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Otolith Sr/Ca ratio complements Sr isotopes to reveal fish migration in large basins with heterogeneous geochemical landscapes

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Abstract The potential use of Sr/Ca and Ba/Ca ratios in fish otolith, as a complement to $^{87}Sr/^{86}Sr$ to study movements of *Prochilodus lineatus,* was evaluated in the La Plata Basin (South America). Water ratios were obtained from samples collected during the high and low water seasons at 42 sites across the La Plata Basin.

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Elemental and isotopic ratios in water were measured by MC-ICP-MS, ICP-MS and ion chromatography, and obtained from available literature. Fish were caught from six different sites with different physiochemical features. Otolith core-to-edge Sr/Ca and Ba/Ca profiles were determined by LA-ICP-MS, while the otolith $^{87}Sr/^{86}Sr$ data set was taken from literature. The predictive classification by rivers according to water Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ ratios (92.5%) was higher than that based solely on $^{87}Sr/^{86}Sr$ (58%), with classification that reached 100% for several rivers. Unlike Ba/Ca, a significant relationship ($R^2 = 0.94$, $p < 0.05$) was found between otolith edge and water Sr/Ca, suggesting that this could be an efficient movement indicator for *P. lineatus*. The Sr/Ca ratio complemented the information provided by Sr isotopes and it was particularly useful in the northwest basin, where the isotopes alone do not allow differentiating between large rivers.

Keywords Calcified structure · Freshwater fish · Geomarkers · Migration indicators · Natural tag

Introduction

Several fish species are known to perform freshwater migrations, including movements between different sub-basins or between different environments in a given basin, such as channels and floodplains (Duponchelle et al. 2016). Knowledge of fish migration patterns enables effective conservation and management strategies to be designed and implemented. Over the last decades, the use of natural markers, such as isotope and trace element signatures in fish otoliths, have been used to reconstruct the life history of many migratory fish (Duponchelle et al. 2016; Avigliano et al. 2020; Hauser et al. 2020). Otoliths are calcified structures located in the inner ear of teleost fish, composed mainly of aragonite (calcium carbonate, ~96%) deposited in an acellular matrix of a fibrous protein called otoline (Campana 1999). As the otolith grows continuously and is metabolically stable, elements deposited at its surface are permanently retained in the calcified structure and not reabsorbed into the animal body. Therefore, several chemical components (e.g., Li, Ba, Mn, Mg, Sr, etc.) registered in otoliths form a detailed chronological record of the environment to which the fish was exposed (Campana 1999; Hüssy et al. 2020). Nevertheless, some elements (e.g., Mn, Se, Zn, etc.) show a complex network of endogenous and exogenous factors that control uptake and incorporation (Sturrock et al. 2015; Thomas and Swearer 2019), hindering its use as a habitat indicator throughout ontogeny (Hermann et al. 2016; Maichak de Carvalho et al. 2020). For this reason, the correct choice of geomarkers and knowledge about the drivers that regulate their incorporation into the otolith is essential to study displacements throughout ontogeny. In marine environments characterized by gradients in temperature and primary production, oxygen and carbon isotopes were proved to be effective in tracing fish movements (Rooker et al. 2014). In estuarine environments with salinity gradients, the most commonly used natural tags in fish otolith are the Sr/Ca and Ba/Ca ratios, which have been shown to be positively and negatively related, respectively, to the salinity for several species (Brown and Severin 2009; Tabouret et al. 2010; Smith and Kwak 2014). In freshwater systems with sub-basins that are geologically heterogeneous, strontium isotope ratios ($^{87}Sr/^{86}Sr$) have allowed tracking the migratory patterns of fish species (e.g., in the neotropical area: Pouilly et al. 2014; Hegg et al. 2015; Duponchelle et al. 2016; Avigliano et al. 2020).

The streaked prochilod *Prochilodus lineatus* (Valenciennes, 1837), a detritivorous and migratory fish which covers distances of more than 1500 km in its lifetime (Sverlij et al. 1993), is one of the most important freshwater fisheries of the La Plata Basin. In relation to extractive fishing, some countries such as Argentina have captured more than 36,000 t/year of this fish (Espinach and Sánchez 2004; MINAGRI 2019). It is thus critical to track the migration of this fish within the La Plata Basin. Recently, the comparison of Sr isotope composition in water and otolith helped reveal fish displacements among sub-basins in the La Plata Basin (Avigliano et al. 2020). Nevertheless, the Sr isotope signature of the water proved to be similar between several large sub-regions of the basin, mainly in the northwest area (Gran Chaco and Andean regions) (Avigliano et al. 2020). Gran Chaco and Andean rivers form a vast and isotopically homogeneous area covering an area of 400,000 km^2 including the lower section of the Paraguay River and two large Andean sub-basins: Pilcomayo and Bermejo rivers. Such similarity imparts significant spatial limitation of Sr isotopes for studying the migration of fish, in particular *P. lineatus* (Avigliano et al. 2020).

A complement to employing otolith Sr isotope ratios for reconstructing fish migration patterns is the use of elemental chemical ratios. This is true, in particular for element ratios that (1) are likely to be only poorly fractionated during incorporation in the otolith and (2) vary across different freshwater environments in the region of study. The X/Ca ratios are most likely the best candidates to fulfill the condition 1. Calcium is the major cation of calcium carbonate material, and X can be chosen to be an element with a geochemical behavior close to that of Ca and that can substitute it in a calcified structure (elements commonly present as a divalent cation in water such as magnesium (Mg^{2+}), strontium (Sr^{2+}), barium (Ba^{2+}), Thomas and Swearer 2019). Regarding condition 2, we note that the distribution of Sr and Ba concentration in freshwater environments of the La Plata Basin has been reported to be heterogeneous and related to electrical conductivity (EC: 23–5508 μS/cm, Sr concentration: 32–886 μg/L and Ba concentration: 11–127 μg/L), especially in the northwest (Avigliano et al. 2019b). This observation suggests that otolith Sr/Ca and Ba/Ca ratios could be a powerful complement to $^{87}Sr/^{86}Sr$ for studying fish displacements. Avigliano et al. (2017b) have already suggested that otolith Sr/Ca ratios could be useful as a salinity indicator in studying *P. lineatus* displacements between freshwater and the estuary. However, the recent description of high levels of salinity and water Sr concentration in the Bermejo and Pilcomayo sub-basins (Avigliano et al. 2019b) cast doubt on this possibility. As a consequence, it is timely to map the variation in water Sr/Ca and Ba/Ca ratio across the La Plata Basin, and to assess the potential of these chemical ratios to infer the displacements of commercially important fish.

The purpose of the present study was to evaluate the potential of Sr/Ca and Ba/Ca ratios in fish otolith, as a complement to Sr isotopes, to study movements of *Prochilodus lineatus* in the La Plata Basin. To achieve this objective, we compare the Sr/Ca and Ba/Ca ratios in water and fish otoliths sampled in the major hydrographic regions of the La Plata Basin, and discuss the observed variations in these ratios across different freshwater environments.

