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Published in:
Canadian Journal of Fisheries and Aquatic Sciences

DOI:
10.1139/cjfas-2016-0153

Published: 01/04/2017

Document Version
Peer reviewed version

Link to publication

Citation for published version (APA):

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Download date: 13. Dec. 2018
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Journal: Canadian Journal of Fisheries and Aquatic Sciences

Manuscript ID: cfas-2016-0153.R1

Manuscript Type: Article

Date Submitted by the Author: 24-Jun-2016

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Keyword: 87Sr/86Sr, ecogeochemistry, Sr isotopes, Liza ordensis, Hephaestus fuliginosus
Temporal and spatial variation in strontium in a tropical river: implications for otolith chemistry analyses of fish migration

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Running head: Riverine strontium and otolith chemistry

Key words: $^{87}$Sr/$^{86}$Sr; Sr isotopes; laser ablation-ICPMS; ecogeochemistry; groundwater; mullet; Liza ordensis; Sooty grunter; Hephaestus fuliginosus
Abstract

Analysis of otolith strontium isotope ratios $^{87}\text{Sr}/^{86}\text{Sr}$ is an increasingly utilised approach for studying fish migration. We analysed surface and groundwater from the Daly River catchment in the wet-dry tropics of Northern Australia over two years. Analyses of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were also conducted for freshwater Sooty grunter ($Hephaestus fuliginosus$) and the putatively diadromous Ord River mullet ($Liza ordensis$). Spatial variation in freshwater $^{87}\text{Sr}/^{86}\text{Sr}$ was high (range: 0.71612-0.78059) and there was strong seasonality in water $^{87}\text{Sr}/^{86}\text{Sr}$, with highest values in the wet season. Temporal variation in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is attributed to seasonal patterns in surface run-off from geological formations with radiogenic compositions versus input from groundwater aquifers interacting with less radiogenic formations. Temporal variation in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios precluded robust inference on movement within freshwater for both species, although movement across salinity gradients by Ord River mullet was clearly identified. We conclude that temporally and spatially replicated water Sr data should be a general requisite for studies that analyse otolith Sr ($^{87}\text{Sr}/^{86}\text{Sr}, \text{Sr/Ca}, \text{Sr/Ba}$) to make inferences about fish movement and migration.
Introduction

Movement and migration by fishes is an important process in many riverine ecosystems, creating ecological connections between spatially distant habitats and functioning as a conduit for the transport of assimilated energy and nutrients across catchments and among terrestrial, freshwater, estuarine and marine ecosystems (Flecker et al. 2010). Although the migrations of riverine fishes are commonly classified into a few broad categories (e.g. anadromy, catadromy, amphidromy, potamodromy), riverine fishes exhibit a wide variety of migration strategies, often with high levels of individual behavioural flexibility (McDowall 1988). Understanding the intricacies of fish migration - and how they influence ecosystem function and productivity - is a key challenge for riverine ecologists, and is fundamental to the effective management and conservation of riverine fish populations (Koehn and Crook 2013).

An increasingly utilised technique for improving our knowledge of fish movement and migration is otolith chemistry analysis. As layers of calcium carbonate accrete on the outer surface of otoliths, dissolved ions from the ambient water are incorporated into the chemical structure, forming a stable chronological record that, at least in part, reflects the ambient water chemistry (Campana 1999). Sr and Ba are the two most commonly used ions for otolith chemistry studies because they are relatively abundant in aquatic environments, are permanently embedded within the otolith crystalline structure via replacement of Ca$^{2+}$, and their concentrations and bioavailability vary among catchments and across salinity gradients (Walther and Limburg 2012; Doubleday et al. 2014). The most common approach in fish migration studies is to measure variations in the concentrations of otolith Sr and/or Ba relative to Ca to identify movements between chemically distinct water bodies (Gillanders 2005). For example, regions of an otolith with relatively low Sr/Ca and high Ba/Ca usually
represent periods of freshwater residence, whilst the reverse pattern occurs during marine
case (McMahon et al. 2013).

Analysis of otolith isotope ratios, particularly $^{87}$Sr/$^{86}$Sr, has also become a common approach
in fish migration studies over recent years. Variations in $^{87}$Sr/$^{86}$Sr are largely due to
accumulation of radiogenic $^{87}$Sr from the slow beta-decay of $^{87}$Rb (half-life 49.6 x 10$^9$ years),
and therefore correlate broadly with the Rb/Sr ratio and/or geological age of the Sr source
(Faure and Mensing 2005). One of the main advantages of $^{87}$Sr/$^{86}$Sr ratios over Sr/Ca and
Ba/Ca is that the $^{87}$Sr/$^{86}$Sr ratios of otoliths directly reflect the source materials, and it is
therefore possible to directly relate water and otolith $^{87}$Sr/$^{86}$Sr (Phillis et al. 2011; Brennan et
al. 2015 a). There are two main approaches for using otolith $^{87}$Sr/$^{86}$Sr to study fish migration.
The first is to trace the movements of fish among locations within freshwater river networks.
This is possible because catchments with different underlying geologies tend to have
distinctive water $^{87}$Sr/$^{86}$Sr ratios, allowing movement between locations to be detected as
variations in otolith $^{87}$Sr/$^{86}$Sr (see Barnett-Johnson et al. 2008; Brennan et al. 2015b). The
second main use of $^{87}$Sr/$^{86}$Sr ratios is to trace the movements of fish across salinity gradients.
Contemporary seawater has a uniform global $^{87}$Sr/$^{86}$Sr ratio of 0.70918 +/- 0.00006
(McArthur and Howarth, 2004), whereas $^{87}$Sr/$^{86}$Sr ratios in fresh water are highly variable
and dependent upon catchment geology. Provided the freshwater system under consideration
has $^{87}$Sr/$^{86}$Sr ratios that are dissimilar to the global marine value, it is possible to use
variations in otolith $^{87}$Sr/$^{86}$Sr ratios to trace movements across salinity gradients (Kennedy et

