins situated adjacent to each other on the Highland Complex. These rivers flow across dry, intermediate and wet zones of Sri Lanka, with river courses having both slope $(>20^{\circ})$ and flat (<20°) areas. Elemental concentrations, averaged over each river basin, show patterns of enrichment and depletion which may relate to localized mineralization conditions, local lithological changes, anthropogenic activities and environmental factors such as local variations in climate and morphology among river basins. Comparison of element concentrations in sediments from the four different lithotectonic units shows that enrichment – depletion patterns can be partly related to rock geochemistry of the associated lithotectonic unit. However, climate and basin morphology also seem to play an important role. Results of Kruskal-Wallis H tests show that both major and trace element levels in sediments from the four different lithotectonic units, as well as from adjacent Uma Oya, Badulu Oya and Belihul Oya basins, are significantly different. Discriminant function analysis appropriately classifies sediments into the four different lithotectonic units with an accuracy of 91.9%. This method also classifies sediments into river basins which share common lithology being situated adjacent to each other in the same lithotectonic unit with an accuracy of 89.5%. This strongly suggests that stream sediment geochemistry is capable of describing the upstream regional scale as well as local scale lithological changes at a great accuracy in complex high-grade metamorphic terrains. In both cases use of channel slope and basin climatic zone as additional variables does not significantly increase overall or individual accuracy in classification.

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1. Introduction

As stream sediments can be considered representative of upstream lithology, they play a significant role in exploration and environmental geochemistry. Geochemical maps have been constructed using stream sediment geochemical data over the world to identify possible sources of anomalous element concentrations (Kautsky and Bølviken, 1986; Thalmann et al., 1988; Reid, 1993; Atsuyuki et al., 2005). However, sediment yield and the geochemistry of river sediments are controlled not only by the physical and chemical weathering of parent rocks, but also by factors such as climatic, hydrological and morphological features of the basin. Incongruent and congruent dissolution, which takes place in the presence of aqueous solutions during penetration through soils and rocks, can result in differences between the chemical composition of a parent rock and its resulting weathering product (Nahon, 1991). Similarly, channel bed morphology

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and bank slope can strongly influence the transportation and sorting of minerals. Sufficiently intense rainfall can initiate bed load transport, bringing the -100 vm fraction into suspension (Fletcher, 1996). The energy slope of the channel bed also positively contributes to the initiation of bedload transport. This will result in a downslope variation in the composition of lag deposits, with deposits that are rich in heavy minerals and coarse materials located in areas with steeper slopes and deposits that contain finer or lighter materials located in flatter areas.

Quantitative studies of the contribution of lithological factors to the geochemistry of stream sediments are however rare. Cannon et al. (2004) attempted to statistically describe the relationship between stream sediment composition and composition of the soils in the north western Wisconsin, USA. Carranza and Martin (1997) have statistically quantified the anomalous geochemical signature of enriched samples from Albay Province, Philippines. Chandrajith et al. (2000) related the geochemistry of stream sediments of the Walawe Basin in Sri Lanka with that of possible source rocks in the

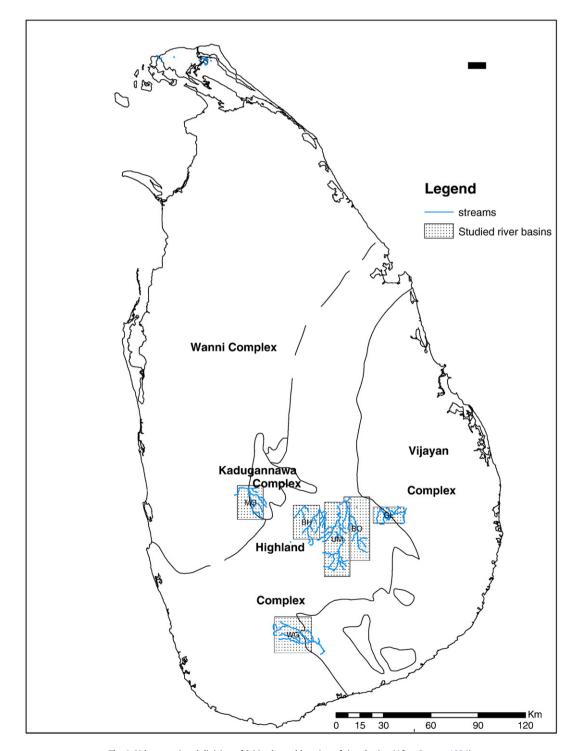


Fig. 1. Lithotectonic subdivision of Sri Lanka and location of river basins (After Cooray, 1994).

region and showed a correspondence between enrichment or depletion of LILE (Rb, Ba, K, and Sr,) and transition metals (Ni, Co) in stream sediments and the average metamorphic rocks of the area. Ohta et al. (2002) used significance tests such as *t*- and *F*-tests to examine the way in which lithology, hot springs, and anthropogenic activity affect elemental concentrations of stream sediment samples in a simple case. Ohta et al. (2004a,b) further applied an analysis of variance (ANOVA) and multiple comparison tests to compare data subsets that were distinguished by parent lithological materials.

This study evaluates the contribution of upstream lithology to the geochemistry of stream sediments in river basins of Sri Lanka. Stream sediments collected by the authors during Phase II and Phase III of the Gem Exploration Project carried out by Institute of Fundamental Studies Sri Lanka were used for this study. In order to quantify the relationship between stream sediment geochemistry and basin lithology, the Walawe, Maha Oya, Belihul Oya Badulu Oya, Uma Oya and Gala Oya river basins, which are situated on different lithotectonic units, have different basin morphologies and flow across different climatological regions, were selected for the study (Figs. 1 and 2).

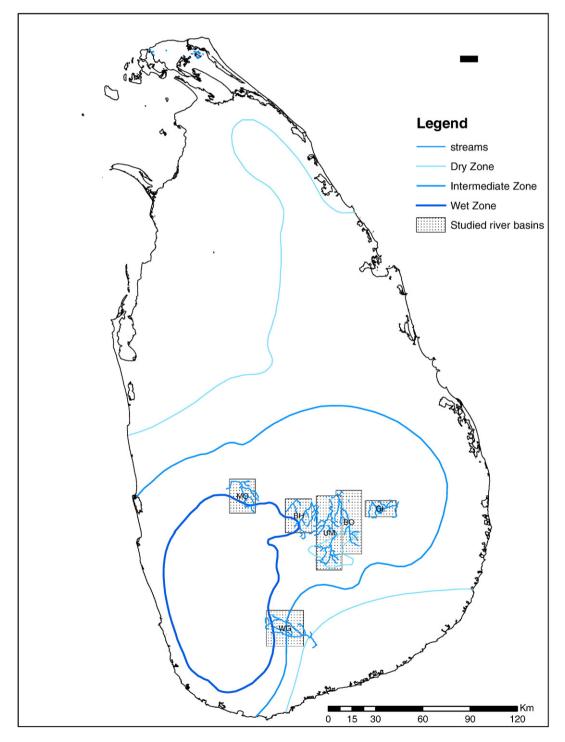


Fig. 2. Climatic zones of Sri Lanka and location of river basins (Source: Survey Department of Sri Lanka, 1988).

