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ANALYSIS AND COMPARISON OF 20 EMPIRICAL EQUATIONS FOR REAERATION RATES IN URBAN RIVERS

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Abstract

Accurate measurements of the pollution in urban basins are essential for the development of effective management strategies. One important parameter is the reaeration rate, which allows for the evaluation of the quality and self-purification rate of water bodies. The reaeration rate can be determined using a variety of methods, such as empirical and semi-empirical equations that can rapidly produce estimates based on hydraulic and hydrodynamic variables. However, depending on the variables, these equations often produce very different results and can lead to underestimated or overestimated values. In order to test these methods, we evaluated 20 empirical equations in three urban rivers in the city of Bogotá and categorized them into four groups. Principal component analyses and a dendrogram analysis were performed to compare the equations, revealing two consistent groups of equations for the three rivers. The first group consisted of equations from Langbein and Durum (LD), Padden and Gloyna (PG), and Bansal (B), while the second group consisted of equations from Owens et al. (OW) and Owens and Gibbs (OG). Equations from Thyseen et al. (TH) and Negulescu and Rojanski (NR-DL) did not present reliable clusters due to the high magnitude of their results compared to the other equations. Finally, the Tsivoglou and Wallance (TW), Grant (G), and Tsivoglou and Neal (TN) equations indicated inverse relationships compared to other equations. Hydraulic variables for velocity and water depth presented the greatest sensitivity and exhibited strong relationships with the magnitudes of the reaeration rates.

Key words: Dendrograms, principal component analysis, reaeration rate equations, urban rivers

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1. Introduction

The exchange of oxygen at the water surface is a natural process that is generally measured through a rate called reaeration (k_a). Reaeration is involved in several environmental processes and is used to estimate existing dissolved oxygen concentration levels and to quantify the self-purification capacity in rivers and lakes through mathematical models (Barnwell et al., 2004; Cox, 2003a, 2003b; Kannel et al., 2011).

Therefore, establishing an accurate reaeration rate is incredibly important in order to avoid

overestimations or underestimations of other values (Gualtieri et al., 2002).

Numerous methods have been developed to determine reaeration rates. Empirical or semi-empirical equations are some of the most commonly used methods, mainly because many of these equations are based on the different hydraulic properties of water bodies (de Souza Inácio Gonçalves et al., 2017). Due to the ease of use, these equations are used worldwide (Haider and Ali, 2010).

Empirical equations are mathematical expressions based on experimental results, whereas semi-empirical equations are based on theories. In

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both cases, the mathematical expressions accurately reflect the measured reference values (Maradei et al., 2015). These equations have been generated through experiments which can result in a wide range of variables, coefficients, and exponents among all of these equations (Jha et al., 2004; Palumbo and Brown, 2014). For this reason, these equations cannot be applied universally, since the equation might be highly sensitive to the different parameters that they are based on (Haider et al., 2013).

In developing countries, there are different forms of pollution and the hydraulic alteration of urban rivers (altering the conditions of self-purification) can be extreme. Specialized software that simulates water quality is therefore becoming increasingly used as a strategy for decision making so much so that in some countries, this practice is already regulated. However, sometimes the differences and similarities between the default reaeration equations that are included in software and those recommended in the literature are unclear. As a result, the operating conditions for the equations are not critically examined, and can generate non-representative values in quality parameters such as dissolved oxygen (DO) (Benson et al., 2014), producing a high degree of uncertainty in their results. For these reasons, it is necessary to expand our knowledge on these reaeration equations and to understand their differences, relationships, and the variables that lead to high sensitivity in the results.

There are a number of comparative studies on reaeration rates. Mohamed et al. (2002) compared reaeration rates by testing the performance of six reaeration equations and one rate measured in the field by simulation with Qual2E. Other studies recommend the O'Connor-Dobbins equation for deep rivers with low velocities and the Owens et al. and Churchill's equations for fast and slow streams. However, Mohamed et al. (2002) found that for the river in their study, the equation that performed the best and that met these two hydraulic and hydrodynamic characteristics was the one proposed by Langbein-Durum. They also found that the Tsvoglou-Wallace equation did not work well for the river in their study. Another study by Aristegi et al. (2009) compared ten different equations and identified large differences in the magnitudes of these equations that occurred mainly in shallow sections of river. Haider et al. (2013) evaluated 29 equations by categorizing them into four groups (groups 1-4) according to their variables. They determined that the best equations after dissolved oxygen simulations for group 1 were Padden and Gloyna, Tsvoglou and Neal for group 2, Lau for group 3, and Gualteri and Gualter for group 4. However, the authors found that the performance between these equations was variable. A mass balance model was calculated by Kalburgi et al. (2015) using dissolved oxygen (DO) and biochemical oxygen demand (BOD) and it was compared with 13 different equations.

Their team found the fewest errors and differences using the equation from Jha et al. (2001). Arora and Keshari (2020) developed their own equation, compared it with classic equations, and concluded that their new equation performed better when using DO.

However, we have not observed the use of multivariate statistical tools for identifying the performance, patterns, differences, and similarities of different equations. These statistical tools would reveal the range of operations of the equations, as well as identify the weight, similarity, and contrast of the different hydraulic variables with which they are calculated. Due to the numerous and varied parameters and measurements that are used to calculate the reaeration rates, this type of multivariate analysis could help simplify the interpretation of the results.