A key premise of both of these approaches is that freshwater $^{87}$Sr/$^{86}$Sr ratios are temporally
stable within a location, thus allowing variation in otolith $^{87}$Sr/$^{86}$Sr ratios to be interpreted as
movement by fish among locations (Elsdon et al. 2008). A small number of studies conducted
in temperate streams have reported stable and predictable water $^{87}$Sr/$^{86}$Sr ratios over seasonal
and annual time scales (e.g., Ingram and Weber 1999; Kennedy et al. 2000; Brennan et al. 2015a). However, significant temporal variation in \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios within rivers and streams has also been reported in some instances (Bastin and Faure 1970; Crook et al. 2013; Douglas et al. 2013). To date, few otolith chemistry studies have explicitly examined temporal variation in water \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios, despite its potential to confound the interpretation of otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio data (Elsdon et al. 2008; but see Brennan et al. 2015a). There is a clear need for better understanding of the processes that drive temporal and spatial variation in freshwater \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios and to assess the consequences of such variation for inferring fish movement based on otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio analyses (Elsdon et al. 2008; Walther and Thorrold 2009; Brennan et al. 2014).

In this study, we examine temporal and spatial variation in water \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in the Daly River system in the wet-dry tropical region of Northern Australia. We use this information to explore potential implications for the interpretation of otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio data using the freshwater Sooty grunter (Hephaestus fuliginosus) and the putatively diadromous Ord River mullet (Liza ordensis) as case studies. The broader consequences of our findings for the interpretation of otolith chemistry data are discussed with regards to the drivers of temporal variation in surface water \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios, particularly catchment geochemistry and seasonal patterns of surface run-off and groundwater discharge.

**Materials and methods**

**Study site**

The study was conducted in the Daly River catchment in the wet-dry tropical region of the Northern Territory, Australia (Fig. 1). The Daly River is one of the largest rivers in northern Australia, draining an area of 52,500 km\(^2\) and extending 500 km from the headwaters to the estuary mouth, where it discharges into the Timor Sea (mean annual discharge 6900 GL; Jolly 2002). Tidal influence on water levels and flows extends upstream as far as Daly River.
Crossing ~105 km upstream of the estuary mouth, whilst salinity may be affected as far upstream as Woolianna (~90 km upstream of estuary mouth) during the dry season. Rainfall in the region comes primarily from the north-west monsoon, as well as from intense rain depressions that form from decaying tropical cyclones. Rainfall is extremely seasonal, with 95% falling in the wet season between November and May.

Surface water flow in the Daly River main channel (known as the Katherine River upstream of the Flora River junction [Fig.1]) is strongly dominated by wet season events, with dry season flows contributing only a small fraction of total annual flows (King et al. 2015). As water levels fall in the dry season, the river progressively breaks into a series of long pools separated by runs and riffles. Dry season flows are dominated by groundwater discharge and progressively increase downstream as baseflows are added from different sources (Lawrie 2014). Three tributaries of the Daly River (Edith River, Fergusson River, Cullen River) were also sampled in the study (Fig. 1a). The Fergusson River flows in a south-westerly direction and enters the Daly River ~380 km by river upstream of the estuary mouth. The Edith and Cullen rivers enter the Fergusson River 35 km and 60 km upstream of the Fergusson-Daly junction respectively.

For much of its course, the Daly River is underlain by sedimentary carbonate-shale-sandstone sequences of the Cambro-Ordovician Daly Basin (Kruse and Munson, 2013). The stratigraphy of this basin comprises, from oldest to youngest, the Tindall Limestone, the Jinduckin Formation, the Oolloo Dolostone and the Florina Formation (Fig. 1b), with a total thickness of ~1 km. These sequences have been folded into a broad basin structure, elongated in a south-east to north-west direction (Fig. 1b) and are locally overlain by Cretaceous sandstone remnants of the Carpentaria Basin. The Tindall and Oolloo are dominantly limestone and dolomite and host major karstic aquifers which are responsible for the bulk of the baseflow in the Katherine and Daly Rivers (Lawrie 2014). Groundwater discharges into
the rivers where they intersect the aquifers. The Jinduckin and Florina formations are composed of siltstone and sandstone with minor limestone layers and only host minor aquifers. Downstream and upstream of the Daly Basin, the Daly/Katherine River system is underlain by ancient crustal basement of the Neoarchean-Proterozoic Pine Creek Orogen (Ahmad and Hollis, 2013). The Pine Creek Orogen is the oldest exposed part of the North Australian Craton and - in the study area - consists of ca. 1860 Ma clastic, carbonate and carbonaceous metasedimentary and volcanic sequences, intruded by ca.1830 Ma granitic plutons. The largest of these, the >2800 km$^2$ Cullen and ~1000 km$^2$ Grace Creek Granites, are major components in the headwaters of the Cullen and Fergusson River, and the Katherine/Daly River, respectively. Aquifers in some of these rocks provide minor discharge to the rivers. Baseflow to the Edith, Fergusson and Cullen rivers is derived from Cretaceous sandstone higher in the catchments. The rivers flow over a variety of Proterozoic rocks with potentially highly diverse present-day $^{87}$Sr/$^{86}$Sr ratios before reaching the sample sites. The largest and most consistent differences, however, are expected between the (i) highly radiogenic but variable run-off from exposed basement and the (ii) much less radiogenic (buffered by marine Sr in limestone and dolostones) and isotopically less variable run-off and groundwater recharge from the Daly Basin.