2. Geology and physiography

The Sri Lankan high-grade Precambrian basement has been divided into three main lithotectonic units, the Highland Complex (HC), Vijayan Complex (VC), and Wanni Complex (WC) and the relatively small Kadugannawa Complex (KC) (Cooray, 1994) (Fig. 1). The HC is comprised of granulite-grade metasedimentary rocks with enclaves of metavolcanic rocks, charnokites and charnokitic gneisses. The VC is composed of amphibolite-grade granitoid gneisses, migmatites and minor metasedimentary xenoliths. Charnokites, charnokitic gneisses, and minor metasedimentary rocks make up the granulite-grade WC. KC is characterised by amphibolite-grade upright synformal structural basins named "Arenas" and surrounding granulite-grade rocks. Biotite hornblende and biotite gneisses, amphibolites, minor quartzofeldspathic gneisses and metaquartzites are the main lithologies of the KC (Cooray, 1994). Depositional age of the precursor sediments of the HC is around 2 Ga while that of WC and VC are around 1.1 Ga. Intrusion of granitoids has taken place from about 665 Ma to 1942 Ma in the HC. Garnitoids in the VC and WC have intruded about 1.1 Ga ago. HC and WC rocks have undergone peak granulite facies regional metamorphism at between 665 and 550 Ma (Kroner et al., 1991). Rocks of the HC shows that they have undergone peak metamorphism at 800-900 °C and 8-9 kbar PT conditions (Kriegsman, 1991). Regional amphibolite-grade metamorphism in the VC has occurred between 456 and 591 Ma (Kroner et al., 1991).

No chemical differences have been observed between metasediments of the northern part of the HC and the WC. Metagneisses of the WC and the HC have high concentrations of elements like Na, Zr, and REE. Chemically, these metasediments represent upper crustal material. Chemically metamorphic rocks of magmatic origin in the HC represent a bimodal basalt-rhyolite association. Basaltic members of this suite are characterised by strong enrichment of Fe₂O₃ and TiO₂, with a concomitant increase in Mn, P, Sr and Nb. Granitic members are depleted in Fe₂O₃ and enriched in SiO₂. This basaltic-rhyolitic association suggests continental rift-related magmatism. Basaltic units represent mantle-derived melts and granitic units represent crustal-derived melts. Alkaline magmatic rocks of the HC and the WC have high concentrations of Na₂O, K₂O, P₂O₅, F, Zr, Pb, Th Sr, and Ba. The KC covers a complete spectrum of basaltic to rhyolitic calc-alkaline series. The data indicate a systematic evolutionary trend from the metabasites to the granitic gneiss. The WC mainly has metabasic to acidic calc-alkaline rocks. These cover a compositional spectrum of tonalitic gneiss to granitic gneiss and are considered to be a subduction-related calc-alkaline series emplaced at a continental margin (Pohl and Emmermann, 1991).

Morphologically, Sri Lanka is divided in to three units based on height and slope characteristics (Vitanage, 1972) including (a) coastal lowlands with elevation ranging from sea level to 305 m and slope ranging up to 15°, (b) uplands with elevations ranging from 305 m to 915 m and slope varying from 10° to 35°, and (c) highlands consisting of a series of well-defined high plains and plateaus rimmed with high mountain peaks where elevation varies from 915 m to 2420 m.

Belihul Oya, Uma Oya and Badulu Oya are three adjacent tributaries of the Mahaweli River situated within the HC (Fig. 1). These adjacent river basins have similar geology. Quartzite, garnetiferous quartzofeldspathic gneiss, marble, calc-gneiss, garnet sillimanite, biotite gneiss, charnokite and charnokitic gneiss are the major lithologies of this region, which is situated on the northern slopes of the Central Highlands (Geological Survey & Mines Bureau, 1996a and Geological Survey & Mines Bureau, 1997). All three rivers originate from elevations over 1500 m and flow across slope ($>5^\circ$) and flat terrains to join the River

Table 1

Detection limits of the	Philips-PW1404 X-ray	fluorescence spectrometer.

Element	Detection limits (dl)
Al (%)	0.2
Ca (%)	0.04
Fe (%)	0.01
Mg (%)	0.01
Mn (%)	0.002
Na (%)	0.01
Ti (%)	0.1
Ba (ppm)	30
Co (ppm)	2
Cr (ppm)	6
Cu (ppm)	5
Nb (ppm)	2
Ni (ppm)	3
Pb (ppm)	3
Rb (ppm)	3
Sr (ppm)	3
V (ppm)	5
Y (ppm)	2
Zn (ppm)	5
Zr (ppm)	10

Mahaweli at an elevation of approximately 200 m. Both Badulu Oya and Uma Oya flow across a drier region with mean annual rainfall of 1500-2000 mm in the eastern central Highlands. The rest of their courses lie within a zone of intermediate mean annual rainfall (2000-3000 mm). Belihul Oya originates in the wet (mean annual rainfall>4000 mm) central mountain region and then flows across hilly terrain with intermediate mean annual rainfall (Fig. 2) (Survey Department of Sri Lanka, 1988). The study area of the Walawe river basin is situated in the HC and extends to the boundary zone of the VC (Fig. 1). This area is mainly composed of charnokite, garnetiferous quartzofeldspathic gneiss, marble, garnet biotite gneiss and garnet sillimanite gneiss (Geological Survey & Mines Bureau, 2001). It begins in the wet southwest mountains, which have elevations over 800 m and mean annual rainfall >4000 mm, and flows across both dry and intermediate lowlands (elevation <100 m) (Fig. 2) (Survey Department of Sri Lanka, 1988). The sampling area within the Maha Oya geologically belongs to both the KC and WC, and the boundary between these units is not well defined (Fig. 1). Migmatitic hornblende biotite gneiss, charnokitic gneiss, granitic gneiss and minor metasedimentary rock units are the main lithologies of this sampling area (Geological Survey & Mines Bureau, 1996b). The Maha Oya River flows from the western slopes of the Central Highlands, which have elevations over 700 m, down to elevations below 100 m. The entire sampling area of the Maha Oya basin is situated within the intermediate climate zone (Fig. 2) (Survey Department of Sri Lanka, 1988). Within the sampling area of the

Table 2

No of samples belongs to each river basin and lithotectonic unit.

Basin	Total	No of san	No of samples							
		Lithotecto	Lithotectonic Unit							
		HC	VC	WC	KC					
BH	310	310								
BO	468	310								
UM	733	310								
GL	190	52	138							
MO	343			319	22					
WG	38	38								

Gala Oya, this river crosses the boundary between the HC and VC and travels through a zone of intermingled rock types (Fig. 1). Charnokite, charnokitic gneiss, garnet biotite sillimanite gneiss, and quartzite are the major lithological units found in the area belonging to the HC, while granitic gneiss, hornblende biotite gneiss, and biotite gneiss are the main rock types on the VC side of the sampling area. Within the sampling area, the Gala Oya flows from an elevation of about 1500 m to 100 m, cascading downhill along steep slopes in the upstream area. The whole Gala Oya basin belongs to the intermediate climatic zone of the country (Fig. 2) (Survey Department of Sri Lanka, 1988).

3. Methodology

Trace and major element concentrations were measured from stream sediment samples collected at an interval of about 0.25 km along the 2nd order or higher streams of the Belihul Oya (BH), Uma Oya (UM), Gala Oya (GL) Badulu Oya (BO), Walawe Ganga (WG) and Maha Oya (MO) river basins. Sampling locations were selected considering the confluence of lower order streams, slope of the channel bed, and minimum disturbance due to sand mining or gem mining. Stream sediment core samples, taken at approximately 0.3 m-0.6 m depth on banks or from the river bed were used in order to minimize the effect of seasonal climatic changes. All stream sediment samples were air dried and divided into two splits using the cone and quarter method. One split was selected for chemical analysis. Samples were then separated using a mechanical sieve shaker into size fractions. The <63 µm sediment size fraction was selected for chemical analysis as this size fraction had the highest concentration of most of the trace elements (Ranasinghe et al., 2002; Horowitz, 1991; Chapman, 1975).

Table 3a

Mean major element concentrations of river basins with respect to Mean upper crustal abundance and mean stream sediment levels, and the results of Kolmogorov–Smirnov Z test for normality.