Materials and methods

Study area

The Paraná and Uruguay rivers are the largest water courses of the La Plata Basin (Fig. 1). The Paraná River (mean discharge ~17,000 m^3/s) runs for 3965 km from the Andes (Argentina, and Bolivia) and the Atlantic Rain Forest areas (Argentina, Brazil, and Paraguay) to the Paraná River Delta (Argentina), and it is partitioned in three hydrogeographic regions (Fig. 1a) depending on watercourse morphology, and ecoregions: upper, middle, and lower Paraná (Tucci and Clarke 1998). The Paraguay River is the main tributary of the Paraná River. It also receives the waters of the sediment-rich Bermejo and Pilcomayo rivers. The Bermejo River (mean discharge ~400 m^3/s) transports around 45% of the total sediment load of the La Plata Basin (~90 Mt/y of suspended sediments; Depetris and Paolini 1988) and has important tributaries such as the San Francisco River. Downstream, the combination of low slope and the input of large sediment loads from the Andean tributaries favor the formation of large floodplains in the middle and lower Paraná River before giving way to a large delta that continues through the Río de La Plata Estuary. On the eastern part of the basin, the Uruguay River (mean discharge ~6000 m^3/s) runs along 1800 km from the Brazilian shield to the Paraná River Delta and is joined by several short tributaries, and forms several successive flooded valleys (Berbery and Barros 2002). The Uruguay River also is partitioned in three hydrogeographic regions (upper, middle, and lower sections, Fig. 1b), depending on watercourse morphology. The Paraná River Delta discharges into the Río de La Plata Estuary (mean discharge ~22,000 m^3/s, Piola et al. 2003). More details on the hydrogeomorphology of the basin can be found in Avigliano et al. (2020).

Water sample collection and chemical analysis

Surface water samples were collected during the high (summer, March 2018) and low (winter, August 2018) water seasons at 42 sites across the La Plata Basin during the same sampling reported by Avigliano et al. (2020). The sampling stations represent different environments such as rivers, streams, floodplain lakes, wetlands, lakes/reservoirs, lagoons, floodplains and the

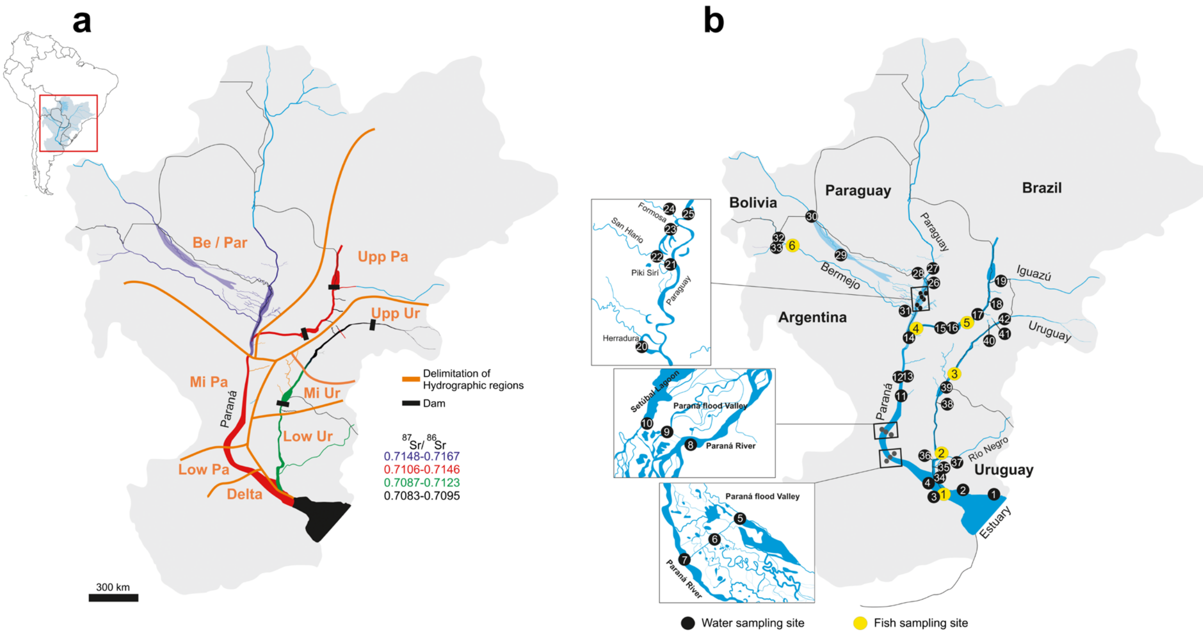

Fig. 1 La Plata Basin map (South America). **a** delineation of $^{87}Sr/^{86}Sr$ regions, **b** Water and fish sampling site distribution. Surface water samples were collected during the high (summer) and low (winter) water seasons at 42 sites. *Prochilodus lineatus* specimens were caught from Río de la Plata Estuary (fish sampling site 1), lower (2) and middle Uruguay (3), middle (4) and upper Paraná (5), and upper Bermejo (6) rivers

estuary (Fig. 1a and Table S1). Water samples were collected at ~0.3-m depth in 500-ml polyethylene-terephthalate bottles pre-cleaned with nitric acid (Merck Pro Analysis). For each season, samples were collected within 3 weeks to minimize effects of possible hydrological variations. Immediately after being collected, samples were stored in darkness at 4 °C and transported to the laboratory. The conductivity was determined ex situ using a Horiba U-52 probe. Water samples were vacuum-filtered through nitrocellulose filters (0.22-μm pore size) and acidified with nitric acid to pH < 2 (Baird et al. 2017).

Water dissolved Ca^{2+} concentrations were measured on specific sample aliquots by ion chromatography, using electrochemical suppression and conductivity detection (IC5000+, ThermoFisher Scientific) in the Institut de physique du globe de Paris at Université de Paris (France). The ion separation was enabled using a specific cation exchange column (IonPac CS16-5 mm, Dionex) and a 31-mM methanesulfonic acid solution as eluent (Sigma-Aldrich). The column temperature was 40 °C and the flow rate 1.2 ml/min. The standard solutions used for quantification were made in the laboratory using mono elemental solutions for ion chromatography (SCP Science), with Ca^{2+} concentrations ranging from 1.2 to 125 μg/g.

Water dissolved Sr^{2+} and Ba^{2+}, and Sr isotopic data was taken from Avigliano et al. (2019b) and Avigliano et al. (2020), and were measured by Quadrupole-ICP-MS and MC-ICP-MS, respectively. These data sets correspond to the same water samples on which calcium was determined here for the first time.

Fish collection and otolith analysis

Prochilodus lineatus specimens ($N = 29$) were caught between February 2011 and November 2014 using trammel nets at six different sites: Río de la Plata Estuary, lower and middle Uruguay, middle and upper Paraná, and upper Bermejo rivers (Fig. 1a and Table S2). Fish collection locations were based on historical knowledge of abundance and the geographical distribution of Sr isotopes in water in order to obtain differentiable signatures (Avigliano et al. 2020). Fish were sacrificed by percussive stunning (Van De Vis et al. 2003), and transported to the laboratory at 4 °C, measured (standard length = SL, 35–58 cm) and their *lapilli* otoliths were extracted.

Otoliths were embedded in epoxy resin and sectioned (thickness 700 μm) transversally at the core plane by using a Buehler Isomet low speed saw (Hong Kong, China). Otolith sections were fixed to glass slides using resin, polished to core and sonicated for 5 min in ultrapure water (resistivity = 18.2 MΩ/cm) (Avigliano et al. 2020). Fish ages were determined by counting otolith *annuli* according to Espinach Ros et al. (2012). The number of *annuli* in the otolith was counted with the sections immersed in water at 40-X magnification.