**Study species**

The Sooty grunter is a non-diadromous freshwater grunter (Family Terapontidae) distributed across tropical northern Australia from the Daly River eastwards to the Burdekin River in Queensland, as well as southern New Guinea (Pusey et al. 2004). Growing to an adult size of up to 5 kg (more commonly 1 kg), they are a popular angling species and an important food and cultural resource for Indigenous people (Jackson et al. 2012; 2014). Previous studies based on direct observation (Bishop et al. 1995) and mark-recapture (Hogan 1994) have suggested that Sooty grunter may undertake spawning migrations within freshwater.
However, the extent and direction of such movements appears variable among locations and dependent on the availability of inundated floodplains and other habitat features (Pusey et al. 2004). The Ord River mullet (Family Mugilidae) reaches ~2 kg and is a euryhaline species that inhabits marine, estuarine and freshwater habitats across northern Australia. They are not commonly targeted by recreational or commercial fishers, but are utilised as a food resource by Indigenous people (Jackson et al. 2012). There is little empirical information on the movements of Ord River mullet, although it has been suggested that they may be diadromous (Linke et al. 2012).

**Water collection and analysis**

Surface water samples for $^{87}\text{Sr}/^{86}\text{Sr}$ ratio analysis were collected between July 2012 and November 2014 from the Daly River, tributaries (Edith River, Cullen River, Fergusson River) and across the salinity gradient of the estuary during the ‘dry’ and ‘wet’ seasons (defined over the study years as June - November and December - April respectively) (Fig. 1). In the freshwater reaches of the main channel and tributaries, up to six temporal replicate samples were collected per site (Table 1). Sampling of surface water across the estuarine salinity gradient was conducted in November 2013 (dry season) and March 2013 (wet season). Groundwater samples from the Oolloo aquifer were obtained in November 2014 from four locations by pumping water from established boreholes maintained by the Northern Territory Department of Land Resource Management.

The salinity of each water sample was measured in the field using a Quanta® water quality meter (Hydrolab Corporation, Loveland, Colorado). This unit has a reported accuracy of +/- 1% and precision of 0.01‰. Most samples were filtered in the field (a few were filtered in the laboratory in Melbourne) using 0.2µm Acrodisc® syringe filters (Pall Corporation, Ann Arbour, USA), stored in acid-washed 50 ml polyethylene bottles, refrigerated at 4°C and transferred to the University of Melbourne for analysis. Based on preliminary estimates of Sr
concentrations (from electrical conductivity data), volumes of 1-40 ml of water were weighed into clean polystyrene beakers, equilibrated with an appropriate amount of high-purity $^{84}$Sr isotopic ‘spike’ ($^{84}$Sr/$^{86}$Sr in the spike is 1530) and dried in a HEPA-filtered fume cupboard. Spiked Sr was extracted using a single pass over 0.15 ml (4 x 12 mm) beds of Eichrom® Sr resin (50-100 µm). Following Pin et al. (1994), matrix elements were washed off the resin with 2M and 7M nitric acid, allowing collection of a clean Sr fraction in 0.05M nitric acid. Sr yields through the column exceed 90% and column blanks are <50 pg Sr. The Sr blank contributed by filtering was simulated in the laboratory using distilled water and found to be 100 pg Sr or less. Based on the signals obtained in the ICP-MS, at least 110 ng of Sr were present in each sample split (usually >400 ng), implying sample to blank ratios of 1100 or higher; blank corrections were therefore insignificant.

Sr isotope analyses were carried out on a Nu Plasma multi-collector ICPMS (Nu Instruments®, Wrexham, UK), with sample introduction in 2% nitric acid via a Glass Expansion® PFA nebuliser (0.05 ml/min uptake) and a first generation Cetac® ARIDUS desolvator (see Maas et al. 2005). Instrumental mass bias was corrected by normalizing to $^{88}$Sr/$^{86}$Sr = 8.37521 and results are reported relative to a value of 0.71023 for the SRM987 Sr isotope standard. Within-run, or internal, precision (2 standard error [SE]) based on at least 30 ten-second integrations is typically better than ±0.00003. The reproducibility, or external precision (2 standard deviation [SD]), of the results is ± 0.00004. This is supported by a triplicate analysis of sample DR-W-071112 which yielded 0.71826, 0.71826 and 0.71825. $^{87}$Sr/$^{86}$Sr ratios in seven analyses of modern seawater Sr (extracted from a live Enewetak Atoll coral, EN-1) ranged from 0.70913 to 0.70917 (average 0.70916±0.00003, 2sd, n=7), consistent with the accepted ratio of 0.70916 (adjusted to SRM987 = 0.71023, McArthur and Howarth 2004).
Sr concentrations obtained by isotope dilution have a high inherent precision (1%) but may only be minimum estimates if Sr contents in the non-acidified water were unstable between collection and analysis. This effect was minimised by low-temperature storage and rapid transfer to the Sr isotope laboratory. A repeat analysis of one sample after mild acidification in the laboratory (to 0.03M nitric acid) did not increase the actual dissolved Sr concentration. The listed concentrations are thus considered to be very close to, or identical with, actual Sr concentrations.

Mixing models of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios (see Phillis *et al.* 2011) over the salinity gradient were calculated for the Daly River in the 2012 dry season and 2013 wet season. End-members used in the models were the least saline freshwater sample from the Daly River main channel in each season (Table 1) and a coastal marine water sample (salinity: 35.8‰, \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio: 0.71918, Sr: 3.6 mg/L) collected on 11th August 2010 at the Adelaide River mouth, approx. 130 km to the east of the Daly River mouth.