Basin		Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Mn (%)	Na (%)	Si (%)	Ti (%)
	Upper crustal abundance ^a	8.15	2.56		2.32	1.49	0.08	2.42	31.13	0.55
	Mean stream sediment ^b	_	_	-	_	_	0.01-0.5	_	_	0.05-1
GL	Ν	190	190	190	190	190	190	190	190	190
	Mean	8.97	1.23	8.00	2.63	0.81	0.17	0.99	23.51	1.06
	Min	5.52	0.69	3.65	1.15	0.46	0.05	0.35	19.83	0.45
	Max	10.59	3.33	12.89	3.92	2.56	0.83	2.82	33.32	5.29
	Std. deviation	0.84	0.38	1.47	0.51	0.27	0.09	0.47	1.85	0.59
	Kolmogorov–Smirnov Z	1.21	2.28	0.67	0.73	2.04	2.46	2.80	2.53	2.67
	Asymp. sig. (2-tailed)	0.11	0.00	0.77	0.66	0.00	0.00	0.00	0.00	0.00
MO	N	343	343	343	343	343	343	343	343	343
	Mean	9.82	1.71	9.01	1.74	1.11	0.17	1.11	18.05	0.94
	Min	6.32	0.53	6.81	1.07	0.44	0.06	0.17	11.97	0.71
	Max	12.41	2.85	14.35	2.65	1.89	1.32	2.23	22.70	4.24
	Std. deviation	0.74	0.47	1.11	0.23	0.28	0.08	0.35	1.38	0.24
	Kolmogorov–Smirnov Z	0.73	0.82	2.11	1.31	1.30	4.19	0.63	1.21	3.78
	Asymp. sig. (2-tailed)	0.67	0.51	0.00	0.07	0.07	0.00	0.82	0.11	0.00
WG	N	38	38	38	38	38	38	38	38	38
	Mean	9.64	1.38	8.03	2.73	0.59	0.10	0.98	23.29	1.41
	Min	8.18	0.41	5.25	1.13	0.28	0.03	0.26	18.97	0.69
	Max	11.10	2.94	12.69	3.45	0.92	0.18	1.68	26.27	4.39
	Std. deviation	0.59	0.60	1.71	0.49	0.16	0.03	0.39	1.60	0.66
	Kolmogorov–Smirnov Z	0.94	0.53	0.74	1.02	0.74	0.64	0.76	0.57	0.92
	Asymp. sig. (2-tailed)	0.34	0.94	0.64	0.25	0.64	0.81	0.61	0.90	0.32
UM	N	733	733	733	733	733	733	733	733	733
0	Mean	11.07	0.93	9.11	1.79	0.51	0.16	0.91	19.63	0.93
	Min	7.84	0.22	4.54	0.65	0.01	0.03	0.02	14.06	0.26
	Max	14.25	2.28	13.54	3.74	1.47	0.66	3.08	23.59	5.65
	Std. deviation	0.91	0.34	1.10	0.47	0.21	0.08	0.45	1.67	0.45
	Kolmogorov–Smirnov Z	0.92	1.55	1.50	0.93	1.35	4.51	1.53	1.84	5.50
	Asymp. sig. (2-tailed)	0.32	0.02	0.02	0.35	0.05	0.00	0.02	0.00	0.00
BH	N	310	310	310	310	310	310	310	310	310
DII	Mean	9.63	1.65	8.74	2.14	0.94	0.14	1.10	19.52	0.74
	Min	6.50	0.30	5.20	0.67	0.01	0.06	0.01	0.00	0.23
	Max	15.64	4.36	14.56	4.32	5.08	0.31	2.68	23.66	1.72
	Std. deviation	1.06	0.58	1.33	0.45	0.51	0.03	0.42	2.23	0.21
	Kolmogorov–Smirnov Z	0.83	1.13	1.36	2.20	3.12	3.09	0.42	2.59	2.63
	Asymp. sig. (2-tailed)	0.83	0.16	0.05	0.00	0.00	0.00	0.82 0.51	0.00	0.00
BO	N	468	468	468	468	468	468	468	468	468
DO	Mean	10.05	1.66	8.72	2.03	0.70	0.14	1.27	21.78	0.87
	Min	4.23	0.20	4.75	0.31	0.70	0.02	0.03	14.52	0.87
	Max	4.25	18.10	4.75	3.31	2.49	2.17	3.16	24.28	11.19
	Std. deviation	1.39	18.10	14.55	0.43	0.28	0.12	0.47	1.05	0.57
	Kolmogorov–Smirnov Z	1.80 0.00	4.96 0.00	1.21 0.11	1.71 0.01	2.48 0.00	5.23 0.00	1.98 0.00	1.88 0.00	5.12 0.00
	Asymp. sig. (2-tailed)	0.00	0.00	0.11	0.01	0.00	0.00	0.00	0.00	0.00

If Asymp. sig. (2-tailed) is -

Bold — normal distribution.

Bold italic – log normal distribution.

Normal letter - non-normal distribution.

^a After Rudnic and Gao (2003).

^b After Rose et al. (1979).

Table 3b

Mean trace element concentrations of river basins with respect to Mean upper crustal abundance and mean stream sediment levels, and the results of Kolmogorov–Smirnov Z test for normality.

Basin		Ba (ppm)	Cr (ppm)	Cu (ppm)	Nb (ppm)	Ni (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
	Upper crustal abundance ^a	624	92	28	12	47	17	84	320	97	21	67	193
	Mean stream sediment ^b	-	5-1000	5-80	5-200	5–150	5-50	-	-	20-500	-	10-200	50-600
GL	Ν	190	190	190	190	190	190	190	190	190	190	190	190
	Mean	1058.01	231	103	37	68	52	142	200	234	45	147	1806
	Min	537.69	44	16	12	22	17	69	99	33	25	81	305
	Max	2958.75	666	304	224	161	77	207	346	554	180	457	13220
	Std. deviation	237.39	74	51	23	24	9	29	38	67	19	51	1486
	Kolmogorov–Smirnov Z	3.09	1.27	1.18	2.07	1.31	1.14	1.11	2.27	1.17	3.32	3.12	2.15
	Asymp. sig. (2-tailed)	0.00	0.08	0.12	0.00	0.07	0.15	0.17	0.00	0.13	0.00	0.00	0.00
MO	Ν	341	341	341	341	341	341	341	341	341	341	341	341
	Mean	918.69	180	66	25	59	20	83	216	280	48	135	1631
	Min	573.08	52	27	11	31	0	28	81	153	26	88	423
	Max	1573.76	509	153	154	96	73	178	493	998	473	421	23358
	Std. deviation	109.62	64	20	9	10	10	13	52	82	26	33	1440
	Kolmogorov–Smirnov Z	0.96	2.04	1.45	2.89	1.04	0.89	1.76	1.32	2.64	4.51	2.45	4.00
	Asymp. sig. (2-tailed)	0.31	0.00	0.03	0.00	0.23	0.41	0.00	0.06	0.00	0.00	0.00	0.00
WG	Ν	38	38	38	38	38	38	38	38	38	38	38	38
	Mean	953.47	187	64	54	44	52	151	227	123	59	218	3094
	Min	561.00	109	26	24	7	31	98	59	7	30	124	726
	Max	1278.00	416	160	124	92	79	201	488	274	105	426	15592
	Std. deviation	194.70	74	29	24	23	13	36	95	57	17	64	2728
	Kolmogorov–Smirnov Z	0.75	1.30	0.94	0.96	0.82	0.58	1.02	1.14	0.68	0.68	0.88	1.59
	Asymp. sig. (2-tailed)	0.63	0.07	0.34	0.32	0.52	0.89	0.24	0.15	0.74	0.74	0.42	0.01
UM	N	733	733	733	733	733	733	733	733	733	733	733	733
	Mean	1006.28	237	85	29	81	54	102	156	241	39	173	1010
	Min	409.06	69	16	10	30	22	46	52	112	16	59	254
	Max	1530.38	627	326	231	144	190	168	413	501	208	638	18721
	Std. deviation	184.53	61	31	19	14	13	22	48	49	12	61	1104
	Kolmogorov–Smirnov Z	1.75	1.91	2.90	5.92	1.07	1.55	0.69	1.50	2.58	3.51	4.58	6.80
	Asymp. sig. (2-tailed)	0.00	0.00	0.00	0.00	0.20	0.02	0.73	0.02	0.00	0.00	0.00	0.00
BH	N	310	310	310	310	310	310	310	310	310	310	310	310
	Mean	1190.65	186	89	21	57	46	108	198	232	37	147	715
	Min	570.94	55	27	9	35	18	55	45	96	23	82	21
	Max	1510.77	394	266	48	95	381	331	407	529	84	506	3585
	Std. deviation	157.93	59	33	6	10	21	22	50	55	6	44	382
	Kolmogorov–Smirnov Z	2.40	0.83	1.98	2.13	1.65	3.99	2.82	3.04	1.59	1.64	3.27	3.29
	Asymp. sig. (2-tailed)	0.00	0.49	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00
BO	N	468	468	468	468	468	468	468	468	468	468	468	468
20	Mean	1042.88	277	96	28	83	53	108	220	233	38	164	1036
	Min	159.58	47	26	8	43	25	21	220	63	17	74	199
	Max	1566.75	958	318	399	192	332	158	384	721	275	1152	28424
	Std. deviation	175.95	107	37	22	132	18	19	56	60	14	71	1543
	Kolmogorov–Smirnov Z	2.02	2.61	2.03	5.24	2.14	4.82	1.17	1.26	2.35	3.19	4.75	6.56
	Asymp. sig. (2-tailed)	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.09	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00	0.00	0.00	0.1.0	0.00	0.00	0.00	0.00	0.00