The Ca, Sr, and Ba concentrations in otolith samples were determined in the Laser and Plasma Spectroscopy Research Lab at Oviedo University through the measurement of $^{43}Ca^{2+}$, $^{88}Sr^{2+}$ and $^{138}Ba^{2+}$ ion signal, respectively, derived from a Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) system, using a 193 nm ArF Excimer system (Photon Machines Analyte G2) coupled to an ICP-QMS Agilent 7700 (Santa Clara, USA). The ablation was performed in scan mode from core to edge. A circular aperture of 30 μm was used at 5 μm/s with a laser repetition rate of 10 Hz and a fluence of 12 J/cm^2 (Avigliano et al. 2017b). The ICP-MS was operated at a power of 1600 W using Helium (flow: 800 mL/min) as carrier gas in the ablation cell, while Argon (900 mL/min) was added before introduction of the laser-induced aerosol into the ICP-MS torch. The $^{238}U/^{232}Th$ and $^{16}O/^{232}Th$ ratios in NIST 612 were used for monitoring the ICP robustness and the oxide formation, showing ratios below 1.2 and 0.4%, respectively. The reference materials NIST610 and NIST612 (trace elements in silicate glass, National Institute of Standards and Technology, USA) were analyzed in triplicate every 10 samples and used as primary and secondary standards, respectively (Pearce et al. 1997; Jochum et al. 2011). A Ca reference value of 38.3 (weight %) was used as an internal standard (IS) (Yoshinaga et al. 2000). Conversion of counts per second (intensity) to concentrations was achieved considering constant Relative Sensitivity Factors ($RSF_x = (I_x/I_{IS})/(C_x/C_{IS})$) in the reference material and in the otolith samples. Reference material recoveries based on NIST612 showed acceptable values for ^{138}Ba (98%) and ^{88}Sr (100%). Elemental Sr/Ca and Ba/Ca molar ratios were expressed in mmol/mol.

The otolith Sr isotopic data set was taken from Avigliano et al. (2020). This data set corresponds to the same otolith samples measured in the present study, which were previously analyzed by a fem-to-second Laser Ablation system (Nexeya SA, Canejan, France) coupled to a MC-ICPMS Nu Plasma (Nu Instruments, Wrexham, UK) under dry plasma conditions. The certified fish otolith reference material (NIESS 22, National Institute of Japan Environmental Studies) was used to check the accuracy and repeatability of the $^{87}Sr/^{86}Sr$ measurements (mean ± 2SD = 0.7093 ± 0.0001, N = 31).

Data analysis

Statistical analyses were performed using the PAST 3.0 and Mystat software

Water chemistry The relationships between water Sr/Ca and Ba/Ca ratios and conductivity were assessed using a power-law function [the relationship between $^{87}Sr/^{86}Sr$ and conductivity was reported by Avigliano et al. 2020]. A Principal Component Analyzes (PCA) was performed to explore possible patterns of variation in Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ ratios between sampling sites. PCA was based on the correlation matrix to remove the scale effect of the variables. A Linear discriminant analyzes (LDA) was performed to test the capacity of $^{87}Sr/^{86}Sr$ and the elemental ratios plus $^{87}Sr/^{86}Sr$ to discriminate between the main rivers and areas differentiated by the PCA. Standardized discriminant coefficients were used to compare the relative importance of the natural tags to classify the samples into the different sub-basins. The predictive ability of the discriminant models was assessed by the leave-one-out cross-validation (jackknifed) method. Prior to the discriminant analyzes, the multicollinearity was tested by calculating the tolerance value (Hair et al. 2014).

Relationship between water and otolith chemistry To test the relationship between elemental ratios composition in otolith and water, linear regression analysis was carried out between otolith edge (~outer 100 μm, corresponding to the most recent life period) and water, for Sr/Ca and Ba/Ca ratios separately.

Otolith chemistry and life history A PCA based on the correlation matrix was performed to explore possible patterns of variation in otolith edge ratios between sampling sites. A discriminant analysis was performed to test the capacity of the geomarkers ($^{87}Sr/^{86}Sr$ and the elemental ratios plus $^{87}Sr/^{86}Sr$) to discriminate between the main capture hydroregions applying a similar statistical approach used for the water samples. In this case, a Quadratic Discriminant Analysis (QDA) was performed for the otolith samples because the homogeneity of variances-co-variances matrices was not met (Box test,

$p < 0.05$). Both the PCA and the QDA were performed with those variables that showed a relationship between the otolith and water.

The variations in elemental and Sr isotopic ratios over the course of individual's life were represented by otolith core-to-edge transects. Additionally, the first annual mark was highlighted on the plots.

Results

Water chemistry

The water Sr/Ca ratio ranged from 2.48 to 8.08 mmol/mol (mean ± SD = 3.91 ± 1.16), while Ba/Ca varied from 0.26 to 2.28 mmol/mol (mean ± SD = 1.34 ± 0.52) (Table S1). A positive relationship was found for Sr/Ca and conductivity ($R^2 = 0.25$, $p < 0.05$) and a negative relationship between Ba/Ca and conductivity ($R^2 = 0.47$, $p < 0.05$), when the two extreme points of the site 1 (upper Estuary) characterized by a relatively high conductivity were excluded (Fig. 2). When these two points from upper estuary were included, significant positive and negative relationships with conductivity were also observed for Sr/Ca ($R^2 = 0.43$, $p < 0.05$) and Ba/Ca ($R^2 = 0.50$, $p < 0.05$), respectively (Fig. 2).

The PCA on water Ba/Ca, Sr/Ca and $^{87}Sr/^{86}Sr$ values from 42 sites showed that the first two components accounted for 80.6% of the total variance of the data set (PC1 = 46.0%, PC2 = 34.1%, Fig. 3). The $^{87}Sr/^{86}Sr$ (eigenvector = 0.72) was the variable that most contributed to the formation of the spatial distribution of the PC1 score, followed by Sr/Ca (0.62), and Ba/Ca (0.30). For the PC2, Ba/Ca (0.88) was the variable that most contributed, followed by Sr/Ca (−0.47), and $^{87}Sr/^{86}Sr$ (0.04). The PCA resulted in the separation of six main groups of sites: 1) the Bermejo and San Francisco sampling sites formed a well-identified group characterized by a high Sr/Ca (≥6.2 mmol/mol) and $^{87}Sr/^{86}Sr$ (0.7149 = 0.7151), and low Ba/Ca (0.97–0.99 mmol/mol); 2) the Pilcomayo area and upper Bermejo presented relatively low Ba/Ca (<0.8 mmol/mol), moderate Sr/Ca ratios (3.1–3.9 mmol/mol) and high $^{87}Sr/^{86}Sr$ (0.7147 = 0.7167); 3) the middle and lower Paraná sites showed overlap with two sites (25 and 26) from the main course of Paraguay River and were characterized by moderate values of Ba/Ca (1.2–1.7 mmol/mol) and Sr/Ca (3.1–3.7 mmol/mol), and high $^{87}Sr/^{86}Sr$ (0.7151 = 0.7154); 4) the tributaries of the Paraguay River and the sites 23 and 27 (Paraguay River) were characterized by moderate values of Ba/Ca (1.6–1.9 mmol/mol), Sr/Ca ratios (3.8–4.4 mmol/mol), and high $^{87}Sr/^{86}Sr$ (0.7148 = 0.7154); 5) the upper Paraná sites also formed a well-identified group characterized by high Ba/Ca (2.1–2.3 mmol/mol), moderate Sr/Ca ratios (3.4–3.5 mmol/mol) and low $^{87}Sr/^{86}Sr$ (0.7125 = 0.7141); 6) the lower Uruguay, the Paraná Delta, and mountain streams with low/intermediate Ba/Ca (0.56–1.57 mmol/mol), low Sr/Ca ratios (2.5–4.2 mmol/mol) and low $^{87}Sr/^{86}Sr$ (0.7072 = 0.7115). Finally, the three points (site 1, 2 and 3) from the estuary were segregated, with point 3 (upper Estuary) characterized by a lower Sr/Ca, and higher Ba/Ca and $^{87}Sr/^{86}Sr$ ratios.

