The hydrochemistry of rivers in KwaZulu-Natal

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Abstract

The chemistry of the major elements of KwaZulu-Natal river water draining the eastern Drakensberg Escarpment was monitored in October 2003 and compared to data obtained previously along the western Drakensberg Escarpment, i.e. the Caledon and Upper Orange Rivers. The data obtained in these two surveys reveal no significant differences in the Mg, Ca, Na, K and HCO_3^- content of rivers draining similar lithologies, despite slightly different climatic regimes and different suspended loads. The implication is that lithology is the dominant control on the major element chemistry of river water draining the Drakensberg. However, in the north-western part of KwaZulu-Natal, drought-stricken at the time of sampling, evaporation-induced concentration results not only in evaporite formation, but dramatic changes in river and stream water chemistry. Elevated levels of minor constituents such as NO_3^- also indicate that in cultivated areas anthropogenic activities have an impact on water quality and composition.

Keywords: KwaZulu-Natal, hydrochemistry, river water, Drakensberg, lithology

Introduction

The chemistry of unpolluted freshwater systems such as rivers is primarily controlled by the lithology of the drainage basin and weathering stoichiometry (Meybeck, 1987; Dupré et al., 2003). Changing land-use patterns in Southern Africa, together with climate change, will almost certainly impact on erosion rates and chemical weathering processes, with important implications for river suspended and dissolved loads (Legesse et al., 2003). Southern Africa in general and the high-relief and erodable sedimentary layers of the Drakensberg Escarpment in particular, are extremely susceptible to such change (Keulder, 1979). Its impact on the quality of freshwater, our most valuable natural resource, can only be assessed and reliably predicted if the fundamental controls on river water chemistry are understood (Day and King, 1995; Scharler and Baird, 2003).

A study of the correspondence between river water strontium isotope ($^{87}Sr/^{86}Sr$) composition and dominant drainage basin lithology in the Orange-Caledon-Vaal River system (De Villiers et al., 2000), demonstrated the extent to which river water chemistry is controlled by lithology. This study investigates whether the relationship between river water chemistry and lithology demonstrated for rivers draining the western Drakensberg Escarpment, i.e. the Caledon and Upper Orange Rivers, holds along the eastern Drakensberg Escarpment. Most of the rivers sampled in KwaZulu-Natal drain rocks of the Karoo Supergroup, i.e. the same lithological provinces as the Caledon and Upper Orange Rivers. Given that catchments along the eastern Drakensberg Escarpment experience higher average annual rainfall than along the western escarpment, this study also provides an evaluation of the possible secondary role of climate on chemical weathering processes and river chemistry. River water runoff provides most of the freshwater used for human, agricultural and industrial utilisation in KwaZulu-Natal, and the results are therefore also of direct relevance to the assessment of water quality for these purposes (DWAF, 1996; Lin et al., 2004).

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Geology of the catchment area

The basal Karoo sequence consists of the Dwyka Formation (tillite-dominated), overlain by the carbonaceous shale, dolomite, mudstone, siltstone and organic-rich layers of the Ecca Group (Smith, 1990; Johnson et al., 1996). Above this is the Permian-Triassic Beaufort Group (alternating calcareous and non-calcareous mudstone), including the coarse sandstone- dominated Upper Triassic Molteno Formation. This is followed by the Elliot and Clarens Formations (fine-grained red beds and yellow sandstone) which in turn are capped by the Drakensberg Group (Jurassic flood basalt). The rivers originating in the easternmost part of KwaZulu-Natal drain primarily rocks of the Natal Group and Natal metamorphic belt.

Climate and geography of the catchment area

Rainfall in KwaZulu-Natal is strongly seasonal with more than 80% falling between October and March (WRC, 2002). This sampling survey was conducted during October, i.e. before the rainy season and additionally, towards the end of one of the most severe droughts on record in the north-western part of KwaZulu-Natal.

In the west, i.e. the vicinity of the Drakensberg Mountain, the terrain varies from high mountains (average altitude of 1 600 m) to undulating hills and lowlands (WRC, 2002). Soils are mostly well-drained. The average air temperature is 15°C, mean annual precipitation (MAP) 720 mm and mean annual runoff (MAR) 195 mm (WRC, 2002). Towards the east the terrain becomes a mix of highly dissected low mountains and lowlands (average altitude 650 m). The average air temperature is 18°C, MAP 890 mm and MAR 100 mm. Soils here consist of a greater proportion of shallow and poorly drained soils. Along the coastal plains the average altitude is < 200 m and the soils consist predominantly of shallow soils on well-weathered rock.