If Asymp. sig. (2-tailed) is –

Bold – normal distribution.

Bold italic – log normal distribution.

Normal letter – non-normal distribution.

^a After Rudnic and Gao (2003).

^b After Rose et al. (1979).

The concentrations of 21 major and trace elements were determined by X-Ray fluorescence spectrometry (XRF) using a Philips-PW1404 spectrometer (Table 1). International standard samples (JSD1, JSD2) and replicates were analyzed after every 10 samples to check the accuracy and precision. With a few exceptions (Ni (12%), Y (15%), Pb (14%) and V (12.5%)), mean deviations between measured concentrations and the reference values were less than 10%. Agreement among the replicate analyses was excellent (relative average deviation < 5%) except for Cu, Co and Pb (between 5 and 10%).

Since the aim of this study was to evaluate the efficacy of stream sediment geochemistry in recognizing upstream lithological changes, the significance of differences between major and trace element geochemical data subsets from sampling locations situated in different basins and in different lithotectonic units were assessed. The number of samples in each subset is shown in Table 2. The normality of the raw data and log-normalized data was tested using a Kolmogorov–Smirnov (K–S)

test) test. It was observed that some data sets could not be normalized even after applying a log transformation. Traditionally, an ANOVA is used in stream sediment geochemical studies to determine the significance of differences between more than two normally distributed data sets (Ohta et al., 2005). When data is not normally distributed, a non-parametric version of the ANOVA (i.e., the Kruskal-Wallis, or K-W test) can be used to examine the significance of differences between data subsets (Gabo et al., 2006). K-W test was performed to recognize whether there was a significant difference between stream sediment elemental concentrations among the four lithotectonic units. In that test "lithotectonic unit" was used as the grouping variable and a value of $\alpha = 0.1$ was used as the level of significance, considering the possible uncertainties in defining the existing boundaries between lithotectonic units. The K-W test was also carried out to recognize significant differences in elemental concentrations among river basins, using "river basin" as the grouping variable and $\alpha = 0.5$ as the significance level.

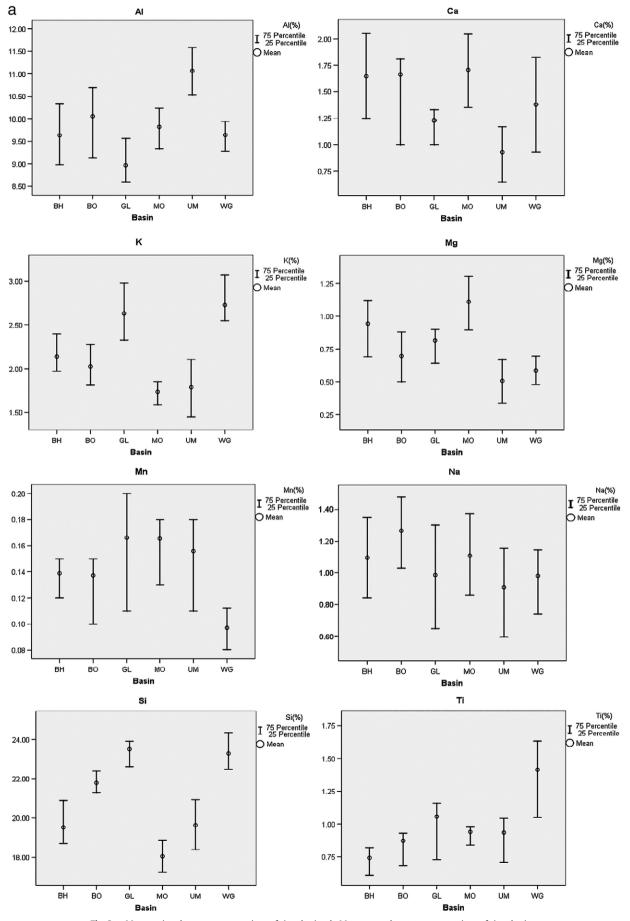


Fig. 3. a. Mean major element concentrations of river basins. b. Mean trace element concentrations of river basins.

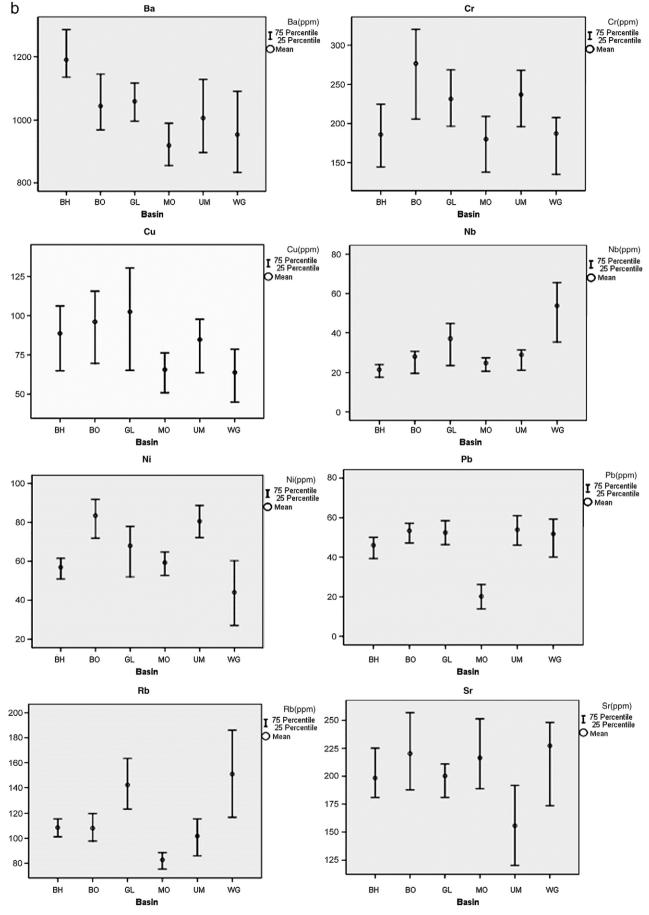


Fig. 3 (continued).

