The strontium isotope distribution in water and fish within major South African catchments

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ABSTRACT

Strontium has 4 naturally-occurring isotopes (^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr) all of which are stable (Faure, 1986). The correlation between the ^{87}Sr/^{86}Sr isotope ratio of lake water and fish fin spine tissue was investigated in 23 lakes within 4 major South African catchments. Data showed that fish within a specific lake all have the same Sr isotope ratio in their fin spine tissue regardless of species, age, sex and condition. The origin of the dissolved Sr fraction in lake water can be either from the natural weathering of upstream geological units or from an upstream anthropogenic source. The Sr isotopic ratios of the water samples were, however, constant over a multi-year period suggesting that the main source may be the more consistent geological environment. The Sr isotope ratio of river and lake water generally increases along the course of the rivers within the tertiary catchments of the areas investigated. In large rivers like the Vaal, where pollution also plays a role, the pattern is much more complicated. In the Olifants River catchment, Lake Middelburg, Lake Witbank and Lake Doornpoort have a similar Sr isotope ratio, which is distinct from Lake Bronkhorstspruit. Lake Loskop which is downstream from these lakes has a Sr isotope ratio between these two extremes, indicating mixing of water from upstream sources. Similarly Lake Arabie (Flag Boshielo), which is even further downstream, shows a Sr isotope composition between the composition of Lake Loskop and the lakes in the Elands River.

Keywords: strontium isotope, ^{87}Sr/^{86}Sr, lake water, fish fin spine, water chemistry, Lake Loskop

INTRODUCTION

Strontium has 4 naturally-occurring isotopes (^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr), all of which are stable (Faure, 1986). Strontium isotope ratios have been used in various applications to link biota to their physical environment. Strontium is an ideal element for this purpose as it is present in high concentrations suitable for analytical applications, while Sr isotope ratios remain independent of biological processes (Capo et al., 1998). The ^{87}Sr/^{86}Sr ratios of natural materials reflect the source of Sr available during their formation (Capo et al., 1998).

Strontium isotope ratios have successfully been used to link elephant bone and ivory to the environment in which these animals lived (Van der Merwe et al., 1990; Vogel et al., 1990). A similar study linked Sr ratio distribution in modern rodents to geology (Hoppe et al., 1999), while Beard and Clark (2000) showed that the Sr isotope composition of skeletal material can indicate the birthplace and geographic mobility of humans and animals.

Lakes are very special habitats as fish migration and movements are limited by dam walls and usually very shallow waters at the inlets. Adult fish are therefore expected to spend their entire lives within a relatively limited area. Penne and Pierce (2006), in a telemetry study of carp in Clear Lake, Iowa, USA, found that carp congregated in a relatively small area in winter, then moved to specific spawning areas in spring and spread out somewhat during the summer and autumn months. Otis and Weber (1982) showed similar results in a carp telemetry study of the Lake Winnebago system, USA, and indicated that carp in a river system occupy restricted home ranges.

It can therefore be hypothesised that bone tissue from fish in South African lakes may have a similar Sr isotope ratio to the aquatic environment they live in. This has been demonstrated in Atlantic salmon from the Connecticut River, Massachusetts, by Kennedy et al. (2002) and in Dolly Varden char from the Yukon Territory by Outridge et al. (2002), using fish otoliths. Strontium is incorporated into bone mass as substituting for calcium in various microcrystalline sites. Palmer and Edmond (1992) state that otolith ^{87}Sr/^{86}Sr ratios directly reflect dissolved ambient ratios, which in freshwater habitats depend on the geological composition of the catchment. Walther and Thorrold (2006) found in an experimental study of juvenile marine mummichogs (*Fundulus heteroclitus*) that the water composition and not the food composition determine the isotope composition of Sr deposited in fish otoliths. Using available South African data (De Villiers et al., 2000; De Villiers and De Wit, 2007), stable geographical distribution patterns in Sr isotope composition of river water can be shown. Douglas et al. (1995) used Sr isotope ratios to link suspended particulate matter in the Murray-Darling River system, Australia, to weathering lithologies in the catchment areas. Preliminary work (Jordaan et al., 2006; Jordaan et al., 2009; Jordaan and Rademeyer, 2009) already indicates a correlation between the Sr isotope ratio of fish fin spine tissue and lake water in South African lakes.

If only the elemental composition of lake or river water in a large catchment is considered, then the mixing of water from two sub-catchments, which can be described by existing mixing models using the water Ca/Sr ratio (Land et al., 2000), may also be reflected in the strontium isotope ratio of fish fin spines. Using the water Cl$^-$/SO$_4^{2-}$ ratio in a mixing model may similarly add information about possible anthropogenic influences.

The aim of this paper is to investigate the relationship in strontium isotope ratios between different fish species and

water within selected South African lakes. The study was undertaken to develop a scientific method (forensic tool) to minimize illegal entries at major South African freshwater fishing tournaments (Jordaan, 2015).

MATERIALS AND METHODS

Description of the project area

The project area consisted of selected lakes within the Vaal, Mgeni, Crocodile (West) and Olifants River catchments (Fig. 1). The selection criteria were different sizes, different sources of pollution and different underlying geological composition.

Collection and preparation of samples

Samples included: water taken on the surface of lakes and fish samples taken mainly by bank and boat angling as well as gill netting (Table 1). Water samples for isotope analyses were collected in 2-L high-density polyethylene (HDPE) containers, acidified with ultrapure HNO_3, cooled and sent to the laboratory for analyses within 24 h. Water samples for anion and metal concentration analyses were collected in 2-L high-density polyethylene (HDPE) containers, not acidified, cooled and sent to the laboratory for analyses within 24 h.

Four fish species were targeted, i.e., common carp (*Cyprinus carpio*), sharptooth catfish, (*Clarias gariepinus*), largemouth bass, (*Micropterus salmoides*) and Mozambique tilapia (*Oreochromis mossambicus*), although minor fish species were also included. Fish samples were collected in plastic containers, packed in ice and brought to the laboratory, where they were frozen to −5°C.

Fish spines from the dorsal or pectoral fins were removed and dried in an oven at approximately 80°C for 14 days. All soft tissues were removed followed by pulverizing in a swing mill.

Chemical analyses

The analytical method for Sr isotope analysis of water samples consisted of filtering 2 L samples through 0.45 μm cellulose nitrate filters and drying in a drying box to concentrate the Sr. The samples were re-dissolved in 10 mL concentrated nitric acid and evaporated to dryness in 50 mL disposable polypropylene beakers on a hotplate – 2 mL 6 M HCl was added, followed by drying on a hotplate. This step was repeated twice to ensure the samples were converted to chlorides. The samples were then centrifuged for 5 min at 2 500 r/min. The samples were purified using 6 mL Bio-Rad AG50Wx12, 200-400# cation resin packed in a 10 mm ID quartz glass column. The resin was cleaned using 30 mL 2.5 M HCl. The samples were carefully transferred onto a resin bed, taking care not to disrupt the resin. Hydrochloric acid was passed through the column, collecting Rb, Sr and the rare earth element fraction. The purified samples were then analysed for Sr isotope ratios using a Finnigan MAT 261 thermal ionization mass spectrometer. The instrument is controlled by Run It 26X software created by Spectromat (Germany).