Sampling of river water for total Sr (mg/L), denoted [Sr] hereafter, was also conducted at a single site (Banyan Farm; Fig. 1) at approximately weekly intervals (n=43) between 7 November 2013 and 25 November 2014. Samples were kept frozen prior to [Sr] analysis. The samples for analysis were acidified with concentrated HNO\(_3\) and then placed in an oven overnight at 60°C. A scan of elemental composition (APHA 2005, method 3125 B), including [Sr], was conducted on an Agilent 7500 series ICPMS operated by Charles Darwin University. The level of detection for [Sr] was 0.1 µg/L (ppb) and results are accurate to within 10%.

**Fish collection**

Sooty grunter were collected by hook and line fishing between July 2013 and April 2014 from the Daly River (n=5; 204-270 mm standard length [SL], 338-511 g), Edith River (n = 10; 265-385 mm SL, 327-1146 g) and Fergusson River (n = 21; 160-328 mm SL, 138-760 g).
Ord River mullet (n=36; 175-395 mm SL, 106-1768 g) were collected by boat electrofishing from the main channel of the Daly River in June and July 2012. Upon capture, fish were immediately euthanised by overdose in Aqui-S (175 mg L\(^{-1}\)) and measured (SL, +/- 1 mm) and weighed (+/- 1 g). The sagittal otoliths were removed in the field and placed into labelled paper envelopes for storage prior to preparation for analysis.

**Otolith preparation and Sr isotope analysis**

Otoliths were embedded in two-part epoxy resin (EpoFix\(^\circledR\), Struers, Denmark) and transversely sectioned to a thickness of ~300 µm through the primordium using a slow speed saw. The sections were polished using lapping film (9 µm), rinsed with deionised water, air dried and mounted on glass slides using epoxy resin. Laser ablation-ICPMS was used to measure Sr isotope ratios (\(^{87}\)Sr/\(^{86}\)Sr) in the otoliths, following the methods outlined in Woodhead et al. (2005). The analytical system consisted of the MC-ICPMS system described above, coupled to a HelEx laser ablation system (Laurin Technic, Canberra, Australia, and the Australian National University) constructed around a Compex 110 excimer laser (Lambda Physik, Gottingen, Germany) operating at a wavelength of 193 nm.

Otolith mounts were placed in the sample cell and the ablation path for each sample was digitally plotted using GeoStar v6.14 software (Resonetics, USA) and a 400× objective coupled to a video imaging system. Ablation transects were run from the otolith core to the proximal edge using a 70 µm laser spot and fluence of ~3 J/cm\(^2\). A pre-ablation was conducted prior to the analysis run to remove any surface contaminants with the laser pulsed at 10 Hz and scanned at 20 µm/sec. The analysis run was then conducted with the laser pulsed at 6 Hz and scanned at 5 µm/sec. Ablation was performed under pure He atmosphere to minimise the re-deposition of ablated material, and the sample was then rapidly entrained into the Ar carrier gas flow. Corrections for Kr and \(^{87}\)Rb interferences were made following Woodhead et al. (2005) and mass bias was corrected by reference to an \(^{86}\)Sr/\(^{88}\)Sr ratio of
0.11940. The data were processed using Iolite Version 2.13 (see Paton et al. 2011) that
operates within IGOR Pro Version 6.2.2.2 (WaveMetrics, Inc., Oregon) with corrections for
potential Ca argide/dimer and Rb interferences and instrumental mass bias. All results were
normalised to an $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of 0.70916 for a modern marine carbonate standard
run concurrently and known from solution ICPMS analyses to have a modern seawater
composition (MacArthur and Howarth 2004). Individual integrations on the mass
spectrometer represent 0.2 second time slices. During data processing a one-second moving
average was employed to smooth the data. The ranges of water $^{86}\text{Sr}/^{86}\text{Sr}$ ratios recorded for
each river (Daly main channel, Edith, Cullen and Fergusson) were overlaid upon the otolith
$^{86}\text{Sr}/^{86}\text{Sr}$ ratio transects of each fish to allow visual assessment of otolith $^{86}\text{Sr}/^{86}\text{Sr}$ ratio
variation in the context of the surrounding environment. A representative selection of the
transect data is presented in the Results and the entire dataset is attached as supplementary
material (S1, S2). Annual growth increment formation in the otoliths of Sooty grunter and
Ord River mullet has not been validated, so it was not possible to directly relate otolith
$^{86}\text{Sr}/^{86}\text{Sr}$ ratios to the age of the fish in the current study.

Results

Water chemistry - freshwater

All water samples collected from freshwater had higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than seawater (Table
1), reflecting the old (Proterozoic-Cambrian) bedrock underlying the catchment. $^{87}\text{Sr}/^{86}\text{Sr}$
ratios in the Edith, Fergusson and Cullen rivers (range: 0.72904-0.78059), in particular, were
very high compared to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio global average runoff value of 0.7119 (Palmer and
Edmond 1989). Sites on the main channel of the Daly-Katherine River (range: 0.71612-
0.74390) had generally lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the three tributaries (Fig. 2). Both the
maximum and minimum $^{87}\text{Sr}/^{86}\text{Sr}$ ratio surface water values for all main channel samples
(i.e., 0.71612 and 0.74390) were recorded at the same site (Galloping Jacks). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
in groundwater from the Ooloo aquifer (bore samples) were lower (range: 0.71514-0.72090) than surface water in the tributaries, but similar to $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios in main channel water during the dry season (Table 1).