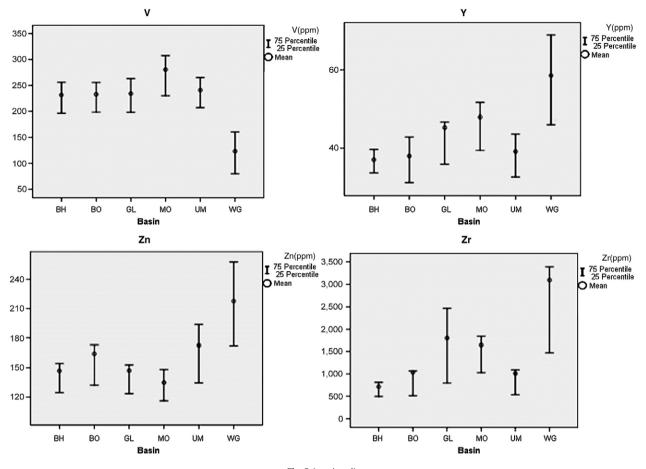


Fig. 3 (continued).

Discriminant function analysis (Rao, 1963) was used to evaluate the efficacy of stream sediment geochemistry in distinguishing source areas. Log-normalized data matrices were used for the discriminant analysis to ensure the homogeneity of variance. Outliers were removed based on critical Mahalanobis distances, but no significant change of the final result was observed. Discriminant function analysis was performed for

Walawe River, Maha Oya and Gala Oya matrix (matrix 1) and for Belihul Oya, Uma Oya, Badulu Oya matrix (matrix 2) separately. The first data matrix indicates the capability of stream sediment geochemical data for discriminating among the four lithological units. For this analysis, 9 major elements (Al, Ca, Fe, K, Mg, Mn, Na, Si and Ti) and 12 trace elements (Ba, Cr, Cu, Nb, Ni, Pb, Rb, Sr, V, Y, Zn, and Zr) were used as

Table 4

Descriptive statistics of major and trace element concentrations of lithotectonic units.

	HC N = 90				VC N=138				KC N=319				WC $N=22$			
	Mean	Min	Max	Stdev	Mean	Min	Max	Stdev	Mean	Min	Max	Stdev	Mean	Min	Max	Stdev
Al (%)	9.20	6.27	11.10	0.87	9.00	5.52	10.59	0.82	9.85	6.32	12.41	0.73	9.41	8.39	11.17	0.66
Ca (%)	1.43	561.00	2958.75	0.47	1.14	537.69	2473.67	0.35	1.71	573.08	1573.76	0.47	1.66	906.78	1179.68	0.43
Fe (%)	8.52	0.41	2.94	1.53	7.67	0.69	3.33	1.40	9.08	0.53	2.85	1.10	8.10	1.07	2.36	0.84
K (%)	2.38	109.00	666.45	0.52	2.83	43.56	408.60	0.42	1.71	51.82	508.51	0.21	2.11	65.68	292.53	0.27
Mg (%)	0.85	26.00	280.48	0.33	0.73	15.68	303.89	0.21	1.11	26.82	153.03	0.27	1.05	31.24	97.55	0.31
Mn (%)	0.14	5.25	12.89	0.09	0.16	3.65	11.24	0.09	0.17	7.01	14.35	0.09	0.16	6.81	9.67	0.05
Na (%)	1.06	1.13	3.45	0.50	0.93	1.15	3.92	0.42	1.10	1.07	2.52	0.35	1.16	1.63	2.65	0.32
Si (%)	23.06	0.28	1.95	1.71	23.73	0.46	2.56	1.82	17.91	0.44	1.89	1.28	20.14	0.59	1.66	1.12
Ti (%)	1.06	0.03	0.58	0.60	1.15	0.05	0.83	0.62	0.94	0.06	1.32	0.24	0.97	0.07	0.26	0.26
Ba (ppm)	1023	0	3	297	1052	0	2	181	909	0	2	105	1062	0	2	75
Cr (ppm)	245	12	124	88	210	18	224	63	182	11	154	64	154	16	49	52
Cu (ppm)	105	7	161	55	90	22	130	45	66	32	96	20	54	31	62	16
Nb (ppm)	36	17	79	23	42	26	73	24	25	0	48	9	27	12	73	9
Ni (ppm)	71	69	201	33	59	69	207	17	60	28	174	10	50	61	178	8
Pb (ppm)	49	19	28	11	54	21	33	9	20	12	21	9	30	18	23	15
Rb (ppm)	129	59	488	33	154	138	346	24	82	81	493	12	95	185	464	22
Sr (ppm)	207	0	4	70	203	1	5	38	214	1	4	51	246	1	2	59
V (ppm)	215	7	554	100	216	33	399	58	284	160	998	83	233	153	399	63
Y (ppm)	46	25	105	17	49	32	180	21	47	26	473	26	55	33	94	19
Zn (ppm)	187	82	457	78	141	81	344	33	135	88	421	34	139	104	190	24
Zr (ppm)	1730	305	15592	2128	2210	532	13220	1551	1607	452	23358	1440	2000	423	6320	1492

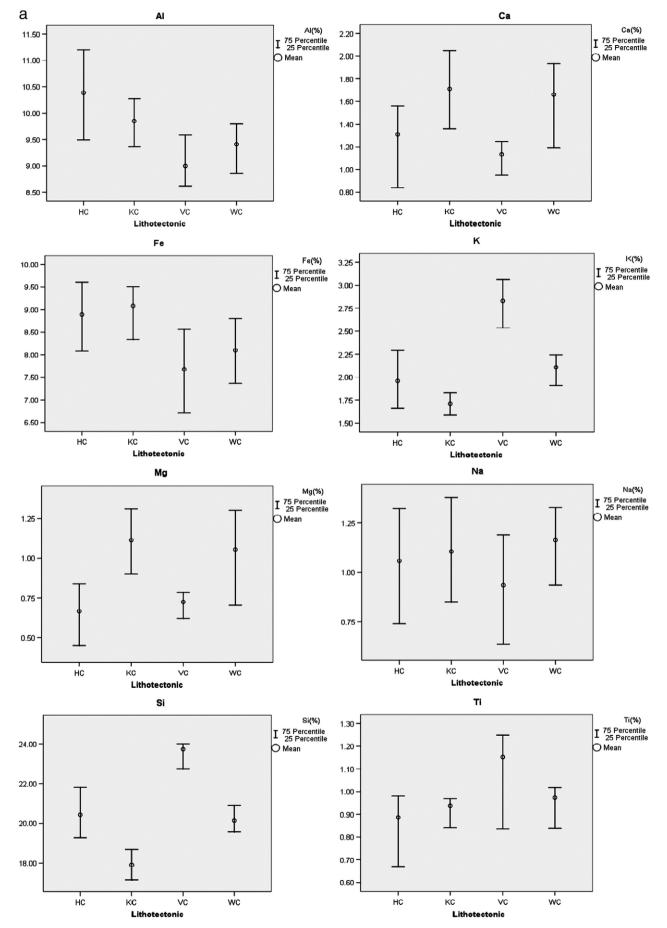
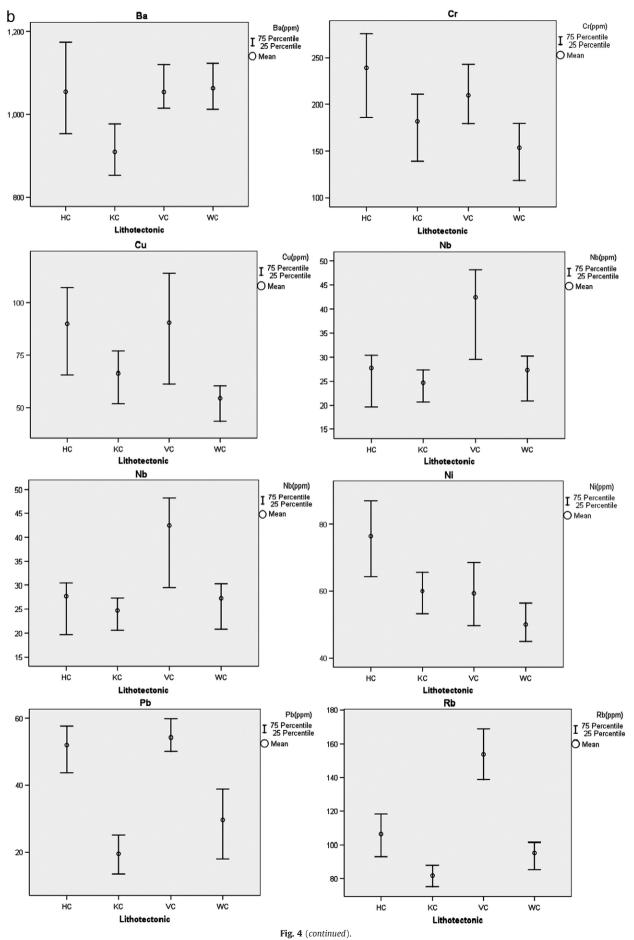