The predictive classification of rivers according to water Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ ratios (LDA, mean% of correct classification =92.5%) was higher than that based solely on $^{87}Sr/^{86}Sr$ values (mean = 58%, Table 1), showing the maximum score of correct classification (100%) for Bermejo, Paraná, Paraguay, Estuary and upper Paraná, and high values (up to 75%) for the rest of the areas. As observed with the PCA, Sr/Ca was the ratio that contributed most to the discrimination (standardized discriminant coefficients: Sr/Ca = 0.17; Ba/Ca = 0.005; $^{87}Sr/^{86}Sr$ = 0.0008).

Water versus otolith chemistry

The otolith edge Sr/Ca ratio varied between 1.01 and 2.18 mmol/mol (1.40 ± 0.44 mmol/mol, Supplementary Material 1). The highest values corresponded to fish caught in the upper Bermejo River (2.18 ± 0.34 mmol/mol) and in the estuary (1.65 ± 0.18 mmol/mol), while the lowest ratios were obtained for the Uruguay (1.08 ± 0.29) and upper Paraná rivers (1.01 ± 0.20 mmol/mol). The otolith edge Ba/Ca ratio ranged from 0.013 to 0.018 mmol/mol (0.016 ± 0.0017 mmol/mol). The lowest values corresponded to the middle Uruguay River (0.013 ± 0.0018) and the upper Paraná River (0.015 ± 0.0028 mmol/mol), and the highest to those obtained from the middle Paraná River (0.017 ± 0.0096 mmol/mol) and the estuary (0.018 ± 0.0067 mmol/mol).

A significant positive linear relationship ($R^2 = 0.94$, slope = 0.29, $p < 0.05$) was found between the Sr/Ca ratios of otolith edge and those of water (Supplementary Material 1). There was no significant relationship between otolith edge and water Ba/Ca ratios ($R^2 = 0.043$, $p > 0.05$). The strong

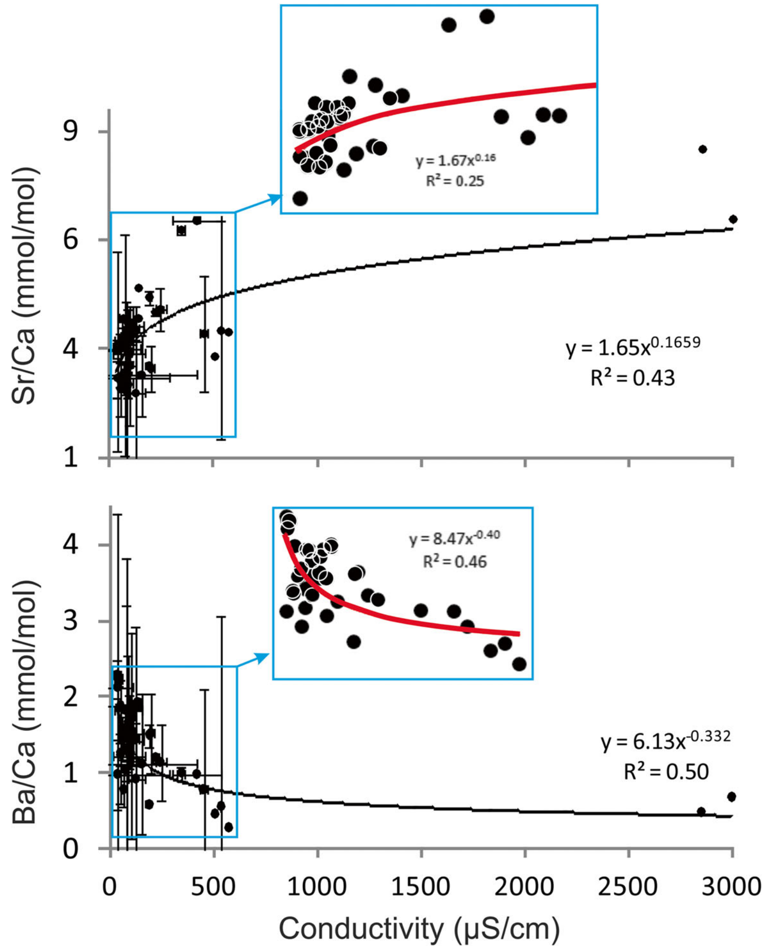

Fig. 2 Relationship between water element/Ca ratios and conductivity. The insets show the relationships excluding the two highest values (Middle Estuary, site 1) recorded for conductivity. Bars indicate the temporal standard deviation

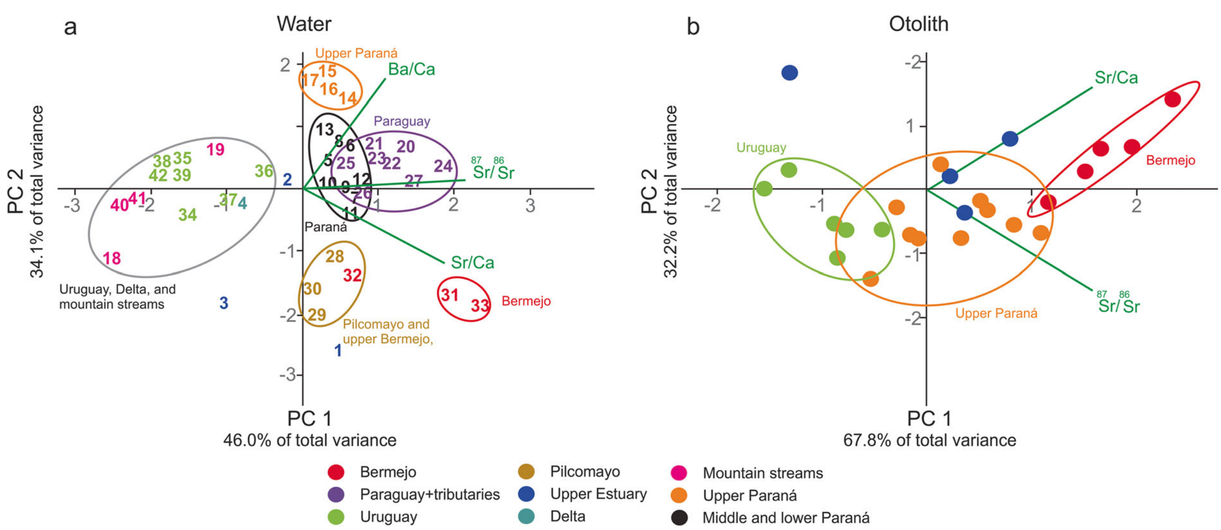

Fig. 3 Principal Component Analyzes based on correlation matrices. **a** results based on water Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ ratios. Numbers correspond to sampling sites (see Fig. 1), **b** results based on otolith edge Sr/Ca and $^{87}Sr/^{86}Sr$ ratios. Otolith Ba/Ca was not included because it did not show a relationship with the water composition. *PC* principal component