The analytical method for Sr isotope analyses of fish fin spine samples consisted of weighing 1 g of pulverized sample into clean, static-free Savillex beakers; 2 mL concentrated nitric acid was added such that the samples were thoroughly wetted. 2 mL 6 M HCl was added and the beakers closed with screw caps. The sample was left to dissolve overnight on a hotplate set at
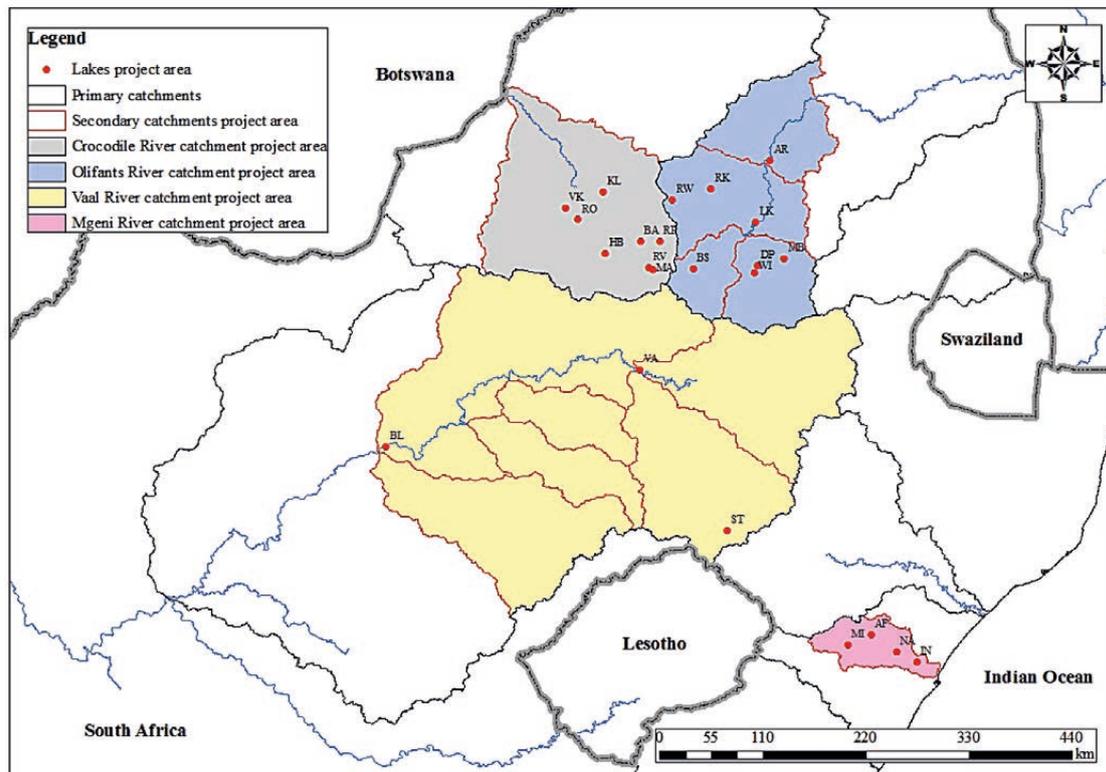

Figure 1

Secondary catchments of the project area. The catchments represented are the Upper Vaal River catchment, the Mgeni River catchment, the Crocodile River (West) catchment and the Upper Olifants River catchment. For codes see Table 1.

TABLE 1

Codes for the different lakes and fish species are indicated. Numbers in the matrix indicate the number of water and fish Sr isotope ratio analyses per lake. Only fish spine tissue is used. Names in brackets indicate samples taken from rivers. (OL) and (SK) are tributaries of Lake Witbank. (VA) and (VE) are tributaries of Lake Bloemhof. 'No sample' is indicated by 'ns'. Wet season is indicated by 'w'. Dry season is indicated by 'd'. Spine tissue is indicated by 's'. Lake water samples were mainly collected between 2007 and 2009. Fish samples were mainly collected between 2007 and 2011. Both sexes were collected during wet and dry seasons. Water samples were mostly collected independently from fish samples.

Target components/species

Catchment	Lake/river/	Code	Water		*Cyprinus carpio* (CC)	*Clarias gariepinus* (CG)	*Micropterus salmoides* (MS)	*Oreochromis mossambicus* (OM)	*Labeo capensis* (LA)	*Labeo rosae* (LR)	*Labeo umbratus* (MO)
Season			w	d				**Both**			
Crocodile (West)	Bon Accord	BA	2	ns	1	ns	n	ns	ns	ns	ns
	Roodeplaat	RP	ns	4	ns	1	n	1	ns	ns	ns
	Klipvoor	KL	3	ns	1	1	n	ns	ns	ns	ns
	Marais	MA	1	ns	1	1	n	ns	ns	ns	ns
	Rietvlei	RV	2	ns	1	1	n	ns	ns	ns	ns
	Hartbeespoort	HB	3	ns	1	1	n	ns	ns	ns	ns
	Roodekopjes	RO	3	ns	1	1	n	ns	ns	ns	ns
	Vaalkop	VK	3	ns	1	ns	n	ns	ns	ns	ns
Olifants	Bronkhorstspruit	BS	ns	3	1	ns	1	ns	ns	ns	ns
	Olifants River	(OL)	1	ns	4	ns	n	ns	ns	ns	ns
	Steenkool River	(SK)	1	ns	ns	ns	n	ns	ns	ns	ns
	Witbank	WI	2	3	ns	ns	3	ns	ns	ns	ns
	Doornpoort	DP	ns	3	1	1	2	ns	ns	ns	ns
	Middelburg	MB	ns	3	ns	ns	2	ns	ns	ns	1
	Loskop	LK	ns	8	50	1	n	6	ns	1	ns
	Rust de Winter	RW	3	ns	1	1	1	ns	ns	ns	ns
	Elands River	EL	1	ns	ns	ns	n	ns	ns	ns	ns
	Rhenosterkop	RK	3	ns	ns	ns	n	1	ns	ns	ns
	Arabie	AR	ns	5	2	1	ns	ns	ns	ns	ns
Vaal	Sterkfontein	ST	3	ns	ns	ns	ns	ns	ns	ns	ns
	Vaal	VA	ns	10	9	4	ns	ns	4	ns	ns
	Vaal River	(VR)	1	ns	ns	ns	ns	ns	ns	ns	ns
	Vet River	(VE)	1	ns	ns	ns	ns	ns	ns	ns	ns
	Bloemhof	BL	9	ns	17	3	ns	ns	ns	ns	ns
Mgeni	Midmar	MI	5	ns	ns	ns	ns	ns	ns	ns	ns
	Albert Falls	AF	2	ns	ns	ns	ns	ns	ns	ns	ns
	Nagle	NA	2	ns	ns	ns	ns	ns	ns	ns	ns
	Inanda	IN	5	ns	1	ns	3	ns	ns	ns	ns

95°C. The samples were removed from the hotplate and allowed to dry to half volume after which another 1 mL of concentrated nitric acid was added and allowed to dry. A further 2 mL of 6 M HCl was added and allowed to dry. This step was repeated twice to ensure the sample was converted to chlorides. The sample was then centrifuged for 5 min at 2 500 r/min. The samples were purified using Bio-Rad AG50Wx12, 200-400# cation resin, followed by analysis on a Finnigan MAT 261 thermal ionization mass spectrometer.

The analytical method for concentration analyses of Sr and Ca in water samples consisted of first filtering samples through 0.45 µm cellulose nitrate filters (Jordaan and Maritz, 2010). Water samples were then diluted 5 times to add the internal standards (In and Ir) and to reduce total dissolved solids. The samples were made up in 2 ml/100 mL HNO_3 to keep analyte elements in solution. Analytical grade HNO_3 and ultra-pure water were used in all preparations. Samples were analysed on a Perkin Elmer SCIEX ELAN DRCII ICP-MS with AS 93 plus auto-sampler.

The analytical method for concentration analyses of Cl^- and SO_4^{2-} in water samples consisted of first filtering samples through 0.45 µm cellulose nitrate filters (Jordaan and Maritz, 2010). Samples were analysed either undiluted or at a dilution factor of 7 times on a Dionex QIC analyser ion chromatograph. The instrument uses an IonPac AG14 (4 × 50 mm) and an IonPac AS14 (4 × 250 mm) column.

Quality assurance

The standard reference material NIST987, used for calibration of the Sr isotope ratio method, produced the following average $^{87}Sr/^{86}Sr$ ratio: 0.710213, range: 0.709915–0.710414, standard deviation: 0.000067, n = 96, which is within the published range of 0.71034±0.00026. A set of samples were analysed at the University of Cape Town on a NU Instruments MC-ICP-MS for verification. An $^{87}Sr/^{86}Sr$ ratio of 0.710300 (n = 8) was obtained for the reference material. A detection limit of 0.2 µg/L Sr, 0.03 mg/L Cl^- and 0.10 mg/L SO_4^{2-} was achieved for concentration analyses of water samples.