Fig. 4. a. Mean major element concentrations of lithotectonic units. b. Mean trace element concentrations of lithotectonic units.



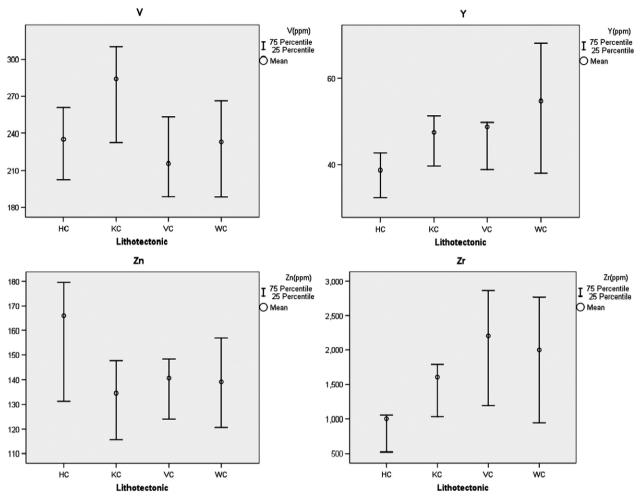


Fig. 4 (continued).

independent variables and samples from each lithological unit (HC, VC, KC and WC) were assigned a unique ID. The second data matrix tests the effectiveness of stream sediment geochemistry for discriminating variations in lithologically similar terrain that span a range of basin morphologies (i.e., slope, flat) and climate zones (i.e., wet, intermediate and dry). This second analysis considers the Belihul, Uma and Badulu basins, which are adjacent to each other. The same elements were used as variables in this analysis, but, in this case, samples from each basin were assigned a unique ID.

Discriminant function analysis was performed with SPSS 14.0 statistical software using lithological unit as the grouping variable for the first matrix and river basin as the grouping variable for the second matrix. Samples from wet, intermediate and dry zones and flat ($<20^\circ$) and slope ($>20^\circ$) regions were assigned different numbers and discriminant function analysis was again carried out for both matrices

using climate zone and channel morphology as two independent variables to see whether these variables can make a significant improvement in interpreting the upstream geology.

4. Discussion

Tables 3a and 3b show the mean major and trace elemental concentrations with respect to upper crustal values and mean stream sediment concentration values in each river basin. This table also shows the standard deviation of the data and results of the normality test. Since the null hypothesis is that population is not significantly different from a normal distribution, values of α less than 0.05 for the asymptotic significance. (2-tailed) of the K–S test indicates a non-normal distribution. From the tables it is clear that some of the variables are not normally distributed, even after log transformation.

Table 5

Results of the Kruskal-Wallis test for lithotectonic units.

	Al (%)	Ca (%)	Fe (%)	K (%)	Ν	lg (%)	Mn (%)	Na (%)	Si (%)	Ti (%)
Chi-square df Asymp. sig.	447. 2 0.		434.14 2 0.00	50.17 2 0.00	167.30 2 0.00		59.77 2 0.00	49.31 2 0.00	212.8 2 0.0		566.57 2 0.00	117.38 2 0.00
	Ba (ppm)	Cr (ppm)	Cu (ppm)	Nb (ppm)	Ni (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
Chi-square df Asymp. sig.	268.16 2 0.00	219.77 2 0.00	34.40 2 0.00	128.21 2 0.00	545.07 2 0.00	153.88 2 0.00	44.59 2 0.00	420.41 2 0.00	13.61 2 0.00	10.22 2 0.01	63.79 2 0.00	34.55 2 0.00

Grouping Variable: Basin.

	Al (S	%)	Ca (%)	Fe (%)	K (%)	1	Mg (%)	Mn (%)	Na	(%)	Si (%)	Ti (%)
Chi-square df Asymp. sig.	114. 3 0.	69 00	159.62 3 0.00	105.27 3 0.00	348.5 3 0.0		189.49 3 0.00	33.34 3 0.00	34.1 3 0.0		423.06 3 0.00	22.71 3 0.00
	Ba (ppm)	Cr (ppm)	Cu (ppm)	Nb (ppm)	Ni (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
Chi-square df Asymp. sig.	157.24 3 0.00	73.46 3 0.00	72.87 3 0.00	147.85 3 0.00	35.27 3 0.00	394.31 3 0.00	374.40 3 0.00	29.52 3 0.00	90.06 3 0.00	10.71 3 0.01	49.30 3 0.00	35.62 3 0.00

 Table 6

 Results of the Kruskal–Wallis test for river basins.

Grouping Variable: Lithotectonic unit.

Tables 3a, 3b and Fig. 3a,b show some noticeable inter-basin variation of elemental concentrations. The graph for Al shows characteristically high values in Uma Oya (Table 3a, Fig. 3a) as high loads of silt added to the Uma Oya due to intensive agriculture with poor soil management practices. Gala Oya has high K and Si values. Similarly, high K, Si and Ti concentrations were observed in the Walawe basin (Table 3a, Fig. 3a). These Ti concentrations in the Walawe basin are higher than the average stream sediment value and much higher than the upper crustal values. Climate may be a significant factor for the abundance of these Si concentrations in Gala Oya and Walawe basins as both flow primarily across the intermediate and dry zones where physical weathering dominates chemical weathering. K feldspar bearing granitic rocks and pegmatite abundant in the Highland-Vijayan boundary zone and in the VC may account for high K levels in sediments of these two river basins. Relatively high Mg concentrations were observed in the Maha Oya basin. Table 3b and Fig. 3b also show high values of Rb, Nb, Y, Zn, and Zr in the Walawe basin, where Zr and Zn exceed the mean average stream sediment value also. Chandrajith et al. (2000) describe high concentrations of REE and HFSE in the Walawe river basin as a product of small, scattered mineralized occurrences. The Highland/ Vijayan boundary runs close to the Walawe basin which is regarded as a highly mineralized zone of mantle derivatives, possibly accounting for the enrichment of the transition elements listed above. The Walawe river basin has a similar characteristic depletion of Ni and V. Badulu Oya shows a marked increase in Ni and Cr levels while Belihul Oya has got high Ba values (Fig. 3b). Possible Ni-Cr mineralization in some parts of the Badulu Oya may account for these values (Ranasinghe et al., 2008). Maha Oya basin, which crosses the Kadugannawa and Wanni Complexes, shows a characteristic depletion of Pb and Rb levels (Fig. 3b). Calc-alkaline rocks of the Kadugannawa Complex are characterised by lower concentrations of Pb than metasediments and alkaline rocks of other lithotectonic units (Pohl and Emmermann, 1991). Similarly, Uma Oya has characteristic lower values of Sr compared to other basins.