Strong seasonal variation in surface water $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios was observed in the main channel, with no overlap between dry season (range 0.71612-0.72065) and wet season (range: 0.72489-0.74390) values across sites and seasons (Fig. 2; Fig. 3). Isotopic variation among sites within the main channel was relatively low in the 2012 dry season (mean: 0.71887, standard deviation [SD]: ± 0.0011), 2012/13 wet season (0.73078 ± 0.0008) and the 2013 dry season (0.71853 ± 0.0011), but there was more variability among main channel sites in the 2013/14 wet season (0.73256 ± 0.0082).

The Edith River showed extreme seasonal variation, from dry season ratios of 0.72904-0.74855 to much higher wet season ratios of 0.7668-0.7805. By contrast, no consistent inter-seasonal variations were observed in the Cullen River (dry: 0.74968-0.75022, wet: 0.74888-0.75133) and at Fergusson River site FR1 (dry: 0.77297-0.77793, wet: 0.77090-0.77618, Fig. 2). However, a single sample taken in July 2013 from location FR2 on the Fergusson River had a much lower $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio (0.7554) than water samples from FR1, indicating strong spatial variation within this tributary.

Weekly water sampling at Banyan Farm revealed strong temporal variation in [Sr], with Sr concentrations decreasing during high flows in the wet season and increasing during low flow periods (Fig. 4). There is a strong negative correlation between natural log-transformed river discharge (cumecs) and [Sr] (Pearson product-moment correlation coefficient = -0.926, P<0.01). [Sr] also varied strongly between sampling occasions at the other sites (Table 1), but relationships between $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios and [Sr] differed among sites. There was a negative correlation in the main channel sites (Pearson coefficient = -0.852, P<0.01), whereas $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios and [Sr] were positively correlated in the Edith River (Pearson coefficient = 0.934,
There were no significant correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and [Sr] in the Fergusson River (Pearson coefficient = 0.587, P>0.05) or the Cullen River (Pearson coefficient = -0.226, P>0.05), although sample sizes were low at these sites.

**Water chemistry - estuarine**

As expected, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decreased substantially, and [Sr] increased, in the estuarine section of the Daly River, due to mixing between seawater and fresh water with contrasting $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and [Sr] characteristics (Table 1, Fig. 5). Modelled $^{87}\text{Sr}/^{86}\text{Sr}$ ratios showed very little change between salinity 36‰ (0.70918) and 5‰ (0.71066), but rose sharply below 5‰ (Fig. 5). Empirical $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values measured at intermediate salinities within the estuary generally aligned closely with predicted values, although a single sample of salinity 0.3‰ collected during the wet season in March 2013 had considerably lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than predicted. Linear regression analysis including all of the estuarine samples demonstrated a strong positive relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the reciprocal of [Sr] ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio = 0.0003[1/Sr] + 0.7091, $r^2 = 0.93$). The variance explained by the regression model was even higher when the outlying March 2013 (wet season) sample was removed ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.0003[1/Sr] + 0.7093, $r^2 = 0.99$). These results support the mixing models’ inherent assumption of conservative mixing between seawater and Daly River freshwater endmembers, although the existence of an outlying value may indicate inputs of freshwater from additional sources into the estuary (i.e., downstream tributaries, run-off from inundated floodplains, groundwater inflow) at particular times and/or locations. Longitudinal patterns of $^{87}\text{Sr}/^{86}\text{Sr}$ in the estuary differed markedly between seasons, with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recorded closer to the estuary mouth in the wet season than the dry season. This reflects the greater input of freshwater into the estuary during the wet season.

**Otolith chemistry**

*Within freshwater - Sooty grunter*
The otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratio transects for Sooty grunter were highly variable both among sites and individuals within sites (Fig. 6; S1). Most transects showed evidence of semi-regular variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting that seasonal variation in water chemistry may have contributed to the observed variation in otolith $^{87}\text{Sr}/^{86}\text{Sr}$. However, the amplitude of these variations was variable even among individuals within the same site (e.g., Fig. 7b versus 7d). The otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratio transects of five fish were fully contained within the range of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured at their collection site (Fig. 7a, b, d, f, h). However, regions of the otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratio transects of the remaining fish were outside the range of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at their collection site, suggesting that movement to other regions may have occurred. In several cases, otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from fish collected in the Fergusson River (site F2) greatly exceeded any water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recorded during the study (Fig. 7i; S1). Presumably, these fish had travelled to more radiogenic regions of the Fergusson River catchment than the collection site during their lives. The strong differences in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between the two water sampling sites on the Fergusson River demonstrate the potential for high spatial variability in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within tributaries of the Daly River, and this variability appears to be reflected in the otoliths of Sooty grunter.

**Across the salinity gradient - Ord River mullet**

Transect analyses of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios confirmed the suggested diadromous life history of Ord River mullet. All 40 individuals analysed had near-core otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to the marine value of 0.70916, reflecting residence in estuarine or marine water during the early life history, followed by a transition into freshwater (see examples in Fig. 7, S2). The subtle response of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to estuarine mixing above 5‰ salinity (Fig. 6) does not allow a definitive discrimination between a predominant residence in seawater or within the estuary during the early life history. After transition to freshwater, otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios varied considerably in a similar manner to Sooty grunter. Semi-regular cycling in $^{87}\text{Sr}/^{86}\text{Sr}$
ratios was apparent in most individuals and appears likely to be driven by annual variation in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within the main channel of the Daly River (where the fish were collected). However, three fish had $^{87}\text{Sr}/^{86}\text{Sr}$ ratios marginally outside the range of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recorded in the main channel, possibly suggesting that they may have undertaken forays into tributaries (Fig. 8b, e) or the estuary (Fig. 8f). Alternatively, this may suggest that our water sampling did not capture the full range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that occurred within the main channel over the lifetimes of these fish.