To evaluate the method used to determine concentrations in water, liquid samples from the SABS Water-Check (Group 1 and Group 3) inter-laboratory proficiency test (South African Bureau of Standards, 2010a, 2010b, 2010c, 2010d, 2010e, 2010f) were regularly analysed. The elements analysed included Al, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Mo, Ni, Si, Sr, V, Zn, As and Se for Group 1, and chloride and sulphate for Group 3. The average Group 1 z-scores obtained for this evaluation are as follows: April 2010, 0.73; July 2010, 0.73 and October 2010, 0.69. The average Group 3 z-scores obtained for this evaluation are as follows: June 2010, 0.77; September 2010, 0.70 and December 2010, 0.60. All z-scores between −2 and 2 are considered satisfactory.

Statistical analyses

The sample codes used are explained in Table 1. A summary of analytical data for water and fish samples (all species) is listed in Table 2. A one-way ANOVA test was used to assess the correlation of Sr isotope ratios between water and fish from lakes in the project area (Table 2). Similarly, the largest dataset from Lake Loskop fish, as well as the results of a one-way ANOVA test used to assess the correlation in Sr isotope ratios between carp and other fish species within the lake, are listed in Table 3. The Single Factor ANOVA function of the software package Microsoft Office Excel was used for the calculation.

RESULTS AND DISCUSSION

Sample identification

In Table 1 the number of species sampled and spine tissues collected for isotope ratio analyses from each lake are represented. The codes provided for the different lakes and fish species are used in all figures and tables. The Olifants River catchment was sampled during both the wet and dry season, while most of the lakes in the other catchments were sampled only during each of the seasons for Ca, Sr and anion concentration analyses. For the purpose of this project the period from August to November is considered the dry season and from December to July the wet season.

The Crocodile River catchment

Figure 2 shows the Sr isotope ratio variation along the Crocodile River system in Gauteng and the North West Province. This system is complicated due to complex geology,
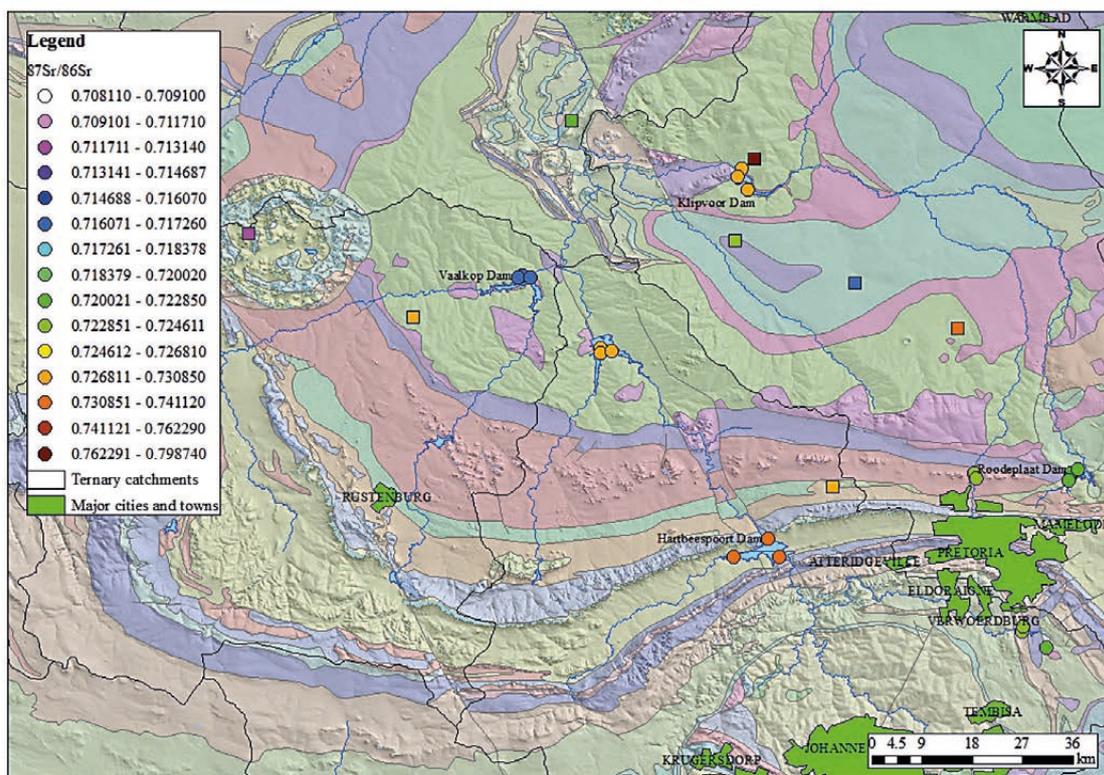

Figure 2

Sr isotope ratios of lake water in the Crocodile River catchment superimposed on the 1:1 000 000 scale geology map of South Africa (Council for Geoscience, 2011), draped over the topography. Square symbols show the $^{87}Sr/^{86}Sr$ ratio of groundwater from McCaffrey and Willis (2001). The colour of the dots/squares represents the $^{87}Sr/^{86}Sr$ isotope ratio as indicated in the legend. Rivers (2nd order and higher) and catchments (ternary) are indicated as blue and black lines respectively.