Table 1 Jackknifed percentages of linear discriminant analysis based on the water Sr/Ca, Ba/Ca, and Sr isotope ratios. *N* = sampling size

	N	Estuary	Middle/Lower Paraná	Uruguay	Paraguay	Bermejo	Upper Paraná	Mountain Stream	Pilcomayo
	$^{87}Sr/^{86}Sr$								
Estuary	3	100	0	0	0	0	0	0	0
Middle/Lower Paraná	10	0	60	0	10	0	30	0	0
Uruguay	8	38	0	25	0	0	25	13	0
Paraguay	8	0	0	0	63	0	0	0	38
Bermejo	3	0	0	0	67	0	0	0	33
Upper Paraná	4	0	25	0	0	0	75	0	0
Mountain Stream	4	0	0	25	0	0	0	75	0
Pilcomayo	3	0	0	0	33	0	0	0	67
Mean									*58*
	Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$								
Estuary	3	100	0	0	0	0	0	0	0
Middle/Lower Paraná	10	0	90	0	0	0	10	0	0
Uruguay	8	0	13	75	0	0	0	13	0
Paraguay	8	0	0	0	100	0	0	0	0
Bermejo	3	0	0	0	0	100	0	0	0
Upper Paraná	4	0	0	0	0	0	100	0	0
Mountain Stream	4	0	0	25	0	0	0	75	0
Pilcomayo	3	0	0	0	0	0	0	0	100
Mean									*93*

relationship found between otolith and water Sr/Ca ratios suggests that this ratio could be an efficient natural indicator for *P. lineatus* migration in combination with $^{87}Sr/^{86}Sr$ ratios, unlike Ba/Ca ratios. For this reason, Ba/Ca transects in otoliths are not discussed in the following part.

Discrimination based on otolith edge chemistry

The PCA and QDA based on the otolith edge were performed with Sr/Ca and $^{87}Sr/^{86}Sr$ ratios (Fig. 3b and Table 2). Otolith Ba/Ca was not included because it did not show a relationship with the water chemical composition.

The PCA showed that the first components accounted for 67.8% of the total variance (PC2 = 32.2%, Fig. 3b), with Sr/Ca and $^{87}Sr/^{86}Sr$ contributing in the same proportion for both PCs (eigenvector = 0.70). While the Estuary samples showed a relatively high dispersion, the rest were grouped into three large groups: Bermejo, upper Paraná and Uruguay rivers. Bermejo samples were mainly associated with high values of Sr/Ca and $^{87}Sr/^{86}Sr$ ratios, while those from Uruguay showed the opposite pattern. With intermediate Sr/Ca and $^{87}Sr/^{86}Sr$ values, the upper Paraná samples were distributed between the Bermejo and Uruguay groups.

The predictive classification of fish based on otolith edge Sr/Ca and $^{87}Sr/^{86}Sr$ ratios (correct classification =79.0%) was higher than that obtained on $^{87}Sr/^{86}Sr$ values (64%, Table 2), showing the maximum score of correct classification (100%) for Bermejo River. The upper Paraná and Uruguay River showed relatively high classification percentages (78–80%), while the lowest value was for the upper Estuary (50%). Sr/Ca was the ratio that contributed most to the discrimination (standardized discriminant coefficients: Sr/Ca = 0.93; $^{87}Sr/^{86}Sr$ = 0.59).

Otolith core-to-edge time series

Otolith core Sr/Ca ratio of fish from the Bermejo River varied from 0.87 to 1.89 mmol/mol for specimens P75,

Table 2 Jackknifed percentages of quadratic discriminant analysis based on the otolith edge Sr/Ca and Sr isotope ratios. *N* sampling size

	N	Estuary	Uruguay	Bermejo	Upper Paraná
	$^{87}Sr/^{86}Sr$				
Estuary	4	0	25	0	75
Uruguay	9	0	67	0	33
Bermejo	5	0	0	80	20
Upper Paraná	10	0	10	10	80
Mean					*57*
	Sr/Ca and $^{87}Sr/^{86}Sr$				
Estuary	4	50	0	0	50
Uruguay	9	11	78	0	11
Bermejo	5	0	0	100	0
Paraná	10	10	10	0	10
Mean					

P78 and P79, and from 1.27 to 2.1 mmol/mol for specimens P76 and P77 (Fig. 4a and Supplementary Material 2a). Considering the complete transects, the Sr/Ca ratio of fish P76 fluctuated between 1.48 and 2.82 mmol/mol (Supplementary Material 2a), while the rest of the specimens showed an increase in the ratio towards the end of life (up to 3.52, Supplementary Material 2a). In contrast, the Sr isotopic ratio showed fewer changes through ontogeny (Supplementary Material 2g).

With the exception of P48 and P51, fish from the middle Uruguay River (upstream) showed otolith Sr/Ca ratios between 0.75 and 1.5 mmol/mol (Fig. 4b and Supplementary Material 2b). Fish P48 and P51 had Sr/Ca ratios exceeding values of 2 mmol/mol (over a short distance for P48 and over a longer distance for P51; Supplementary Material 2b). The $^{87}Sr/^{86}Sr$ ratio also showed peaks in these two fish (Supplementary Material 4h).

Fish from the lower Uruguay River were characterized by relatively low Sr/Ca ratios (around 1 mmol/mol) (Fig. 4c and Supplementary Material 2c), except specimens P46 and P45 which had ratios >1.5 over a significant distance. On the contrary, the Sr isotope ratios of the otolith core were variable among individuals (Supplementary Material 2i). All fish showed a partial overlap of the Sr/Ca transects, especially in the outer 1000 μm of the otolith (Supplementary Material 2c).

For the upper Paraná River (Yacyretá Reservoir, Fig. 4d and Supplementary Material 2d), a relatively variable otolith core Sr/Ca ratio was observed, ranging from 0.76 to 1.89 mmol/mol. The Sr/Ca profiles partially overlap for all fish, except for P71, which presented higher Sr/Ca values, with a peak that exceeded 5 mmol/mol within the core area (Supplementary Material 2d). This Sr/Ca peak was not reflected in the isotopic pattern (Supplementary Material 2j). The otolith Sr isotopic ratio of upper Paraná River fish showed a tendency to decrease over time (Supplementary Material 2j). Specifically, fish P70 and P71 showed a pronounced drop in $^{87}Sr/^{86}Sr$ approximately 1 year of life (Fig. 4d and Supplementary Material 2j). The drop in $^{87}Sr/^{86}Sr$ observed in fish 70 matched with an increase in the Sr/Ca ratio (Fig. 4d).