Discussion

The results of this study demonstrate substantial temporal variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within sites on the Daly-Katherine River and associated tributaries. This finding has important implications for the interpretation of otolith chemistry data, as it demonstrates that variation in otolith core-to-edge $^{87}\text{Sr}/^{86}\text{Sr}$ ratio profiles may be concurrently influenced by within-site variation in water chemistry and fish movement among chemically distinct habitats.

Variability of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

There was strong spatial variation in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among the surface water sampling sites on each sampling occasion. However, considerable overlap among sites occurred across seasons, which was primarily due to the high temporal variability in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within the Edith River and the main channel of the Daly-Katherine River (particularly at the Galloping Jacks site). Water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Cullen and Fergusson rivers were relatively stable over time and did not overlap. With the exception of a single dry season sample from the Edith River, there was no overlap between the tributaries and the main channel of the Daly-Katherine River.

Changes in the relative inputs of surface run-off versus groundwater inflow across seasons (wet versus dry) appear to be the primary driver of the observed temporal variation in riverine
$^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Groundwater and surface runoff Sr concentrations and isotopic ratios are determined by the age and composition of rock and soil with which they have had contact (Clark and Fritz, 1997). Since $^{87}\text{Sr}$ is the product of radioactive decay of its parent isotope $^{87}\text{Rb}$, old rocks with high Rb content will tend to have more radiogenic (i.e. higher $^{87}\text{Sr}/^{86}\text{Sr}$) Sr isotope ratios. The geology of the headwater regions of the Daly River (i.e., outside the Daly Basin) consists of Proterozoic sedimentary rocks, granite and volcanics, with areas of Cretaceous sandstone (Fig 1b; Tickell 2011). These rocks impart a highly radiogenic signature on surface runoff and groundwater in the region, which accounts for the relative high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the tributaries. During the wet season, the radiogenic surface runoff enters the Daly River main channel via tributaries, resulting in elevated riverine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In the dry season, surface runoff into the main channel is negligible and discharge into the river becomes dominated by groundwater, primarily from the Tindall and Ooloo aquifers (Lawrie 2015). As the Tindall and Ooloo formations are mainly comprised of limestones and other marine calcareous rocks, with low Rb content, they impart a less radiogenic signature on the groundwater, resulting in lowered riverine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios during the dry season. This seasonal variation in the relative proportion of discharge into the main channel from groundwater and surface runoff thereby creates an oscillating pattern in riverine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with annual periodicity.

A further source of complexity in $^{87}\text{Sr}/^{86}\text{Sr}$ dynamics in the Daly River catchment is spatial variation in groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Although strong variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among aquifers with different geochemical characteristics is common (Frost and Toner 2004), considerable variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios has also been shown to occur within aquifers. Indeed, analysis of small-scale spatial variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of groundwater is an increasingly utilised approach for tracing sub-surface flow pathways within aquifers (e.g., Brenot et al. 2008). In a study of the Ooloo aquifer, Tickell (2011) described three distinct
regions based on sampling of groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and other chemical properties. The first region, located close to the Daly River in the lower catchment, had groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~0.706. In the second groundwater domain, located more distal to the Daly River channel, water $^{87}\text{Sr}/^{86}\text{Sr}$ was higher (~0.715), indicating water-rock interactions with more siliceous sediments, such as the overlying Cretaceous aquifer. Groundwater in the third region near Oolloo Crossing was more radiogenic (~0.718-0.725) than the first two groups, reflecting upward leakage from the underlying Jinduckin Formation. This was the region from which groundwater samples were taken in the current study. These observations, along with those of the current study, demonstrate the spatial complexity of surface and groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within the Daly River catchment. Whilst our water sampling was conducted over a very large spatial extent, representation of the catchment remained incomplete and otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios outside of the range of sampled water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were recorded. This emphasises the need for temporally replicated sampling across all potential habitats utilised by the fish under investigation to characterise catchment-scale $^{87}\text{Sr}/^{86}\text{Sr}$ dynamics.

**Interpretation of otolith chemistry data**

Strong seasonal and spatial variation in fresh water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and [Sr] has the potential to affect the utility of otolith chemistry data for making inferences about fish movement and migration (see Elsdon et al. 2008). In the current study, overlap in water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between the Edith and Fergusson rivers over space and time made it impossible to confidently distinguish between fish movement among tributaries and temporal variation in water chemistry based on otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratio transects. In a minority of cases, the magnitude of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variation was strongly suggestive of large-scale movement between tributaries and the main channel. For example, significant portions of the transects of two fish collected from the Fergusson River (Fig 7e, g) reflected the chemistry of
the main channel of the Daly River, with values resembling the Fergusson River occurring
only immediately prior to capture (i.e. near the otolith margin). However, the relative
influences of temporal and spatial variation in water \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios could not be
differentiated in most cases, even where large (>0.010) variations in otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios
were observed, thus limiting our ability to make detailed inferences on fish movement within
fresh water based on the otolith chemistry data.

This finding raises significant issues for the interpretation of otolith chemistry data generally,
as many previous otolith chemistry studies do not report on water chemistry or contain only
very limited spatial and temporal replication (see Elsdon et al. 2008). For example, Walther
et al. (2011) used otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios and Sr/Ba ratio transect data without supporting
water chemistry data to make inferences about the movements of barramundi \textit{Lates calcarifer}
in northern Australia (coincidentally including the Oolloo Crossing site on the Daly River).
Walther et al. (2011) observed strong variation in otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios and Sr/Ba along
core-to-edge profiles of barramundi and applied a global zoning algorithm to divide otolith
profiles into relatively homogenous zones separated by distinct ‘zone breaks’. These were
then used to infer movement by barramundi among chemically distinct ‘habitats’ over the life
history.