Catchment	Lake		Water ^{87}Sr/^{86}Sr	Spine ^{87}Sr/^{86}Sr	p-value	Cl (mg/L)	SO$_4^{2-}$(mg/L)	Ca (µg/L)	Sr (µg/L)
	BA	Ave	0.724298±0.000021	0.725934	0.01	5.3±0.1	44.9±0.1	36 734±34	154.6±1.2
		Range	0.724277–0.724319			35.2–35.4	44.8–45.0	36 700–36 768	153.4–155.7
	RP	Ave	0.721756±0.000570	0.723950±0.000357	0.02	57.9±2.3	38.3±2.3	34 258±333	104.0±5.9
		Range	0.720788–0.722244	0.723593–0.724308		55.4–61.5	36.1–42.2	33 753–34 636	96.4–112.8
	KL	Ave	0.729329±0.000027	0.729945±0.000023	0.00	41.8±0.2	33.2±0.3	28 960±185	134.6±0.8
		Range	0.729296–0.729361	0.729922-0.729968		41.6–42.1	32.9–33.6	28 816–29 220	133.7–135.7
	MA	Ave	0.722486	0.722950±0.000387	0.61	74.6	62.2	30 981	112.3
		Range		0.722564–0.723337					
	RV	Ave	0.724020±0.000126	0.723606±0.000084	0.11	45.1±0.0	42.2±0.2	28 248±284	99.4±0.6
Crocodile		Range	0.723894–0.724146	0.723523–0.723690		45.1–45.1	42.0–42.3	27 964–28 532	98.8–99.9
	HB	Ave	0.734467±0.000172	0.734409±0.000851	0.94	50.5±0.6	42.7±1.1	35 927±690	139.1±1.3
		Range	0.734228–0.734628	0.733557-0.735260		49.7–51.2	41.7–44.1	35 260–36 877	137.3–140.4
	RO	Ave	0.730135±0.000228	0.730639±0.000104	0.11	67.6±1.3	57.3±0.7	35 456±174	154.2±3.3
		Range	0.729903–0.730446	0.730535–0.730743		66.5–69.4	56.7–58.3	35 302–35 698	150.3–158.3
	VK	Ave	0.716612±0.000420	0.719744	0.03	101.6±0.4	80.9±1.1	36 208±1 340	251.3±6.9
		Range	0.716304–0.717206			101.1–102.1	80.2–82.4	34 581–37 862	242.8–259.8
	BS	Ave	0.730204±0.000080	0.730170±0.000016	0.67	17.6±0.2	14.5±1.1	22 550±1 343	93.0±4.8
		Range	0.730093–0.730278	0.730153-0.730186		17.4–17.8	13.7–16.1	21 395–24 434	89.1–99.7
	OL	Ave	0.723241	0.722898±0.000028	0.00	12.0	56.7	22 066	164.6
		Range		0.722863-0.722929					
	SK	Ave	0.723642			32.3	262.0	79 573	1450.9
	WI	Ave	0.725340±0.000177	0.725666±0.000206	0.09	15.0±1.4	163.4±14.0	42 398±1 706	343.4±12.2
		Range	0.725112–0.725583	0.725437–0.725936		13.0–17.0	150.8–188.7	40 272–44 771	331.4–364.2
	DP	Ave	0.725551±0.000111	0.726807±0.000450	0.01	17.6±0.2	152.9±0.4	42 124±486	341.3±1.5
		Range	0.725395–0.725637	0.726275–0.727398		17.4–17.8	152.3–153.3	41 508–42 697	339.5–343.1
	MB	Ave	0.724975±0.000262	0.725649±0.000139	0.03	22.0±0.5	367.1±13.2	77 119±2 299	577.8±16.3
Olifants		Range	0.724611–0.725217	0.725519–0.725841		21.6–22.7	349.2–380.8	75 234–80 355	562.9–600.6
	LK	Ave	0.729044±0.000533	0.730938±0.000965	0.00	14.8±2.3	148.6±35.6	36 348±5 918	210.1±29.1
		Range	0.728487–0.730027	0.728734–0.732730		11.7–17.2	105.0–197.4	27 641–46 866	166.9–258.0
	RK	Ave	0.746904±0.000034	0.747130	0.04	19.8±0.1	5.5±0.1	14 274±177	95.7±0.5
		Range	0.746878–0.746953			19.7–20.1	5.4–5.6	14 033–14 453	95.4–96.5
	EL	Ave	0.746191			11.4	5.7	7 138	38.5
	RW	Ave	0.745912±0.000175	0.743131±0.002406	0.18	10.8±0.0	6.1±0.1	6 825±117	37.6±0.2
		Range	0.745670–0.746077	0.740344–0.746215		10.7–10.8	6.0–6.1	6 701–6 982	37.4–37.8
	AR	Ave	0.737776±0.000111	0.737649±0.000923	0.80	31.6±0.9	114.8±2.2	36 856±788	211.6±1.7
		Range	0.737636–0.737935	0.736389–0.738571		30.4–32.8	112.0–117.2	35 927–38 087	209.2–214.3
	ST	Ave	0.712373±0.000006			1.2	3.1	8 490±30	62.8±0.3
		Range	0.712366–0.712381					8 454–8 528	62.4–63.0
	VA	Ave	0.713325±0.001095	0.713546±0.000622	0.53	6.0±3.1	11.4±6.6	14 529±3 948	90.9±27.1
Vaal		Range	0.712485–0.715752	0.712540–0.714877		2.5–12.2	6.1–27.0	10 708–24 987	60.4–150.6
	VR	Ave	0.721668			70.2	209.5	72 259	190.2
	VE	Ave	0.715666			14.6	12.6	20 930	173.1
	BL	Ave	0.718412±0.000653	0.718617±0.000306	0.28	34.0±21.2	79.7±42.7	29 874±7 295	121.3±52.0
		Range	0.717728–0.719725	0.717775–0.719280		9.4–66.8	30.9–145.3	20 977–41 519	64.0–201.1
	MI	Ave	0.712383±0.000163			4.1±0.1	1.4±0.2	4 375±556	34.0±4.0
		Range	0.712174–0.712644			4.0–4.2	1.2–1.7	3 464–4 965	27.2–38.3
	AF	Ave	0.714522±0.000030			6.6±0.3	2.9±0.0	4 906±22	34.9±0.2
Mgeni		Range	0.714492-0.714552			6.3–6.9	2.8–2.9	4 884–4 928	34.6–35.1
	NA	Ave	0.717628±0.000015			13.5±0.3	4.3	5 645±989	36.5±6.3
		Range	0.717613–0.717642			13.2–13.7		4 656–6 634	30.3–42.8
	IN	Ave	0.718552±0.000244	0.718489±0.000628	0.86	31.1±1.3	16.6±0.7	12 674±1 358	64.3±7.2
		Range	0.718241–0.718923	0.717410–0.718970		28.8–32.6	15.9–17.5	10 058–13 940	50.1–69.9

TABLE 2
Average (± standard deviation) Sr isotope ratio of lake water and fish fin spines (all species) from lakes in the project area.
Average (± standard deviation) Ca, Sr and anion content of lake water from the project area.
Codes for the lakes and number of samples (*n*) are explained in Table 1.

but in general shows a slight increase in Sr isotope ratios as water moves downstream within tertiary catchments. Lake Roodekopjes is inconsistent with this pattern, as it has a slightly lower value than Lake Hartbeespoort, which is approximately 50 km upstream. The Lake Vaalkop tertiary catchment contains the Pilanesberg alkali intrusive complex which is different in both composition and age to the geology of the Lake Hartbeespoort/Roodekopjes system. This may explain the very distinct Sr ratio of the Lake Vaalkop water.

The Olifants River catchment

The Sr isotope ratio of water samples from different localities in the Olifants River catchment shows a very distinct pattern (Fig. 3). Water within tertiary catchments of the Olifants River system generally shows a slight increase in the $^{87}Sr/^{86}Sr$ isotope ratio downstream. When water from two different tertiary catchments is combined the Sr isotope ratio shows an intermediate value between the values of the two sources. In the Olifants River catchment, water from the Witbank and Middelburg sub-catchments is similar. When combined with water from the Bronkhorstspruit sub-catchment the intermediate ratios of Lake Loskop result. Lakes in the Elands River catchment have much higher Sr ratios than that of the Olifants River catchment and result in the intermediate Sr isotope ratio of water in Lake Arabie, located downstream of the confluence of the two systems. Figure 3 shows that catchments with similar geology produce similar isotope ratios in the rivers that drain them, while different geology can produce quite distinct Sr ratios in others.

The Orange/Vaal River catchment

Figure 4 shows the Sr isotope ratios in the massive Orange/Vaal River system (some data from De Villiers et al., 2000; De Villiers and De Wit, 2007). When looking at the Upper Orange and Caledon River catchment a similar pattern emerges, with a slight increase in the Sr isotope ratio within tertiary catchments. This part drains the relatively uncomplicated Karoo stratigraphy and is very similar to the Mgeni River which drains eastwards from the same Karoo stratigraphy. The Lower Orange River shows a mixed ratio of water from the Upper Orange and the Vaal Rivers. Further downstream, variation in Sr isotope ratios is limited to confluences of major tributaries.