For the middle Paraná fish (Fig. 4e and Supplementary Material 2e), core Sr/Ca ratios ranged from 0.72 to 1.64 mmol/mol. Moreover, Sr/Ca increased throughout ontogeny for all fish, being more pronounced in specimens P1 and P2 (up to 3.1 and 3.4 mmol/mol, respectively; Fig. 4e and Supplementary Material 2e). In contrast, the isotopic ratio showed a tendency to decrease in all fish (Supplementary Material 2k). The specimens P1, P2 and P73 showed $^{87}Sr/^{86}Sr$ values at the beginning of the profiles compatible with the Paraguay-Pilcomayo-Bermejo isotopic conglomerate (Supplementary Material 2k). In particular, the P2 fish showed a pattern compatible with movements from the Bermejo to the Paraná (even towards the Uruguay River) (Fig. 4k), agreeing with the ascending pattern of Sr/Ca (Supplementary Material 2e).

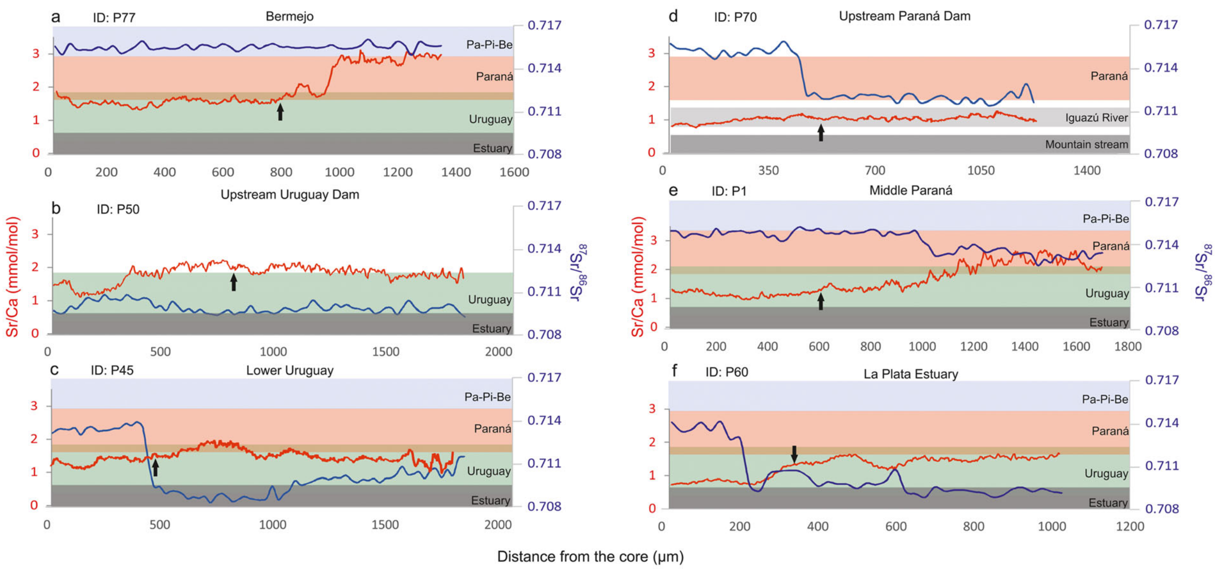

Fig. 4 Representative profiles of *Prochilodus lineatus* otolith Sr/Ca (this paper) and $^{87}Sr/^{86}Sr$ (Avigliano et al. 2020) ratios obtained by LA-ICP-MS. The shaded areas correspond to the range in water $^{87}Sr/^{86}Sr$ as a function of the potential migratory corridor (for fish coming from reservoirs, only reference values from upstream are shown) according to Avigliano et al. (2020). The arrows indicate the position of the first annulus. Par-Pi-Be: Paraguay-Pilcomayo-Bermejo system

For fish P60, P61, P62, and P64 caught in the upper estuary, the Sr/Ca ratio showed an increase throughout ontogeny (from 1 to 2 mmol/mol) (Fig. 4f and Supplementary Material 2f). In addition, fish P60, P62, and P64 showed a similar pattern of decreasing $^{87}Sr/^{86}Sr$ values during the ontogeny (Supplementary Material 2l), but P61 had low Sr/Ca ratios near birth and then Sr/Ca ratios (Supplementary Material 2f) characterized by Sr/Ca ratios between.

Discussion

Distribution of Sr/Ca, $^{87}Sr/^{86}Sr$ and Ba/Ca in the main hydroregions

The PCA and LDA (Fig. 3 and Table 1) showed that it is possible to separate different hydroregions of the basin based on water Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ ratios. According to the statistical approaches, Sr/Ca ratios had a greater ability for the separation of the areas from the northeast of the La Plata Basin (Bermejo, Pilcomayo and Paraguay rivers), which have a relatively similar Sr isotopic ratio (Avigliano et al. 2020).

The range of Sr/Ca and Ba/Ca ratios found in the present study were concordant to those reported for other basins around the world (Brown and Severin 2009). Typical Sr/Ca ratios in aquatic systems are 0.27 to 9.2 (mean = 2.39) mmol/mol for rivers and their estuaries, and 8.17 to 8.87 mmol/mol for seawater (Brown and Severin 2009). Most of the world's major freshwater basins such as the Congo, Ganga, Orinoco, Mississippi, and Yukon rivers are characterized by Sr/Ca ratios between ≈1 and ≈9 mmol/mol (Brown and Severin 2009), a range comparable to that obtained in this study. Values of Ba/Ca ratios obtained here for the La Plata Basin were also comparable with those reported previously for fluvio-estuarine systems, with ratios of 0.005 to 6.4 for freshwater, and of 0.009 to 0.1 mmol/mol for estuarine/seawater (Elsdon and Gillanders 2005; Hamer et al. 2015; Mohan and Walther 2015).

A striking feature of our dataset is the opposite relationship observed between conductivity versus Sr/Ca ratio (positive trend), and between conductivity versus Ba/Ca ratio (negative trend) (Fig. 2). A positive relationship between the water Sr/Ca ratio and salinity has been reported in several river basins such as the Indigirka, Indus, Mississippi, and Río de La Plata (lower basin part), where the strongest slope corresponds to the estuary area (Zlokovitz et al. 2003; Brown and Severin 2009; Avigliano and Volpedo 2013). However, inverse relationships have also been found for a few basins such as the St. Johns rivers (USA) (Brown and Severin 2009) and the Wyuna Creek (Australia) (Hamer et al. 2015).

Dissolved Sr concentration and Sr/Ca ratios in river are largely controlled by the presence of carbonate rocks in the drainage basins, which tends to result in higher Sr concentrations but lower Sr/Ca ratios (Palmer and Edmond 1992). Rivers draining carbonate rocks are also expected to display high conductivity, because of the fast dissolution rates and high solubility of carbonates compared to silicate minerals (Brantley et al. 2008). Nevertheless, several alternative sources of dissolved Sr and Ca to rivers can complicate this simple picture, such as the deposition of marine-sourced atmospheric salts, anthropogenic inputs, or the presence of evaporite rocks in the basin. Additionally, processes such as the formation of secondary carbonates can fractionate Sr and Ca (Bickle et al. 2015). This complexity is the most likely cause for the diversity of Sr/Ca vs. conductivity relationships reported in the literature. Although Sr concentration in seawater is fairly high in any case, Sr concentration in river water, and associated Sr/Ca ratio, vary widely depending on the geological setting, such that it can be either lower than (as is the case overall of La Plata Basin) or higher than seawater as reported by Elsdon and Gillanders (2005), Joung and Shiller (2014) and Mohan and Walther (2015).