Re-examination of the data of Walther et al. (2011) in the context of the water \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio
data presented here provides an informative perspective on this approach to interpreting
otolith \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio data (Fig. 8). Similar to our results for the diadromous Ord River mullet,
Walther et al. (2011) effectively identified the transition from saline to fresh water in
barramundi from the Daly River, with a zone break corresponding to the transition from
estuarine/marine to fresh water \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios occurring for all fish during the early life
history (Fig. 8). This finding agrees well with current understanding of barramundi life
history (Russell and Garrett 1985; McCulloch et al. 2005). Walther et al. (2011) also
identified at least one zone break in the freshwater phase of all six Daly River barramundi
examined, with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among most ‘habitats’ differing by ~0.003-0.010 (Fig. 8).

Only one of the seven zone breaks identified in the fresh water phases of the otolith profiles exceeded 0.010 (~0.045, Fig. 8f).

There appears little doubt that fish movement explains at least some of the observed variation in otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fish in the Daly River in the current study and the study of Walther et al. (2011). This is particularly the case for the very large shifts observed in otolith $^{87}\text{Sr}/^{86}\text{Sr}$ profiles of some fish. However, our analysis shows that variations in otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the magnitude used by Walther et al. (2011) to statistically derive zone breaks in the freshwater phase of barramundi would be expected to occur as a result of seasonal variation in water chemistry, even if the fish had remained entirely stationary. Water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were >0.010 higher in the wet season than the dry season along the length of the Daly-Katherine River (Fig. 3) and individual sampling sites varied by up to 0.028 among seasons (Table 1). Based on these observations, we conclude that the application of global zoning algorithms and similar statistical techniques to derive estimates of fish movement should be treated cautiously unless there is complimentary information on the temporal variability of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to support their validity. The strong seasonal variation in [Sr] (Fig. 4) suggests that similar concerns may also apply for the interpretation of trace element ratios (e.g. Sr/Ca, Sr/Ba).

Unless the potentially confounding effects of temporal variability in water chemistry can be discounted based on empirical evidence, our findings suggest that robust inference regarding fish movement requires an understanding of the association between sampled otolith material and the water chemistry of the study system at the time the material was deposited. In systems with seasonally oscillating water chemistry, this could potentially be achieved by careful alignment of otolith chemistry profiles against validated annual increments with
known deposition times (not available in the current study). Seasonal otolith chemistry data derived this way could then be examined with regards to spatial patterns of water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios across the study system within seasons. Bataille et al. (2014) provide an example of the approaches available for modelling riverine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the catchment scale. However, even in situations with highly predictable seasonality in water chemistry, disentangling the influence of temporal water chemistry variation versus fish movement is a complex task requiring detailed consideration of the spatio-temporal dynamics of the study system, as well as otolith crystallisation rates and the otolith sampling methodology itself (e.g., laser spot sizes and the growth period integrated within each measurement). To date, such detailed linking of otolith chemistry to ambient environmental conditions has seldom been attempted at large spatial scales (but see Brennan et al. 2015b).

When considering the generality of our findings, it should be recognised that fresh water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Daly River catchment are high (up to 0.7806) compared with the global mean of 0.7119 (Palmer and Edmund 1989). The seasonality of rainfall in northern Australia’s wet-dry tropics is also much more extreme than temperate areas. Nonetheless, the Daly River example serves to amplify the effects of an issue that is likely to apply to the majority of rivers, lakes, wetlands and estuaries that experience temporal variation in the relative importance of surface run-off versus groundwater input (Sophocleous 2002). Thus, while temporal variation may be more subtle in systems with lower water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and less extreme seasonal variability in rainfall, the implications of our findings have broad significance for the interpretation of otolith chemistry data. Based on our observations, we conclude that presentation of temporally and spatially replicated water Sr data should be a general requisite for studies that use analyses of otolith Sr ($^{87}\text{Sr}/^{86}\text{Sr}$, Sr/Ca, Sr/Ba ratios) to make inferences about fish movement and migration.

Acknowledgments
We gratefully acknowledge the traditional custodians of the lands upon which this study was conducted, the Wagiman, Jawoyn and Malak Malak people, and thank them for providing access to their land. We thank Lizzie Sullivan (Wagiman traditional owner) and Troy Baruwei, Janet Ellis, Ryan Barrowei, Traven Shields, Mike Alengale, Lee Jambalily (Jawoyn Ranger Program) for their assistance with fish and water collection. We thank Ben Lewis and the Jawoyn Association for organising the consultation with traditional owners. Quentin Allsop, Wayne Baldwin and Jonathon Taylor of the Department of Primary Industries and Fisheries are also thanked for assistance with fish collection and otolith preparation. Roger Farrow conducted the pumping of bore water samples and Julia Schult and Matt Majid took Sr water samples at Banyan Farm for the Department of Land Resource Management. Damien McMaster assisted with production of the map. Funding for this work was provided by the Australian Government’s National Environmental Research Program (Northern Australia Hub). This research was conducted under Charles Darwin University Animal Ethics Committee permit A12023.

References


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Table 1: Water chemistry of samples collected from the main channel of the Daly-Katherine River, tributaries of the main channel and the Oolloo aquifer during the study. Site codes for map in Fig. 1 are shown in brackets. “na” = data not available.