The Vaal River (Fig. 4) shows the most complicated and varied Sr isotope ratio pattern of all the systems investigated. In this case smaller sub-catchments need to be evaluated to follow the variation in Sr isotope ratios. Figure 5 shows the Vaal River from Lake Vaal in the east to Lake Bloemhof in the west. The map indicates 2nd and higher order rivers as well as tertiary catchments. Lake Vaal is very large and has two inlets. There is a clear difference in Sr isotope ratios of water from the Vaal River side versus the Wilge River side. Water is well mixed in the western part of the lake closest to the dam wall. The Vaal River between Lake Vaal and Lake Bloemhof shows a large variation in Sr isotope ratios. This is mostly related to the large number of tributaries joining the Vaal River in this area. Tributaries have very distinct Sr isotope ratios, possibly related not only to the underlying geology but also to industrial pollution from the Vereeniging and Vanderbijlpark areas. Lake Bloemhof (Fig. 5) also has two inlets but seems to be dominated by the Vaal River as it has a higher flow rate than the Vet River. The Vet River does have a distinct Sr isotope ratio 10 km upstream from Lake Bloemhof.
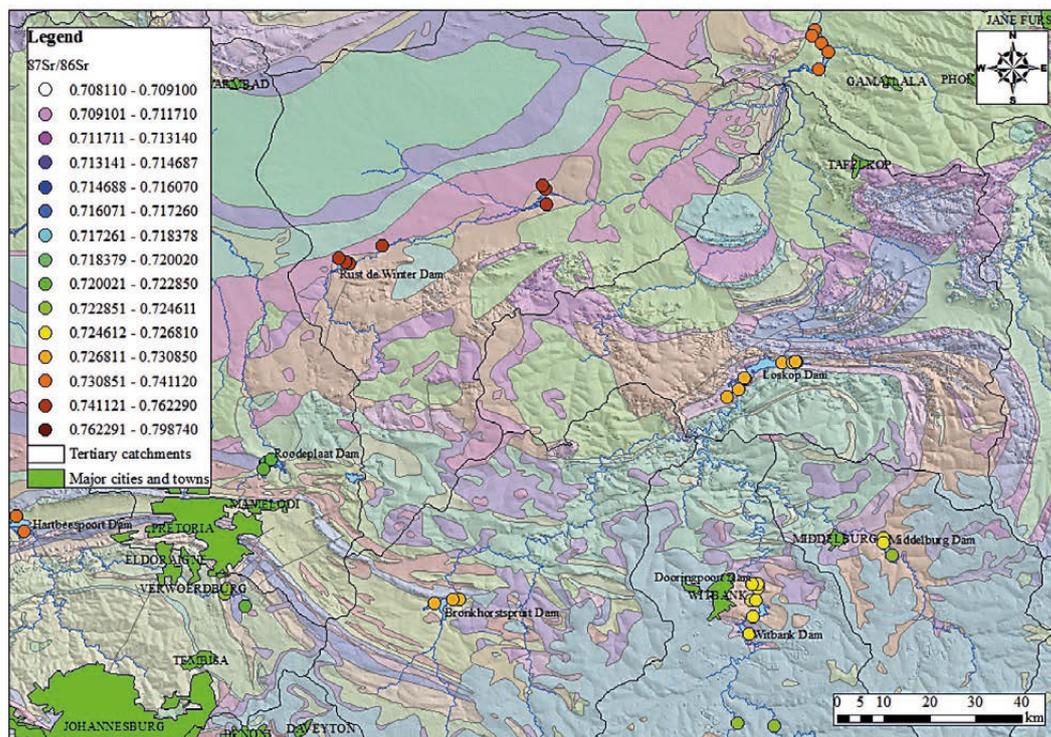

Figure 3

Sr isotope ratios of lake and river water in the Olifants River catchment superimposed on the 1:1 000 000 scale geology map of South Africa (Council for Geoscience, 2011), draped over the topography. The colour of the dots represents the $^{87}Sr/^{86}Sr$ isotope ratio as indicated in the legend. Rivers (2nd order and higher) and catchments (ternary) are indicated as blue and black lines respectively.
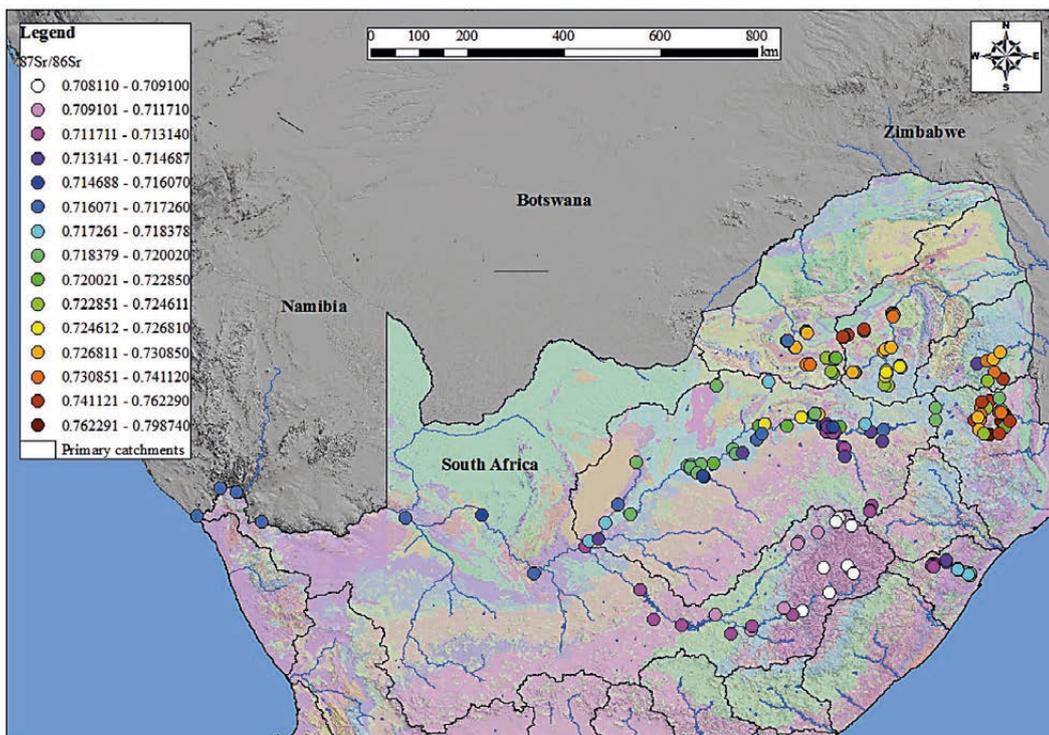
Figure 4

Sr isotope ratios of lake and river water in the Orange/Vaal, Crocodile, Olifants and Mgeni River catchments, superimposed on the 1:1 000 000 scale geology map of South Africa (Council for Geoscience, 2011), draped over the topography. Some data from the Orange/Vaal catchment from De Villiers et al. (2000). Swaziland data from De Villiers and De Wit (2007). The colour of the dots represents the ⁸⁷Sr/⁸⁶Sr isotope ratio as indicated in the legend. Rivers and catchments are indicated as blue and black lines, respectively.
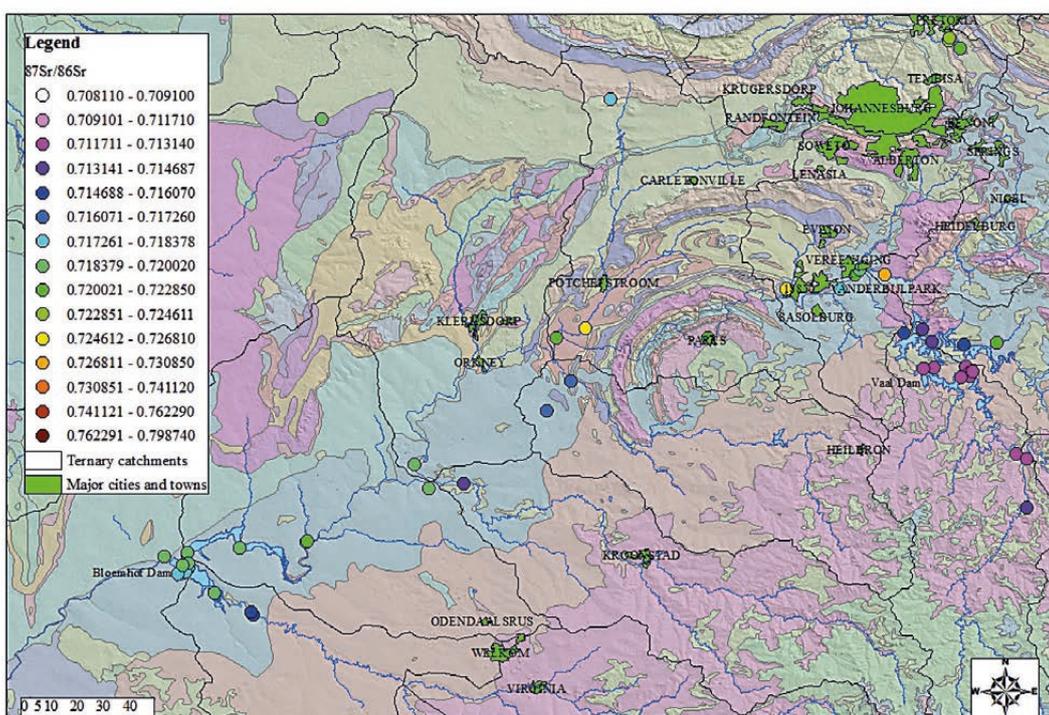
Figure 5

Sr isotope ratios of water in Lake Vaal and Lake Bloemhof superimposed on the 1:1 000 000 scale geology map of South Africa (Council for Geoscience, 2011), draped over the topography. Some data from the Orange/Vaal catchment from De Villiers et al. (2000). The colour of the dots represents the ⁸⁷Sr/⁸⁶Sr isotope ratio as indicated in the legend. Rivers (2ⁿᵈ order and higher) and catchments (ternary) are indicated as blue and black lines, respectively.