Like in our study, an inverse relationship between Ba/Ca and conductivity has been reported for several basins and estuaries around the world such as the Adour River (France) (Tabouret et al. 2010), the Negro River (Avigliano et al. 2019a), the Mississippi River and in the Gulf of Mexico (USA) (Joung and Shiller 2014; Mohan and Walther 2015), and estuaries in Australia (Elsdon and Gillanders 2005). Although little is known about the controls on Ba abundance in freshwater, lithology is expected to play a control over water Ba/Ca ratio. Unlike Sr, river dissolved Ba is mostly derived from silicate rocks (Charbonnier et al. 2020; Gou et al. 2020). In addition, Ba is much more sensitive than Sr to secondary processes including the formation of clays and oxides (Dalai et al. 2002; Das and Krishnaswami 2006; Gong et al. 2019) or biological uptake (Bullen and Chadwick 2016; Charbonnier et al. 2020). Although it is beyond the scope of this work to clearly identify the controls on river dissolved Ba/Ca ratios, it can be hypothesized that the presence/absence of carbonate rocks in the studied basins (leading to high conductivity but low Ba/Ca ratios) exerts the strongest influence on the widespread inverse relationships between conductivity and Ba/Ca ratios. The widespread observation of inverse relationships between Ba/Ca ratios and conductivity stems from the fact that the concentration of Ba in lower estuary and seawater (the high-conductivity end member) is relatively low compared to that usually observed in continental waters (Wolgemuth and Broecker 1970; Tabouret et al. 2010).

Are water Sr/Ca and Ba/Ca ratios reflected in otolith?

In our data set, Sr/Ca ratio of water samples was correlated with that of edge otolith, but no correlation was found for Ba/Ca ratio. This means that among the two elemental ratios; only Sr/Ca could be used as an efficient tracer of *P. lineatus* migratory patterns, at least in the case of La Plata Basin. Nevertheless, the Ba/Ca baseline in water presented in this study could be used to study the migration of other fish species, for which an association between the environmental concentration and a calcified structure would be demonstrated.

Positive relationships between otoliths and water Sr/Ca have been reported especially for diadromous or euryhaline fish (Brown and Severin 2009; Tabouret et al. 2010; Avigliano and Volpedo 2013; Arai and Chino 2017), although there are relatively few studies regarding freshwater species (e.g. Brown and Severin 2009). By contrast, the accurate record of water Ba/Ca ratios by otolith seems to be less systematic. Although several examples of positive relationships between Ba/Ca of otolith and water have been reported for diadromous or euryhaline fish (Tabouret et al. 2010; Mohan et al. 2015), many species do not show such a relationship, even those for which a relationship was observed for Sr/Ca (e.g. Avigliano et al. (2018) and Rohtla et al. (2014)). However, some species, like *Morone saxatilis* from river habitats, show a significant positive relationship between otolith and water for the Ba/Ca ratio but not for the Sr/Ca ratio (Mohan et al. 2015).

Brown and Severin (2009) indicated that several species experiencing exposure to a wide range of salinity generally exhibit strong relationships between otolith and water element/Ca ratios. However, the relatively small range of Ba/Ca ratios covered by the freshwater environments of our datasets is most likely too limited for otoliths to record faithfully the water Ba/Ca ratio in the La Plata Basin. Indeed, although a negative relationship between the otolith Ba/Ca and salinity has been found in many species (Tabouret et al. 2010; Mohan et al. 2015), this was not the case for others such as *Genidens barbus* (Avigliano et al. 2017a) and *Odontesthes bonariensis* (Avigliano et al. 2018), for which the incorporation of Ba/Ca in otoliths can be highly sensitive to runoff or rainfall.

Tracing fish migration combining Sr/Ca and Sr isotope ratios

Because otolith did not record conservatively the water Ba/Ca ratio, in this work only Sr/Ca and $^{87}Sr/^{86}Sr$ ratios were used for tracing fish migration. In general, the otolith edge chemical composition showed a good ability to classify the fish in their respective catch areas, suggesting that Sr/Ca and $^{87}Sr/^{86}Sr$ are good habitat indicators for *P. lineatus*. The classification ability was shown to be relatively low for the estuary, which could be explained by the influence of the Paraná River water discharged into the estuary, temporal variation in the water chemical composition, and the relatively low number of fish samples.

Simultaneously considering the distribution of the two faithful habitat indicators, it was possible to hypothesize different ontogenetic migration patterns according to Sr/Ca and $^{87}Sr/^{86}Sr$ variations along the otolith. Figure 5 schematizes possible chemical otolith profiles based on the Sr/Ca distribution found in this work and the Sr isotopic baseline. Considering the two "extreme" signatures of the basin, more radiogenic (^{87}Sr-enriched) values and high Sr/Ca ratios are expected for the Bermejo River region, while low $^{87}Sr/^{86}Sr$ and high Sr/Ca ratios characterize the estuary. In the rest of the sub-basins, different combinations of low and intermediate Sr/Ca and Sr isotope ratios are expected (Fig. 5). The Bermejo River is an illustrative example that shows the complementary potential of Sr/Ca and $^{87}Sr/^{86}Sr$ ratios to reveal migration patterns. The Bermejo-Pilcomayo-Paraguay area presents highly radiogenic waters (high $^{87}Sr/^{86}Sr$ values) in all the tributaries sampled by Avigliano et al. (2020). Unlike the other rivers of this region, the Bermejo River waters showed higher Sr/Ca signatures. Therefore, the otolith of a fish moving between the Paraguay River and the Bermejo River may present a relatively constant profile of $^{87}Sr/^{86}Sr$ but a variation in the Sr/Ca profile; with higher values during the time it spent in the Bermejo River (Fig. 5, type 2; Supplementary Material 2). The movements suggested by both markers in the Bermejo-Pilcomayo-Paraguay area are consistent with the limited independent information available for *P. lineatus*. For example, fish tagged at the Paraguay-Paraná confluence performed downstream migrations (Bonetto and Pignalberi 1964; Bonetto et al. 1981; Sverlij et al. 1993). Bonetto et al. (1971) reported that tagged specimens at the Bermejo-Paraguay confluence do migrate downstream and upstream towards the Andes, moving more than 700 km upstream. This evidence supports the existence of a migratory corridor between these rivers, as revealed by otolith Sr/Ca and $^{87}Sr/^{86}Sr$ time-series (Fig. 5, migratory pattern 2, and Supplementary Material 2).

Some fish caught upstream of the Uruguay (e.g., P48, P51, Fig. 4d and j) and Paraná (e.g., P69 and P71, Fig. 4d and j) dams showed relatively variable Sr/Ca or $^{87}Sr/^{86}Sr$ patterns, specially within the first year of life. It suggests that they were exposed to environments with different geochemical features, despite the fact that no great environmental variations of these markers have been found in our sample set upstream from the dams (Avigliano et al. 2020). In addition, theses variations were not reflected simultaneously in both natural tags in otolith and water. Then, it is possible that these signatures stem from still unmapped environments in this region, or that significant seasonal variability remains yet to be documented.

The otolith Sr/Ca profiles for fish from the lower Uruguay River showed relatively small variation throughout ontogeny, nevertheless, the otolith $^{87}Sr/^{86}Sr$ profiles were highly variable (Fig. 4c and i). This suggests movements between environments with relatively homogeneous salinity but heterogeneous in relation to radiogenic features, for example between sub-basins such as the Paraná, the Uruguay and the estuary.