TABLE 1 River water sampling locations in KwaZulu-Natal				
Sample	**River name**	**Latitude**	**Longi-tude**	**Dominant Formation/Group**
KZN_1	Elands River	29°40'S	30°04'E	Drakensberg
KZN_2	Mkomazi River	29°45'S	29°50'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_3	Mzimkhulu River	29°46'S	29°29'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_4	Pholela River	29°56'S	29°31'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_5	Mkhomazana River	29°39'S	29°32'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_6	Umkomaas River	29°36'S	29°33'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_7	Nhlathimbe River	29°33'S	29°34'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_8	Nzinga River	29°28'S	29°55'E	Molteno, Elliot, Clarens & Beaufort
KZN_9	Mooi River	29°14'S	30°00'E	Molteno, Elliot, Clarens & Beaufort
KZN_10	Bushmans River	29°01'S	29°55'E	Molteno, Elliot, Clarens & Beaufort
KZN_11	Tugela River	28°45'S	29°25'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_12	Tugela River trib	28°37'S	29°05'E	Drakensberg, Molteno, Elliot, Clarens & Beaufort
KZN_13	Klip River	28°34'S	29°44'E	Beaufort
KZN_14	Busi River	28°15'S	30°06'E	Beaufort
KZN_15	Blood River	27°50'S	30°35'E	Dwyka & Ecca
KZN_16	Mkuzi River	27°40'S	31°30'E	Dwyka, Ecca, Natal and Pongola
KZN_17	Pongola River	27°28'S	31°35'E	Dwyka, Ecca, Natal and Pongola
KZN_18	Mkuzi Village pump	27°41'S	32°08'E	Natal Group/metamorphic belt/Pongola Supergroup
KZN_19	Mkuzi GR tap water	27°41'S	32°09'E	Natal Group/metamorphic belt/Pongola Supergroup
KZN_21	Mfolozi River	28°29'S	32°11'E	Natal Group/metamorphic belt/Pongola Supergroup
KZN_22	Mhlatuze River	28°46'S	31°59'E	Natal Group/metamorphic belt/Pongola Supergroup

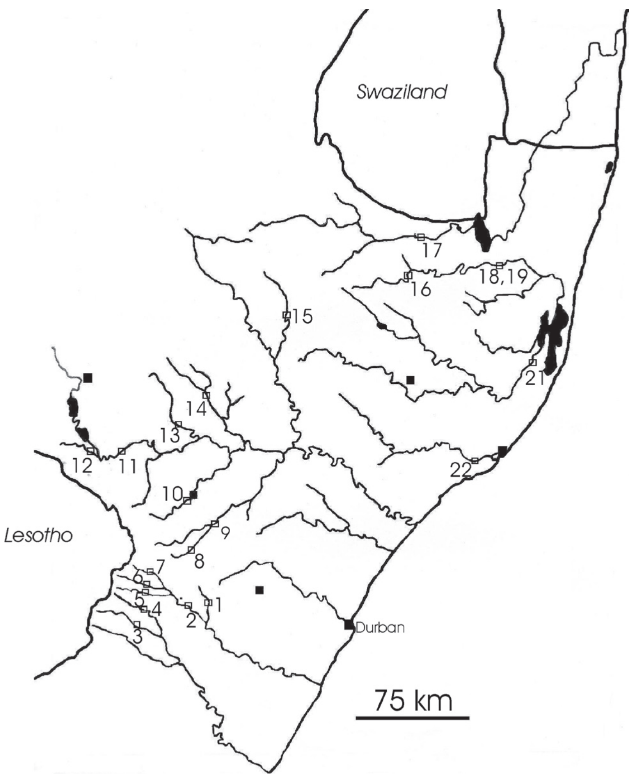

Figure 1
Map of KwaZulu-Natal sampling stations

The average air temperature is 20°C; MAP is 890 mm and MAR 120 mm.

Sampling and analytical methods

Sampling locations and ancillary information are listed in Table 1 and shown in Fig. 1. Samples KZN1 to KZN12 in western KwaZulu-Natal drain rocks and sediments belonging to the Karoo Supergroup, as do KZN13 to KZN15 in the north-western part of the province. Samples KZN16 to KZN22 drain Karoo sediments as well as lithologies belonging to the Natal Group and Natal Metamorphic Belt, i.e. a complicated mixture of different rock types.