The Mgeni River catchment

Figure 6 shows the Sr isotope ratios of water from 4 lakes within the Mgeni River in KwaZulu-Natal. This system appears much simpler as it is contained within one tertiary catchment which shows a slight increase in Sr isotope ratios moving downstream from Lake Midmar towards Lake Inanda. The river is approximately 130 km long and passes over several distinct geological units which may contribute to the Sr isotope ratio of the river water.

TABLE 3
Average (± standard deviation) Sr isotope ratio of spine tissue from different fish species sampled in Lake Loskop. Other species are compared to carp (CC). Significance regarded as $p < 0.05$. For codes see Table 1.

Lake	Species		Spine ^{87}Sr/^{86}Sr	p-value
LK	CC	Average	0.730928±0.000953	
		Range	0.728923–0.732730	
		n	42	
	CG	Average	0.728734	0.03
		n	1	
	OM	Average	0.731388±0.000632	0.27
		Range	0.730440–0.732303	
		n	6	
	LR	Average	0.730879	0.96
		n	1	

Fish

Data obtained during the project indicated a correlation (although not in all cases statistically significant), between the ^{87}Sr/^{86}Sr isotope ratio of fish spine tissue and the lake water in which the fish lived while developing these tissues (Table 2). In the Mgeni and Orange/Vaal River catchments the Sr ratio of fish and water were statistically the same. In the Olifants and Crocodile River catchments population sizes were too small for comparison, except at Lake Loskop where the Sr ratios of fish and water were statistically different. In Lake Loskop the Sr ratios of different fish species were not significantly different (Table 3).

When plotting the average ^{87}Sr/^{86}Sr ratios of fish spine tissue against the average ^{87}Sr/^{86}Sr ratios of water (Fig. 7), a significant linear regression ($r = 0.98$, $p < 0.005$) was obtained. The error bars indicate the total range of values for each locality. The range of values for water samples from any specific lake is generally smaller than the range of values for fish samples from that same lake. It is, however, not influenced by the specific fish species (Table 3), the sex of the fish, the age of the fish and the season in which the fish were caught, as fish were collected from both sexes, both seasons and different ages, yet still produced a limited range of Sr isotope ratios for each lake. The Sr ratios were in some cases determined over a 4-year period in which time there were no significant changes in these ratios (Table 1).

Fish spine tissue from Lake Rust de Winter showed a relatively large variation in ^{87}Sr/^{86}Sr ratio, while the water had a relatively small range. It is not clear what causes this large range in fish spine tissue data or why most of the data plot below
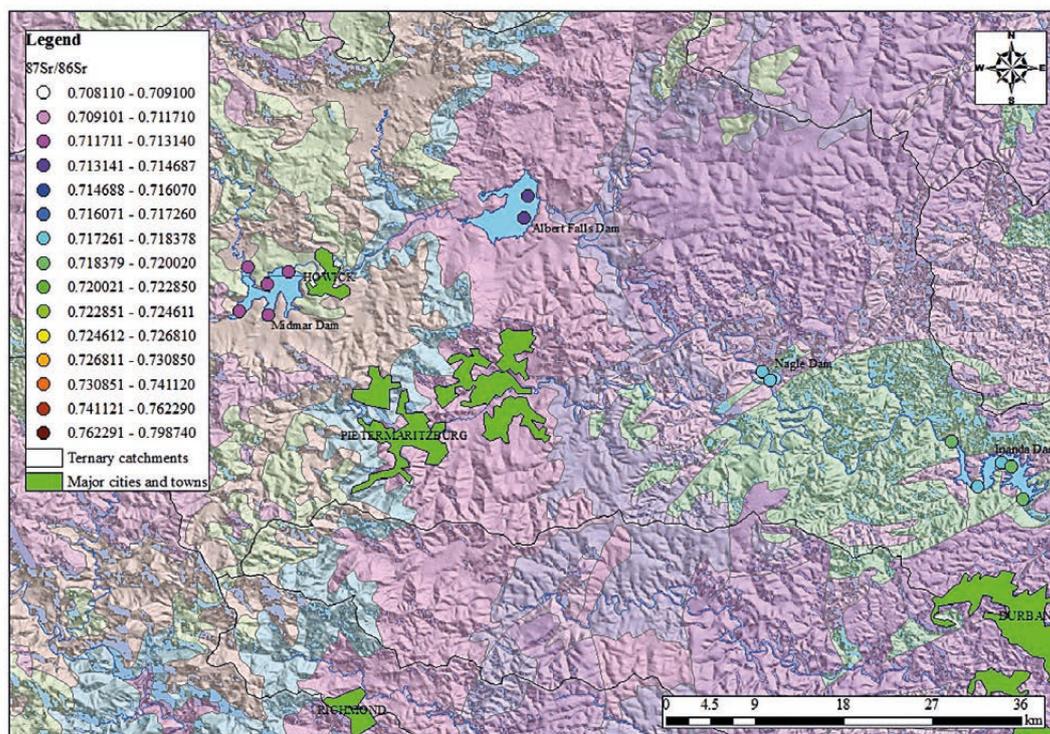

Figure 6
Sr isotope ratios of lake water in the Mgeni River catchment superimposed on the 1:1 000 000 scale geology map of South Africa (Council for Geoscience, 2011), draped over the topography. The colour of the dots represents the ^{87}Sr/^{86}Sr isotope ratio as indicated in the legend. Rivers (2nd order and higher) and catchments (ternary) are indicated as blue and black lines, respectively.

the regression line in Fig. 7. Samples from Lake Loskop, Lake Roodeplaat, Lake Bon Accord and Lake Doornpoort all plot slightly above the regression line in Fig. 7. Even though only a limited number of spine samples were analysed from each individual lake, the data range for each lake indicates that this shift in the data may be real and not related to an analytical artefact.

The relatively large spread in data from Lake Vaal (Fig. 7) is due to a difference in Sr isotope ratios between the Vaal and the Wilge Rivers that feed the lake. Fish were mainly collected during fishing competitions at the Jim Fouché resort on the Wilge River inlet side, although sampling was not restricted to this area. Lake Bloemhof shows a similar situation although the lake is dominated by the Vaal River.

Influence of inter-catchment water transfers on Sr isotope ratios

Middleton and Bailey (2005) describe 28 major inter-catchment water transfer schemes for South Africa. These systems include domestic and industrial water supply schemes, hydro-electric power generation schemes and irrigation schemes. These systems either transport water directly from one catchment to another or transport water for domestic or industrial use that reaches destination rivers as waste water (DWAF, 2004).

The most significant of these schemes is water from the Lesotho Highlands Project which is transferred into the Vaal River catchment and then pumped from Lake Vaal to Johannesburg and Pretoria to end up in the Crocodile River catchment. Water from the Lesotho mountains has a distinctly low $^{87}Sr/^{86}Sr$ isotope ratio (0.709) compared to other more local Lake Vaal tributaries (0.715) (Fig. 4). Therefore the Wilge River side of Lake Vaal, where the water from Lesotho is received, also has a lower $^{87}Sr/^{86}Sr$ isotope ratio than the Vaal River side.