The geochemistry of stream sediments reflects the influence of dominant parent rock in the particular lithotectonic unit in many cases. While many features of stream sediment geochemistry are

Table 7

Classification table of discriminant function analysis carried out using lithotectonic unit as the grouping variable.

GEOLTYP			Predic	ted group	hip	Total	
			HC	VC	KC	WC	
Original	Count	HC	81	8	0	1	90
		VC	13	125	0	0	138
		KC	0	0	298	21	319
		WC	0	0	2	20	22
	%	HC	90	9	0	1	100
		VC	9	91	0	0	100
		KC	0	0	93	7	100
		WC	0	0	9	91	100

92.1% of original grouped cases correctly classified.

consistent with the elemental concentrations in the parent rocks, in some cases, parent rock lithology does not fully explain variations in sediment geochemistry. In these cases, local mineralization or enrichment and depletions due to basin morphology and differential weathering conditions may account for such changes. VC sediments have comparatively high K and Si, (Table 4, Fig. 4a). As mentioned in the above discussion, enrichment of K should be due to K feldspar rich granitic rocks and pegmatites in the region while enrichment of Si may be related to weathering rather than geological origin because the VC and intermediate and dry zones overlap each other. KC and WC sediments are depleted in Si and K, consistent with the low quartz and K feldspar bearing migmatitic hornblende biotite gneiss dominated rocks in the area (Table 4, Fig. 4a). Pohl and Emmermann (1991) have recorded comparatively lower SiO₂ and K₂O values from common tonalitic gneiss, metabasites and enderbites from KC. WC sediments are enriched with Ba and Sr (Table 4, Fig. 4b). The chemical composition of the WC rocks, which include syenitic gneisses, granitic gneisses, metabasites, and monzonitic gneisses, show a strong enrichment of Ba and Sr. HC has elevated levels of Pb, Ni, Zn and low Y and Zr, while KC has comparatively high values of V and low values of Pb and Rb (Table 4, Fig. 4b). Metasedimentary rocks in the HC show an

Table 8

Structure matrix of discriminant function analysis carried out for the stream sediment geochemical data matrix of lithotectonic units using lithotectonic unit as the grouping variable.

Structure Matrix			
	Function		
	1	2	3
Si (%)	0.52	0.05	0.34
Rb (ppm)	0.45	-0.21	0.03
K (%)	0.39	-0.26	0.34
Pb (ppm)	0.23	0.03	0.15
Mg (%)	-0.19	0.07	0.04
Zn (ppm)	0.07	0.33	0.00
Zr (ppm)	0.03	-0.25	0.10
Nb (ppm)	0.16	-0.17	0.00
Ca (%)	-0.16	0.17	0.08
Mn (%)	-0.04	-0.15	0.00
Ti (%)	0.05	-0.12	0.02
Ba (ppm)	0.11	-0.06	0.42
Cu (ppm)	0.10	0.13	-0.33
Cr (ppm)	0.08	0.16	-0.31
Sr (ppm)	-0.03	-0.03	0.31
Ni (ppm)	0.00	0.08	-0.28
Fe (%)	-0.13	0.19	-0.27
Y (ppm)	-0.01	-0.08	0.24
V (ppm)	-0.12	-0.14	-0.15
Al (%)	-0.14	0.03	-0.14
Na (%)	-0.06	-0.16	0.13

Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions.

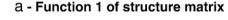
Bold – largest absolute correlation between each variable and any discriminant function.

enrichment of Pb $(12 \pm 7-27 \pm 14 \text{ ppm})$ when compared to dominant rock types in other terrains and, as discussed above, the calcalkaline rocks of KC are relatively depleted in Pb (Pohl and Emmermann, 1991). VC sediments have higher levels of Pb, Nb and Rb (Table 4, Fig. 4b).

Kruskal–Wallis test was performed for all the elements in sediments from Uma Oya , Badulu Oya and Belihul Oya basins which are situated next to each other in the same lithotectonic unit (HC). The results from this test (see Table 5) show that, for all of the elements considered, the asymptotic significance, α , was equal to 0.00 which is less than the critical level of significance $\alpha = 0.05$ set for the test. The null hypothesis for this test is that the mean elemental concentrations of sediments in the three basins situated in the HC are not significantly different. Therefore it is clear that there are significant differences of major and trace element concentrations among the basins. These results strongly indicate that both major and trace element data highly depends on local lithology representing small scale geochemical changes.

The same test was performed to compare the major and trace element concentrations in sediments from different lithotectonic units, with the results shown in Table 6. The null hypothesis for this test is that the mean elemental concentrations of sediments in the four lithotectonic units are not significantly different at a level of significance $\alpha = 0.1$. Results show that all 9 major and 12 trace elements have $\alpha = 0.00$ and hence the null hypothesis is rejected proving that, for each element, the concentration is significantly different in at least one of the lithotectonic units.

The classification matrix of the discriminant function analysis (Rao, 1963) for the Walawe, Maha Oya and Gala Oya data matrix (matrix 1) is shown in Table 7. It shows that geochemistry of stream sediments classifies sampling locations into the four lithotectonic units with an overall accuracy of 92.1%. The most significant misclassifications include the assignment of approximately 9% of HC samples as VC and vice versa, and the assignment of approximately 7% of KC samples as WC, and vice versa. Inspection of these specific cases shows that more than 50% of the misclassified samples lie on the uncertain and broad boundaries between lithotectonic units. This result demonstrates that geochemistry of stream sediments is an extremely powerful tool in recognizing highgrade metamorphic terrains. The structure matrix shows that function 1 which describes 91.7% of the total variance contains high positive correlations with Si, Rb and K (Table 8, Fig. 5a). This may represent granitic gneiss abundant with K feldspar, and biotite. Function 2, responsible for 7.1% of the variability, has relatively high negative correlations with Zn (Fig. 5b). Function 3 describes 1.2% of the variance and has relatively high positive correlation with Ba, and Sr (Fig. 5c), and relatively high negative correlation with metallic elements Cu and Cr. Scatter plots of function 1 vs function 2 and the territorial map also clearly show the classification of sampling locations into the lithotectonic units (Fig. 6a). It indicates that function 1 discriminates sediments of HC and VC together from KC and WC together. Higher function 1 values of HC and VC relate to the abundant granitic and feldspathic rocks in these lithological units. Function 2 which has a negative correlation with Zn helps to



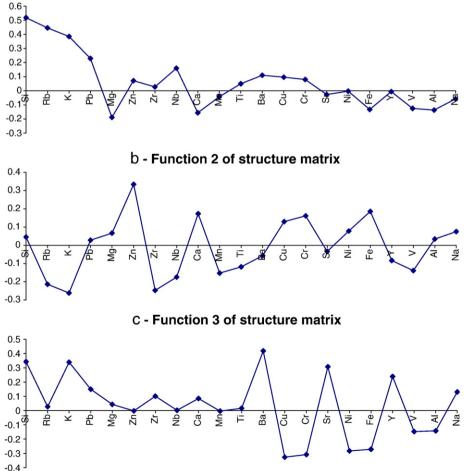


Fig. 5. Plot of pooled within-groups correlations between discriminating variables vs standardized canonical discriminant functions 1–3 of the structure matrix from discriminant function analysis of stream sediment geochemical data matrix of lithotectonic units.