All of the samples contained very low levels of suspended material, estimated at below 20 mg/ℓ for all samples. The low total suspended (TSS) content of the samples can probably be ascribed to the dry/drought and low-flow conditions during the time of sampling.

Water samples were collected in high-density polyethylene sampling bottles. Within 12 h after collection the samples were filtered through 0.45 µm filters, a fraction acidified and kept for trace metal analysis, and pH, conductivity and alkalinity measurements performed on a non-acidified fraction. Back in the laboratory (within a week after sampling) analysis of major cation and anion analyses was carried out using a DIONEX ICS90 single-channel ion chromatograph. The certified reference material ION-20 (medium-hard lake water) was analysed to evaluate analytical accuracy, which was within 2 to 5% for all components reported.

TABLE 2
Chemistry of KwaZulu-Natal river and stream water

Sample	River	pH	Cond mS	TDS mg/ℓ	HCO_3^- µM	F^- µM	Cl^- µM	NO_3^- µM	PO_4^{3-} µM	SO_4^{2-} µM	Na^+ µM	K^+ µM	Mg^{2+} µM	Ca^{2+} µM	$\%(\Sigma^- - \Sigma^+)/\Sigma^-$
KZN_1	Elands	7.13	0.04	53	537	11.1	68	44	11.79	16	157	16	104	126	9
KZN_2	Mkomazi	6.95	<0.01	74	719	4.7	30	163	2.42	16	188	15	140	223	2
KZN_3	Mzimkhulu	7.08	<0.01	53	555	2.1	28	94	0.32	8	121	11	95	152	10
KZN_4	Pholela	7.26	<0.01	48	555	1.6	41	13	0.32	5	106	11	100	143	3
KZN_5	Mkhomazana	7.03	<0.01	50	580	1.6	23	22	<0.10	11	138	9	82	144	8
KZN_6	Umkomaas	7.39	<0.01	66	792	1.6	11	14	<0.10	12	149	8	120	203	5
KZN_7	Nhlathimbe	7.33	0.04	63	731	2.1	16	24	<0.10	13	145	9	109	207	2
KZN_8	Nzinga	7.42	<0.01	36	429	1.6	12	3	<0.10	10	123	13	60	93	5
KZN_9	Mooi	6.86	0.03	69	530	2.6	104	236	<0.10	12	197	40	147	177	1
KZN_10	Bushmans	7.23	<0.01	57	605	2.1	22	79	<0.10	11	135	15	110	171	2
KZN_11	Tugela	7.29	<0.01	63	706	3.2	26	51	<0.10	19	135	17	109	181	11
KZN_12	Tugela trib.	6.99	<0.01	62	731	2.1	20	6	<0.10	23	133	9	109	200	5
KZN_13	Klip	7.24	0.2	222	2.143	8.4	319	252	0.11	107	574	37	512	661	-1
KZN_14	Busi	9.21	1.74	2.075	21.434	123.7	980	10	3.05	1.207	25 408	128	209	274	-6
KZN_15	Blood	7.39	0.18	219	2.169	12.1	464	7	<0.10	98	1.177	80	528	408	-10
KZN_16	Mkuzi	7.36	0.07	96	958	17.4	302	5	<0.10	25	507	18	187	159	9
KZN_17	Pongola	7.63	0.2	249	2.648	10.5	419	8	<0.10	106	1 233	44	577	421	1
KZN_18	Mkuzi pump	6.56	1.51	1.286	3.530	18.4	14.634	2.468	<0.10	224	9 957	11	1 793	2.496	12
KZN_19	Mkuzi tap	6.76	<0.01	62	366	3.2	376	78	<0.10	56	259	25	46	210	15
KZN_21	Mfolozi	8.05	0.88	856	6.557	16.3	4.977	10	<0.10	319	6 094	72	2.115	1.298	-7
KZN_22	Mhlatuze	7.80	0.38	350	2.269	13.7	2 389	11	<0.10	214	3.052	71	586	439	-1

Results and discussion

Hydrochemistry

The hydrochemistry results are summarised in Table 2. Conductivity is low (< 0.1 mS) in surface water draining Karoo Supergroup lithologies, with the exception of the rivers in the north-western part of KwaZulu-Natal (KZN13 to KZN17) and those draining the coastal belt (KZN18 to KZN22). The same trend is observed for the total dissolved solid (TDS) content of surface waters. TDS values of 219 to 2 075 mg/ℓ were observed in the north-west (KZN13 to KZN15), where severe drought conditions prevailed during the time of sampling. High TDS values also characterise surface water along the coastal belt (KZN18 to 22).