Water is also transferred to the Olifants River catchment to supply coal-fired power stations in the Upper Olifants River region. This water is, however, not returned to the Olifants River system (Van der Merwe, 2011). These pumping schemes should therefore contribute in some degree to the chemical characteristics of the water in rivers and lakes in South Africa. The amount of water displaced through these schemes is, however, relatively constant and should therefore have a constant
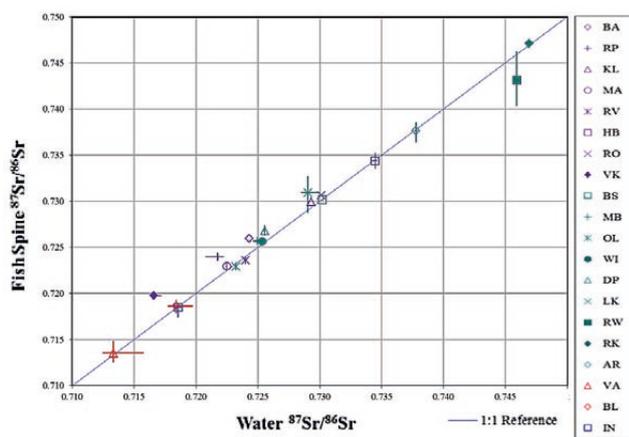

Figure 7

Average Sr isotope ratios of water and fish from the project area. Solid line indicates 1:1 reference line. A linear regression of all data produced a R^2 value of 0.98, whether forced through zero (y = 1.00x) or not (y = 0.93x + 0.05). Error bars indicate total range of data for each locality. For codes see Table 1.

influence on the natural water chemistry. Correlating fish to lake water should therefore be possible despite the fact that the water may contain significant anthropogenic components.

Geological significance and Sr isotope ratios

If Rb and Sr are incorporated into rock at its formation and the system remains closed, the amount of ^{87}Sr increases over time as radioactive ^{87}Rb decays. Older rocks will therefore, in general, have higher $^{87}Sr/^{86}Sr$ ratios than younger rocks with the same initial Rb/Sr ratio (Capo et al., 1998). The utility of the Rb-Sr isotope system results from the fact that different minerals in a given geological setting can have distinctly different $^{87}Sr/^{86}Sr$ ratios as a consequence of different ages, original Rb/Sr values and the initial $^{87}Sr/^{86}Sr$ ratios. Strontium derived from minerals through weathering reactions will have the same $^{87}Sr/^{86}Sr$ as the initial mineral. Differences in $^{87}Sr/^{86}Sr$ in catchment waters will therefore either depend on differences in mineralogy along contrasting flowpaths or on the relative amounts of Sr weathered from the same suite of minerals (Kendal et al., 1995). According to Faure (1986) Rb-bearing minerals are generally more resistant to weathering than Sr-bearing minerals. Strontium is therefore more readily lost from rocks exposed to weathering than Rb and the $^{87}Sr/^{86}Sr$ ratio of Sr that goes into solution is generally lower than the $^{87}Sr/^{86}Sr$ ratio of the unweathered rock. Faure (1986) does however note exceptions to this generalization.

Figure 4 shows 4th and higher order rivers superimposed on the 1:1 000 000 geology map of South Africa. When evaluating the regional systems, it is noted that the origins of the Caledon, Orange, Mgeni and Wilge Rivers are all situated in the middle and upper regions of the Drakensberg. In all of these rivers a very similar Sr isotope pattern emerges, regardless of the direction in which the river drains (some data from De Villiers et al., 2000). These rivers originate in or close to the Drakensburg basalts, then flow into older successions of the Karoo sedimentary sequence until they finally reach significantly older basement lithologies. The $^{87}Sr/^{86}Sr$ ratios of water samples increase from approximately 0.709 at the top to 0.715 at the base of the Karoo sequence. Where the Vaal River drains lithologies older than the Karoo sediments it has a Sr ratio of approximately 0.715 to 0.720, which is maintained in the Lower Orange River. There are however many local variations to this pattern. Fisher and Strueber (1976) found a similar situation in the Susquehanna River and its tributaries that drain large areas of Pennsylvania and Maryland in the USA. They observed that the $^{87}Sr/^{86}Sr$ ratio varies irregularly along the river as a result of mixing with water from tributaries. Pollution from anthropogenic sources may play a role in portions of the Vaal River, but this is likely a minor contributor to the Sr ratio of a large river. Several inter-catchment water transfers to and from the Vaal River may also contribute to a more irregular Sr isotope pattern.

The Swaziland rivers show a very complex pattern as they drain a very complicated geology (data from De Villiers and De Wit, 2007). The patterns are very different from the rivers draining the Drakensberg lavas and sediments. Primary river water in an area subject to active erosion will show a much closer relationship with the geology than massive rivers that flow for hundreds of kilometers and show only average Sr isotope ratios.

The Crocodile River system (Fig. 2) originates mostly in the Transvaal sediments and then continues through the Bushveld complex. This gives all the tributaries a similar Sr isotope ratio. Lake Vaalkop has two inlets and is very different to the rest of the system. The Hex River (southern inlet) is similar to the rest

of the catchment but the Elands River (western inlet) originates near the Pilanesberg alkali complex. This may contribute to the much lower Sr isotope ratio of Lake Vaalkop. The Crocodile River system is also the destination of inter-catchment water transfers from Lake Vaal. This may contribute to the difference between water that originates locally and water that has a larger component of water from Lake Vaal. (Fig. 3).

In the Olifants River catchment (Fig. 3), tributaries originate in, geologically, very distinctive sequences. The Middelburg and Witbank sub-catchments originate in the older portions of the Karoo sequence and are very different from the Bronkhorstspruit sub-catchment, which originates in mostly Transvaal sequence lithologies. This can clearly be seen in the Sr isotope ratios, which combine to give Lake Loskop an intermediate Sr isotope ratio. The Elands River originates in the Bushveld igneous complex and is very different from the Olifants River. The Sr isotope ratio of the Elands River is therefore higher (0.747) than the water in Lake Loskop (0.729). A mixing of these sources results in the Sr ratio of 0.738 at Lake Arabie further downstream (Table 2). The Sr isotope ratio of water in a river system is therefore mostly determined by the geology at the origin of the river were most weathering occurs (De Villiers et al., 2000). Further downstream it is determined by the contributions from tributaries which gain their Sr isotope ratio in a similar fashion. Sr isotope data from rocks in the upper catchment of the Olifants River are limited. Barton et al. (2004) investigated Sr isotope ratios in glauconite from quartz-rich sediments of the Witbank coalfield above the Number 4 and Number 5 coal seams. The $^{87}Sr/^{86}Sr$ ratios ranged from 0.751 to 0.922 for glauconite from the Vryheid formation, from 1.165 to 1.241 for coarse-grained detrital muscovite, and was 1.201 for coarse-grained detrital biotite from strata closely associated with the glauconite-bearing beds.

Published Sr isotope data from global lakes and rivers is very limited. Comparing the Sr isotope data from South African rivers on a mixing diagram (Fig. 8) to the limited amount of data from international examples listed by Faure (1986), Edmond (1992), Harris et al. (1998), Galy et al. (1999), Dalai et al. (2003), Négrel et al. (2004) and De Villiers and De Wit (2007), it can be seen that the Olifants and Crocodile River systems correspond to rivers draining the Himalayas, while the Orange/Vaal and Mgeni River systems fall within the field of global rivers. De Villiers and De Wit (2007) noted that rivers draining Swaziland also correspond to Himalayan examples. Rivers draining catchments dominated by K-granites have higher $^{87}Sr/^{86}Sr$ ratios (average 0.767) while Achaean Na-rich gneisses (average 0.731) and volcano-sedimentary sequences (average 0.735) have lower values. Edmond (1992) concluded that the average fluvial $^{87}Sr/^{86}Sr$ ratio (excluding Himalayas) is 0.710.