In the middle Paraná River, otolith profiles were consistent with movements from more radiogenic waters but lower in Sr/Ca ratio (for example the Paraguay River) to water masses characterized by a higher Sr/Ca and a lower Sr isotopic ratio (maybe the lower Paraná or the Delta) (migratory pattern 3 and 5 represented in Fig. 5 and Supplementary Material 2).

For fish caught in the upper estuary, the use of Sr/Ca brought additional more detailed description to the patterns suggested by the isotopes. For example, the isotope profile suggested movements between the Paraná, the Uruguay and the estuary for fish P61. However, the increasing Sr/Ca ratio implies displacements from lower to higher salinity, from the lower Paraná or Uruguay, to the upper estuary. Other fish such as P60, P62 and P64 showed Sr/Ca and $^{87}Sr/^{86}Sr$ patterns consistent with movements towards the lower part of the basin (Fig. 4f and l, and Supplementary Material 2), as

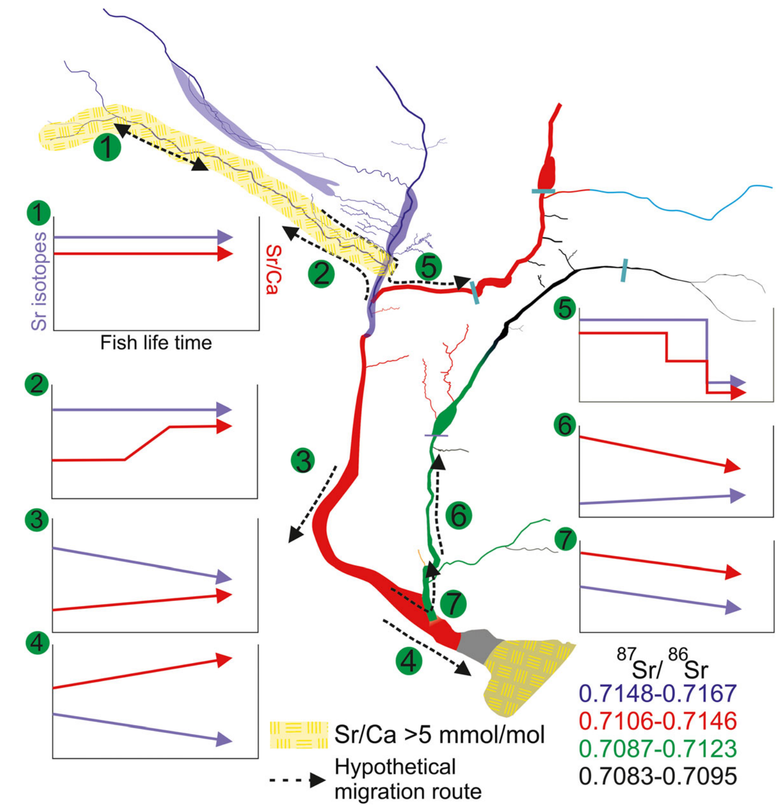

Fig. 5 Hypothetical migratory patterns and corresponding otolith Sr/Ca (this paper) and $^{87}Sr/^{86}Sr$ (Avigliano et al. 2020) profiles, based on the integration of both geochemical markers in water and otoliths

represented in Fig. 5 (migratory pattern 3). Avigliano et al. (2017b) have suggested displacements between freshwater and the estuary for *P. lineatus*, based on the Sr/Ca ratio in otolith and water. These authors have assumed that the highest values of Sr/Ca in water corresponded to the external part of the estuary (like many fluviomarine systems; Brown and Severin 2009), and have thus attributed otolith Sr/Ca peaks with incursions into estuaries. The present study showed that the occurrence of high Sr/Ca in water of some particular sub-basins, like the Bermejo, can impart high Sr/Ca values in the otolith, and can sometime overcome the high Sr/Ca ratios of the estuary. Therefore, reinterpreting the results of Avigliano et al. (2017b) in the light of the present study, many of the fish analyzed in the latter study could have migrated to water systems with the same characteristics as the Bermejo River, rather than to the estuary. This discussion highlights the importance of the simultaneous use of multiple otolith markers, and the need to generate more complete maps for these markers in river basins.

Conclusion

The Sr/Ca ratio complemented the information provided by Sr isotopes. The Sr/Ca ratio was particularly useful in the northwest section of the basin, where the water Sr isotopes do not allow differentiation of large rivers such as the Bermejo and Paraguay rivers. In that region, the Sr/Ca ratio measured in otoliths suggested that *P. lineatus* migrates between areas of different salinity but displays the same Sr isotope signature (maybe between the Bermejo, Pilcomayo, Paraguay and Paraná rivers). The simultaneous use of both markers is also interesting in the lower basin, where they showed opposite but complementary tendencies. Interpretation of geochemical markers in otoliths is strongly dependent on environmental baselines, and we thus recommend intensifying Sr/Ca and $^{87}Sr/^{86}Sr$ studies in waters in order to improve existing geochemical maps. Because the hydrological conditions could affect the chemical composition of the water, mapping will be further improved through seasonal monitoring at strategic points in the La Plata Basin. Subsequently, this methodology could be used to reconstruct the life history of

P. lineatus, this information being an important input for the development of management policies on a provincial or regional scale.

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Code availability Not applicable.

Authors' contributions Not applicable.

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Declarations

The authors declare not to have any interest conflicts. *Prochilodus lineatus* is not protected under wildlife conservation laws (local legislations, IUCN, or CITES). As the Consejo Nacional de Investigaciones Cientificas y Técnicas (CONICET) does not possess a formal animal research ethics committee regarding the fish welfare and sampling protocols, fish handling during sampling was performed following guidelines of the ethical committee of the UFAW Handbook on the Care and Management of Laboratory Animals (http://www.ufaw.org.uk). Collection fish was authorized by the local Wildlife and Fisheries Authority guidelines and policies (Ministerio de Ecología y Recursos Renovables of Misiones Province, Law XVI N° 47, N° 509/07 and 052/18, Dirección de Recursos Naturales of Corrientes Province, Law 1863/54, and Comisión Administradora del Río Uruguay, RS27 /04). The fish in this study were not a part of faunal surveys and they did not employ any type of experimental procedure, surgery or chemical agents that would induce injury on the collected organisms.

Ethics approval *Prochilodus lineatus* is not protected under wildlife conservation laws (local legislations, IUCN, or CITES). As the Consejo Nacional de Investigaciones Cientificas y Técnicas (CONICET) does not possess a formal animal research ethics committee regarding the fish welfare and sampling protocols, fish handling during sampling was performed following guidelines of the ethical committee of the UFAW Handbook on the Care and Management of Laboratory Animals (http://www.ufaw.org.uk). Collection fish was authorized by the local Wildlife and Fisheries Authority guidelines and policies (Ministerio de Ecología y Recursos Renovables of Misiones Province, Law XVI N° 47, N° 509/07 and 052/18, Dirección de Recursos Naturales of Corrientes Province, Law 1863/54, and Comisión Administradora del Río Uruguay, RS27/04). The fish in this study were not a part of faunal surveys and they did not employ any type of experimental procedure, surgery or chemical agents that would induce injury on the collected organisms.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest There are no conflicts of interest.

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