Sodium, Mg and Ca are the dominant cations in all the water samples analyzed, with HCO_3^- Cl^- and SO_4^{-2} providing the charge balance (Table 2). In western KwaZulu-Natal river waters draining Karoo lithologies contain almost equivalent amounts of Na and Ca (35 to 40% of each) with Mg only slightly less abundant. This is similar to what is observed for rivers draining western Drakensberg Karoo sequences (De Villiers et al., 2000). Sodium, however, is the dominant cation in the drought-stricken north-western part of the province and along the coastal belt, by a factor of two in most cases (Table 2, KZN13 to KZN22). Bicarbonate is the dominant anion in all waters draining Karoo Supergroup lithologies. Along the coastal belt, however, HCO_3^- and Cl^- concentrations are equivalent, and Cl^- is the dominant anion in the Mkuzi Village pump (ground) water sample (Table 2).

Ionic ratios

The ion ratios (mole/mole) for Mg, Ca, Na and K are listed in Table 3. In western KwaZulu-Natal N and Ca are present in approximately equivalent concentrations, followed closely by Mg. Average values for the cation ratios in water draining the eastern Drakensberg Escarpment are almost identical to those measured in Orange and Caledon River waters that drain the western Drakensberg escarpment (Table 3; De Villiers et al., 2000). Superimposed upon these relative cation abundance values, are definitive trends in Mg/K and Ca/K values (Fig. 2). High Mg/K and Ca/K values (> 25) reflect the Mg- and Ca-rich composition of basalt and dolerite (Keulder, 1979), in contrast to the more K-rich sand- and mudstones of the Karoo Supergroup sedimentary sequences (Keulder, 1979). The highest Mg/K and Ca/K values found are those of KZN6, 7 and 12, i.e. the sampling sites closest to the central and northern Drakensberg area. The lowest Mg/K and Ca/K, in contrast, are those of KZN1, 8 and 9, i.e. the sampling sites that originate within the Karoo sedimentary sequences well below the Drakensberg basalt sequence. Since Drakensberg basalt is found only above an altitude of approximately 1 800 m along the escarpment, the results suggest that Mg/K and Ca/K can be used as indicators of the relative altitude from which river water along the escarpment was sourced. However, the presence of dolerite dykes, compositionally similar to Drakensberg basalt, at lower altitude may complicate the use of these ratios as source indicators.

The chemical composition of river water in

TABLE 3 Cation ratios (mole fraction) in KwaZulu-Natal river water samples				
Sample	Mg	Ca	Na	K
KZN_1	0.26	0.31	0.39	0.04
KZN_2	0.25	0.39	0.33	0.03
KZN_3	0.25	0.40	0.32	0.03
KZN_4	0.28	0.40	0.29	0.03
KZN_5	0.22	0.39	0.37	0.02
KZN_6	0.25	0.42	0.31	0.02
KZN_7	0.23	0.44	0.31	0.02
KZN_8	0.21	0.32	0.43	0.05
KZN_9	0.26	0.32	0.35	0.07
KZN_10	0.26	0.40	0.31	0.04
KZN_11	0.25	0.41	0.31	0.04
KZN_12	0.24	0.44	0.30	0.02
KZN_13	0.29	0.37	0.32	0.02
KZN_14	0.01	0.01	0.98	0.00
KZN_15	0.24	0.19	0.54	0.04
KZN_16	0.21	0.18	0.58	0.02
KZN_17	0.25	0.19	0.54	0.02
KZN_18	0.13	0.18	0.70	0.00
KZN_19	0.08	0.39	0.48	0.05
KZN_21	0.22	0.14	0.64	0.01
KZN_22	0.14	0.11	0.74	0.02
KZN-W avg.	0.25	0.39	0.33	0.03
KZN-NW avg.	0.18	0.19	0.61	0.02
KZN-coast avg.	0.17	0.20	0.61	0.02
Upper Orange avg.	0.26	0.35	0.35	0.04