A linear correlation on a mixing diagram is typical of many river systems where a high Sr, low $^{87}Sr/^{86}Sr$ end member, derived from carbonate, is mixed with a low Sr, high $^{87}Sr/^{86}Sr$ end member, derived from silicate (Palmer and Edmond, 1992).

The Mgeni River system shows a gradual increase in the Sr isotope ratio as well as in the Sr content moving downstream from Lake Midmar, to Lake Albert Falls, then to Lake Nagle and Lake Inanda (Fig. 8). The Vaal River system does not show such clear trends as the system is massive and has numerous tributaries with very different Sr characteristics. The present data however correspond very well with the Vaal River data of De Villiers et al. (2000). The data from De Villiers et al. (2000) for the Lower Orange River plots centrally within all the available data for the upstream parts of this river system, possibly indicating that the Lower Orange River composition represents

mixing of all the upstream components (Fig. 8).

The Crocodile River system shows much clearer mixing properties. Lake Loskop falls on a mixing line between Lake Bronkhorstspruit and Lake Witbank/Middelburg. Lake Arabie falls on a mixing line between Lake Loskop and Lake Rhenosterkop. This is a precise representation of the field observations. Lake Rhenosterkop, the Elands River and Lake Rust de Winter show the same linear downstream trend as the Mgeni River system. Variation in Sr concentration data in the Crocodile River system is limited. Clear linear mixing trends are difficult to identify.

Land et al. (2000) used element ratios rather than element concentrations for mixing models when investigating a small catchment situated within the Kalix River watershed in northern Sweden. Figure 9 (after Land et al., 2000) shows the $^{87}Sr/^{86}Sr$ vs. Ca/Sr for the project area. Mixing trends in data from all four large catchments are essentially similar to trends described on the $^{87}Sr/^{86}Sr$ vs. 1/Sr plot (Fig. 8). Figure 10 shows the $^{87}Sr/^{86}Sr$ vs. Cl$^-$/SO$_4^{2-}$ data on a mixing diagram. It includes the possibility of chloride and sulphur from possible anthropogenic pollution sources. Again, mixing trends in data from all four large catchments are essentially similar to trends described on the $^{87}Sr/^{86}Sr$ vs. 1/Sr plot (Fig. 8). Data are however less spread out and mixing relationships are clearer.

Figure 8
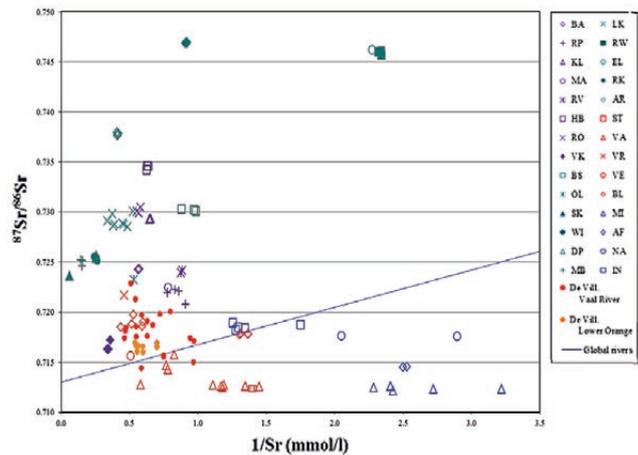
All water data from project area. Orange and Vaal River data from De Villiers et al. (2000). For codes see Table 1.
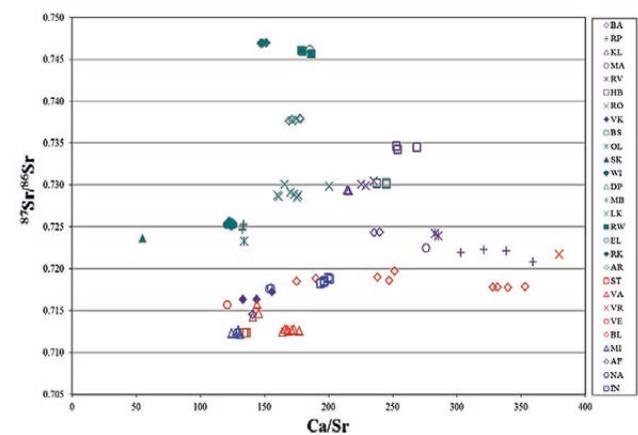

Figure 9

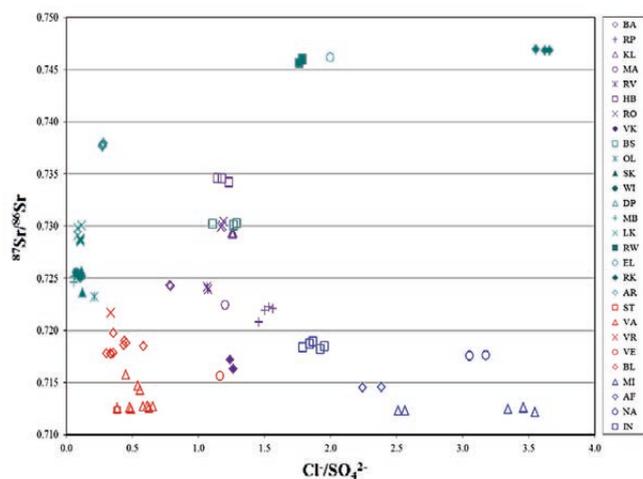*All water data from project area. For codes see Table 1.*

Figure 10
All water data from project area. For codes see Table 1.

CONCLUSIONS

Sr isotope ratios of water samples were in all cases determined on the dissolved Sr fraction. The origin of this fraction can therefore be either from the natural weathering of upstream geological units or from upstream anthropogenic sources. An investigation of the Vaal and Orange Rivers by De Villiers et al. (2000) showed that much of the Sr isotope ratio of the river is determined by the isotope ratio of the predominant geological strata in the upper part of the catchment (where active weathering is taking place). In the upper Olifants River system there is certainly ample proof of additions to the river water from mine, municipal or industrial sources. The Sr isotopic ratios of the water samples were however constant over a 3-year period (2007–2009), suggesting that the main source may be the more consistent geological environment. Anthropogenic Sr sources vary along the course of a river, but individual anthropogenic sources may be more constant over time than expected. Most of the larger fish that were analysed (carp above 4 kg) were also older than 5 years (Balik et al., 2006; Sedaghat, 2013) indicating that a relatively constant Sr source may have been available to them for several years. In larger lakes with only one major inlet the Sr isotope ratio is very constant, even close to the inlet. In large lakes with two major inlets like Lake Vaal or Lake Bloemhof, slight differences may exist between the inlets.

The Sr isotope ratio of fish spine tissue shows a remarkable correlation with the Sr isotope ratio of the lake water in which these fish lived. It correlates much better than any single element and may therefore be used to establish a link between the fish and lake water. It also shows that the Sr isotope ratio systematics is constant over the multi-year span of the project and that the season in which samples were taken did not contribute any variability. The establishment of a chemical link between fish and lake water provides a forensic tool to eliminate illegal entries at major South African fishing tournaments.

Inter-catchment water transfers are relatively constant and should have a constant influence on the natural water chemistry. Correlating fish to lake water should therefore be possible despite the fact that the water may contain anthropogenic components.

In the Olifants River catchment, Lake Middelburg, Lake Witbank and Lake Doornpoort have a similar Sr isotope ratio, which is distinct from Lake Bronkhorstspruit, primarily due to differences in catchment geology. Lake Loskop, which is downstream from these lakes, has a Sr isotope ratio between these two extremes, clearly indicating mixing of water from upstream sources. Similarly, Lake Arabie, which is even further downstream, shows a Sr isotope composition between the composition of Lake Loskop and the lakes in the Elands River, again indicating mixing. The Sr isotope composition of a single lake may therefore be the result of several factors that may give a lake and the fish living within it a distinctive character.

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