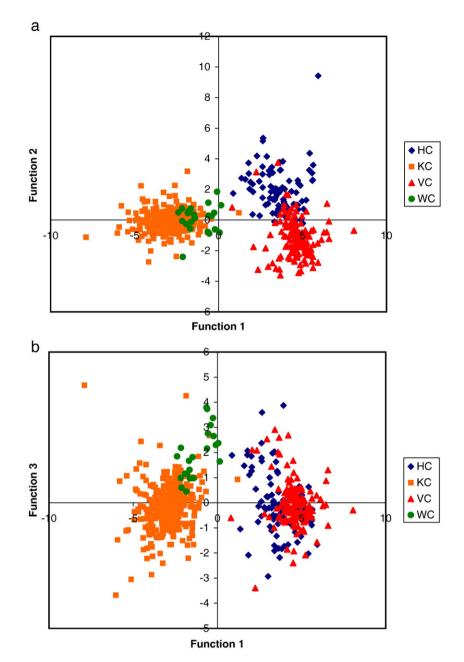


Fig. 6. Plot of (a) canonical discriminant functions 1 vs 2 (b) canonical discriminant functions 1 vs 3 from discriminant function analysis of stream sediment geochemical data matrix of lithotectonic units.

Table 9

Classification table of discriminant function analysis carried out for the stream sediment geochemical data matrix of lithotectonic units including climate zone and channel morphology as two independent variables and lithotectonic unit as the grouping variable.

GEOLTYP			Predic	Predicted group membership					
			HC	VC	KC	WC			
Original	Count	HC	75	14	0	1	90		
		VC	6	132	0	0	138		
		KC	0	0	300	19	319		
		WC	0	0	2	20	22		
	%	HC	83	16	0	1	100		
		VC	4	96	0	0	100		
		KC	0	0	94	6	100		
		WC	0	0	9	91	100		

92.6% of original grouped cases correctly classified.

Table 10

Classification table of discriminant function analysis carried out for the stream sediment geochemical data matrix of adjacent river basins using river basin as the grouping variable.

Classificatio	on results(^a)								
		Basin	Predicted	Predicted group membership To					
			BH	BO	UM				
Original	Count	BH	294	2	14	310			
		BO	2	429	37	468			
		UM	25	78	630	733			
	%	BH	94.8	0.6	4.5	100			
		BO	0.4	91.7	7.9	100			
		UM	3.4	10.6	85.9	100			

89.5% of original grouped cases correctly classified.

Table 11

Structure matrix of discriminant function analysis carried out for the stream sediment geochemical data matrix of adjacent river basins using river basin as the grouping variable.

Structure matrix		
	Function	
	1	2
Ni	0.53	-0.11
Cr	0.30	0.13
Ba	-0.27	0.21
Pb	0.13	-0.07
Nb	0.12	-0.07
Zr	0.08	-0.02
Sr	0.01	0.62
Si	0.29	0.53
Al	0.20	- 0.53
Ca	-0.07	0.43
Mg	-0.29	0.41
Na	0.04	0.38
K	-0.13	0.31
Fe	0.02	-0.17
Rb	-0.04	0.16
Cu	0.03	0.16
Mn	0.01	-0.11
Zn	0.10	-0.11
Ti	0.10	-0.11
V	0.02	-0.08
Y	0.03	- 0.06

Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions.

Bold - largest absolute correlation between each variable and any discriminant function.

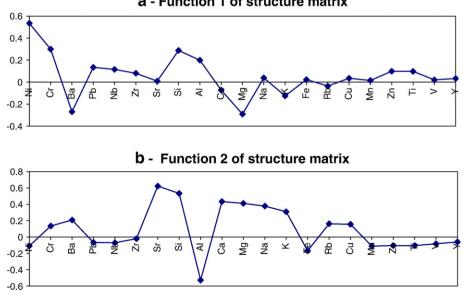
discriminate HC from VC because HC is enriched with Zn with respect to the VC (Fig. 4b). Scatter plot of function 1 vs function 3 (Fig. 6b) shows that WC has higher function 3 values than KC. As discussed above WC rocks rich in Ba and Sr account for this discrimination. The addition of channel morphology and climate as variables increases overall accuracy only up to 92.6%. It increases the accuracy of VC and KC while significantly decreases the accuracy of HC (Table 9).

The classification matrix derived from discriminant function analysis of the Uma Oya, Badulu Oya and Belihul Oya data (matrix 2) is shown in Table 10. For the data considered in matrix 2, the accuracy of classification was 89.5% (Table 10). Samples from the Belihul Oya basin, which is isolated from both other basins, were discriminated with the highest accuracy of 94.8%. Uma Oya basin, which is situated adjacent to Badulu Oya and at the middle of the three basins, has the lowest accuracy in classification (85.9%), with 10.6% of locations misclassified into the adjacent Badulu Oya basin and 3.4% misclassified into the Belihul Oya basin. However, as all three basins share common geology, these results prove that stream sediment geochemistry is a powerful tool for distinguishing the identity of source rocks based on their local chemical variations. Functions 1 and 2 of the structure matrix explain 68.5% and 31.5% variance respectively. Function 1 has high positive loading for ore-forming elements such as Ni and Cr (Table 11, Fig. 7a). As Table 3b and Fig. 3b show Ni and Cr of Badulu Oya and Uma Oya were higher than of Belihul Oya basin. Function 2 has positive loadings for Ca, Si, Sr and Mg and Na high negative loading for Al (Table 11, Fig. 7b). As discussed above, average Al value is higher in Uma Oya basin because of high silt content due to poor soil management in agriculture. Calc gneisses and marble, which contain abundant Ca, Sr and Si, are more abundant in the Badulu Oya basin than in the Uma Oya basin. The scatter plot of function 1 vs function 2 and the territorial diagram also show a strong discrimination of sampling locations among groups (Fig. 8). Addition of basin morphology and climate as variables does not improve overall classification but slightly changes individual basin-wise classification.

5. Conclusions

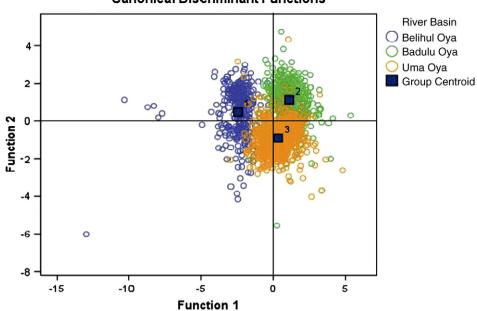
According to the results of this analysis, there is a significant increase in Al in sediments of the Uma Oya basin, Ti, Zr, Y, Zn and Nb in the sediments of the Walawe river basin, and Ni and Cr in the sediments of the Badulu Oya basin. There is a depletion of Pb in Maha Oya basin. Localized mineralization and anthropogenic factors may account for these enrichments and depletions. It is evident that sediments derived from the HC are rich in Pb and Zn while the VC are enriched in K, Si, Pb and Rb. WC stream sediments have higher levels of Ba and Sr, while sediments from KC are enriched with V and depleted in K, Si and Pb.

These observed variations are partly explained by the geochemistry of dominant country rocks in the particular lithotectonic unit.



a - Function 1 of structure matrix

Fig. 7. Plot of pooled within-groups correlations between discriminating variables vs standardized canonical discriminant functions 1-2 of the structure matrix from discriminant function analysis of stream sediment geochemical data matrix of adjacent river basins.



Canonical Discriminant Functions

Fig. 8. Plot of canonical discriminant functions 1 vs 2 from discriminant function analysis of stream sediment geochemical data matrix of adjacent river basins.

However, it seems that weathering and basin morphology partially control the distribution pattern of certain elements. This study clearly proves that levels of both major and trace elements are significantly different among lithotectonic units and also among adjacent river basins belonging to the same lithotectonic unit, indicating that stream sediment geochemistry is a representation of large scale as well as local scale chemical variations of the upstream lithology. Discriminant function analysis strongly suggests that stream sediment geochemistry is capable of describing the upstream regional scale lithological changes with an accuracy of >90% and local scale lithological changes with an accuracy >89%. Although stream morphology and climatic factors contribute in controlling the stream sediment geochemistry, they do not improve discrimination at these scales for these regimes which are dominated by more strong and complex lithological variations. However, the use of additional variables, such as stream morphology and climatic factors, in lithologically more simple terrains might improve the effectiveness of stream geochemistry in describing the upstream lithology.

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