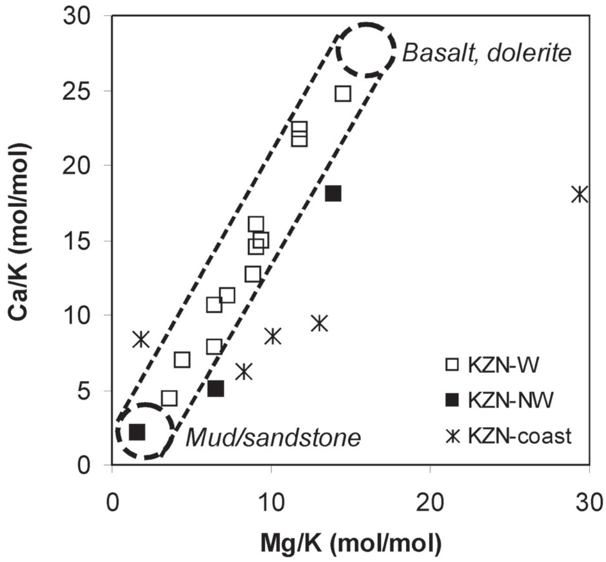

Figure 2
Relationship between Mg/K and Ca/K of KwaZulu-Natal river water

the drought-stricken north-western part of KZN suggests that evaporation-induced concentration results in relatively lower calcium and Mg levels, with Na becoming the dominant cation (Table 3). These ion ratio changes together with high dissolved ion concentrations imply the formation of Ca and Mg evaporite mineral phases. Calcium and Mg carbonates are typically precipitated out first during evaporite formation from natural water bodies (Harvie et al., 1984). The high solute content of KZN-14 (Table 2) suggests that super-saturation with respect to Ca (and Mg) carbonate mineral phases has been reached, i.e. that evaporite mineral formation has commenced. Along the coastal belt, Na becomes the dominant cation (Table 2). The dissolution of soluble Na mineral phases of seawater intrusion along the coastal belt is also suggested by elevated Cl^- and SO_4^{-2} levels (Table 2).

Water quality for human consumption

Target Water Quality Range values for human consumption exist for the following of the chemical species analyzed: Ca, Cl^-, F, Mg, NO_3^- and N (DWAF, 1996). Several samples exceed one or more of these criteria: Ca (KZN18 and 21), Cl^- (KZN18, 21 and 22), F^- (KZN14), Mg (KZN18 and 21), NO_3^- (KZN2, 9, 13 and 18) and Na (KZN 14, 18 and 21). There are no potential health effects related to the elevated Ca, Mg and Cl^- levels present, but the levels measured during this sampling survey will result in increased scaling and erosion of, e.g. domestic appliances. Elevated Na levels can be undesirable for infants or person on a Na-restricted diet, in addition to affecting the taste of the water. The F^- levels found at KZN-14 can result in tooth damage and mottling of dental enamel.

The most problematic of the water quality parameters analysed, from a human health perspective, is NO_3^-. The levels of NO_3^- found in samples KZN-2, 9 and 13 can result in rare instances of methaemoglobinaemia in infants (DWAF, 1996). These sample locations all receive runoff from agricultural areas and fertilisation is the most likely origin of the high NO_3^- present. Of all the samples analysed the Mkuzi Village pump-water sample has the highest NO_3^- levels, 2 468 μM compared to the 323 μM limit above which methaemoglobinaemia occurs in infants, in addition to mucous membrane irritation in adults.

Elevated PO_4^{3-} levels were also found at several locations: KZN1, 2 and 14 the most noticeable. These elevated values do not coincide with that for NO_3^-, i.e. the presence of agricultural runoff. It more likely reflects usage of stream-water upstream for domestic purposes by rural communities, such as domestic laundry.

Conclusions

The chemistry of river water draining the western and eastern Drakensberg Escarpment is remarkably similar. This is to be expected on the one hand, given that the rivers drain similar lithologies, but also surprising given the pronounced differences in suspended sediment load during the times of sampling. Equilibrium cation-exchange reactions between dissolved and suspended phases such as clays have been proposed as a potentially important secondary control on river water chemistry. In high turbidity rivers cation-exchange reactions can in fact be the dominant control on river chemistry. Despite the fact that the Orange-Caledon River is the 4th most turbid in the world, the results presented here suggest that cation-exchange reactions do no impact significantly on the major element chemistry of rivers draining the Drakensberg.

One of the most promising aspects of the results presented here is that the correspondence between cation ratios and lithology demonstrated along the western Drakensberg Escarpment by de Villiers et al. (2000) holds along the eastern escarpment. Element ratios such as Mg/K, Ca/K, Mg/Na etc. are relatively easy to measure and a much better alternative than time-consuming and expensive $^{87}Sr/^{86}Sr$ proxies of water origin. The combined correspondence between lithology and altitude in the Drakensberg provides a relatively easy method by means of which water movement can be traced from different source areas in hydrological studies, in this area.

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