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<th>Main channel</th>
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<th>EC (ms/cm)</th>
<th>Sal (‰)</th>
<th>Sr (mg/L)</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr})</th>
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Figure legends

Figure 1: (a) Map of study region showing sampling sites (open circles) and bore water sampling sites (red circles). Site codes: Galloping Jacks (GJ), Cullen River (CR), Fergusson River (FR1, FR2), Edith River (ER), Claravale Crossing (CC), Oolloo Crossing (OC), Daly Crossing (DC), Woolianna (WO), Banyan Farm (BF), estuary sites 1-6 (E1, E6; sites E2-E5 not labelled for clarity). (b) Block diagram showing Daly Basin and underlying structure of major aquifers. Florina Formation (green), Oolloo Dolostone (light blue), Junduckin Formation (pink), Tindall Limestone (aquamarine). Australia’s coastline data was obtained from Geoscience Australia (Geoscience Australia, 2004). Surface hydrology and catchment boundary data was supplied by the Department of Land Resource Management, Copyright - Northern Territory of Australia.

Figure 2: Seasonal (dry versus wet) variation in surface freshwater $^{87}\text{Sr}/^{86}\text{Sr}$ in the main channel of the Daly/Katherine River and three major tributaries. For clarity, values within season are offset and lines are drawn between the seasonal medians or single values for each site. Details of the samples are presented in Table 1. Site “FR2” which was only sampled on one occasion is not included.

Figure 3: Longitudinal profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ along the main channel of the Daly-Katherine River from the most upstream site (Galloping Jacks) to the estuary mouth in the dry season 2012 and the wet season 2013.

Figure 4: Total Sr (black symbols) versus daily river discharge (unbroken line). Water samples were collected approximately weekly from Banyan Farm on the Daly River main channel between November 2013 and November 2014.

Figure 5: Mixing models (lines) of water $^{87}\text{Sr}/^{86}\text{Sr}$ across salinity gradient in the Daly River in the dry season of 2012 (a) and the wet season of 2012/13 (b). Symbols represent empirical...
samples collected from intermediate salinities within the estuary in November 2012 and March 2013 (Table 1).

**Figure 6:** Core-to-edge transects of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ in Sooty grunter collected from the Daly River (a-d), Edith River (e-g) and Fergusson River (h-l). The dashed line labelled “SW” represents seawater $^{87}\text{Sr}/^{86}\text{Sr}$; shaded areas show the ranges of water $^{87}\text{Sr}/^{86}\text{Sr}$ recorded at each of the regular water sampling sites (Daly River main channel = “MC”, Edith River = “ER”, Cullen River = “CR”, Fergusson River = “FR1”); the unbroken straight line represents the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the single sample taken from a second site within the Fergusson River (“FR2”).

**Figure 7:** Core-to-edge transects of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ in Ord River mullet collected from the Daly River main channel. The dashed line labelled “SW” represents seawater $^{87}\text{Sr}/^{86}\text{Sr}$; shaded areas show the ranges of water $^{87}\text{Sr}/^{86}\text{Sr}$ recorded at each of the regular water sampling sites (Daly River main channel = “MC”, Edith River = “ER”, Cullen River = “CR”, Fergusson River = “FR1”); the unbroken straight line represents the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the single sample taken from a second site within the Fergusson River (“FR2”).

**Figure 8:** Core-to-edge $^{87}\text{Sr}/^{86}\text{Sr}$ otolith data from barramundi collected at Oolloo Crossing (redrawn from Walther *et al.* 2011, Figure S1) overlaid on water chemistry data collected in the current study. Black lines show the otolith $^{87}\text{Sr}/^{86}\text{Sr}$ transect data and grey lines show modelled habitat occupation and shifts using a global zoning algorithm (Walther *et al.* 2011). The dashed line labelled “SW” represents seawater $^{87}\text{Sr}/^{86}\text{Sr}$; shaded areas show the ranges of water $^{87}\text{Sr}/^{86}\text{Sr}$ recorded at each of the regular water sampling sites (Daly River main channel = “MC”, Edith River = “ER”, Cullen River = “CR”, Fergusson River = “FR1”); the unbroken straight line represents the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the single sample taken from a second site within the Fergusson River (“FR2”).
Figure 1
Figure 2

- Main channel
- Cullen
- Edith
- Fergusson

Season
- Dry 2012
- Wet 2013
- Dry 2013
- Wet 2014

$\frac{^{87}Sr}{^{86}Sr}$
Figure 3

Dry 2012
Wet 2013
Figure 4
Figure 5

(a) Dry 2012

(b) Wet 2013
Figure 6

(a) Daly

(b) Daly

(c) Daly

(d) Daly

(e) Edith

(f) Edith

(g) Edith

(h) Fergusson

(i) Fergusson

(j) Fergusson

(k) Fergusson

(l) Fergusson

$\frac{\text{Sr}}{\text{Sr}}$

Distance from core (µm)
Figure 7

(a) 
(b) 
(c) 
(d) 
(e) 
(f) 

Distance from core (µm)

0.70
0.71
0.72
0.73
0.74
0.75
0.76
0.77
0.78
0.79

0 200 400 600 800 1000 1200

87Sr / 86Sr
Figure S1: Core-to-edge transects of otolith $^{87}$Sr/$^{86}$Sr in Sooty grunter collected from the Daly River, Edith River and Fergusson River.
**Figure S1 (cont):** Core-to-edge transects of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ in Sooty grunter collected from the Daly River, Edith River and Fergusson River.
Figure S1 (cont): Core-to-edge transects of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ in Sooty grunter collected from the Daly River, Edith River and Fergusson River.
Figure S2: Core-to-edge transects of otolith $^{87}\text{Sr}/^{86}\text{Sr}$ in Ord River Mullet collected from the Daly River.
Figure S2 (cont): Core-to-edge transects of otolith $^{87}$Sr/$^{86}$Sr in Ord River Mullet collected from the Daly River.
Figure S2 (cont): Core-to-edge transects of otolith $^{87}$Sr/$^{86}$Sr in Ord River Mullet collected from the Daly River.