In this study, we evaluated 20 reaeration equations in three urban rivers in the city of Bogotá with varying hydraulic and hydrodynamic characteristics to evaluate, analyse and compare their performance and variability through the use of principal component analyses (PCA) and dendrograms. These analyses allowed us to determine if there are groupings and the differences between variables. The analyses performed in this study also shed light on the importance of the selection and determination of reactor equations.

2. Case studies

2.1. Geographic location

Bogotá is the capital of Colombia and the largest urban centre in the country. It is located in Eastern Cordillera in the Andes at an altitude of 2630 meters above sea level (m.a.s.l). It has a total area of 177,598 hectares (ha), of which 30,736 ha are urban, 17,045 ha are urban-rural and 129,815 ha are rural. The population growth in the last 40 years has accelerated, from more than 2 million inhabitants in 1973 to more than 8 million in 2019. This growth has mainly occurred in urban areas, in which 99.92% of the total population of Bogota lives.

Economically, Bogotá generates 26% of the country's Gross Domestic Product and has one of the largest business platforms in the nation. Hydrographically, the city is composed of the middle basins of the Bogotá River, which are drained by four main rivers: Salitre-Torca, Fucha and Tunjuelo (Peña-Guzmán et al., 2016) (Fig. 1a). These rivers receive residual discharge from different residential, industrial and commercial activities, and the local environmental authority is currently working to improve the quality of this rivers and develop strategies to reduce pollutant loads. One of these strategies is the determination of dissolved oxygen concentrations as an indicator of water quality in rivers using mathematical models (Peña-Guzmán et al., 2017).

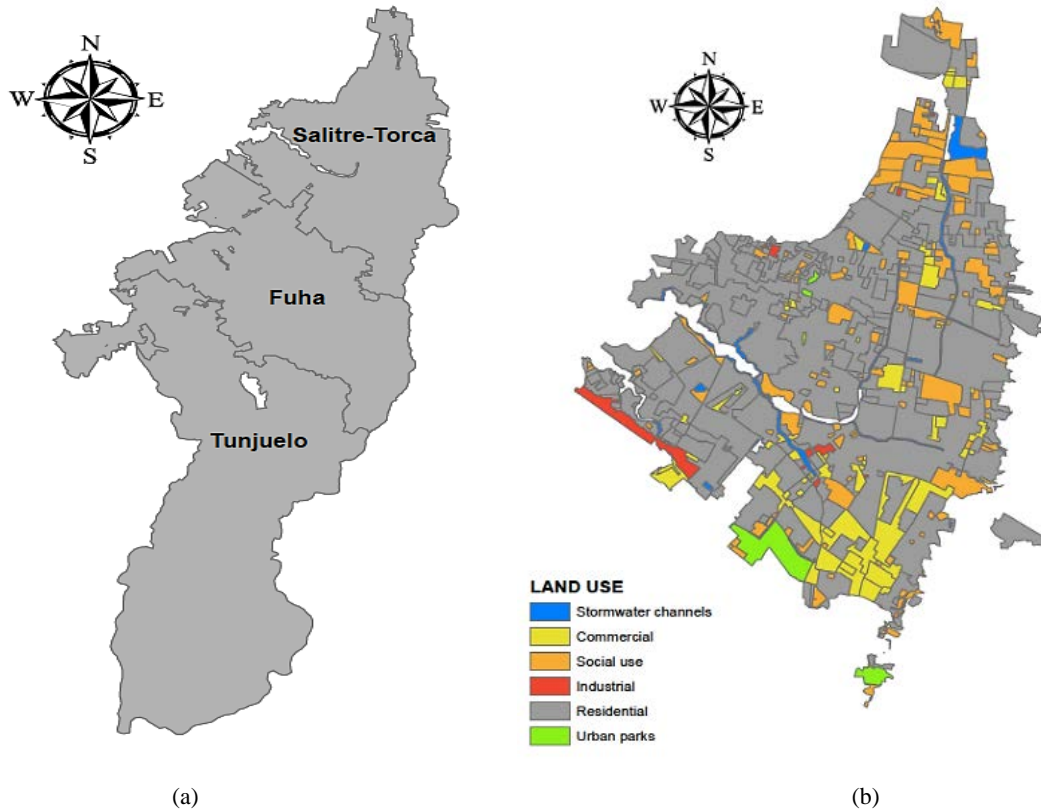


Fig. 1. (a) Urban catchments in Bogotá, (b) Land use of Salitre and Torca catchments

Table 1. Locations of measurements collected along the Torca, Molinos, and La Vieja Rivers

River	Site	Latitude	Longitude	Altitude (m.a.s.l)
Torca	1	4° 43' 39.37''	74° 01' 29.49''	2611
	2	4° 43' 44.5''	74° 01' 35.35''	2607
	3	4° 44' 01.54''	74° 02' 12.64''	2602
	4	4° 46' 11.43''	74° 02' 16.62''	2594
	5	4° 46' 44.47''	74° 02' 27.35''	2588
Molinos	1	4° 41' 11.71''	74° 02' 01.16''	2605
	2	4° 41' 21.30''	74° 02' 10.54''	2603
	3	4° 41' 37.08''	74° 02' 23.20''	2567
	4	4° 41' 52.62''	74° 03' 43.54''	2493
La Vieja	1	4° 38' 58.69''	74° 02' 53.16''	2707
	2	4° 39' 03.19''	74° 02' 56.96''	2710
	3	4° 39' 03.25''	74° 02' 58.97''	2695
	4	4° 39' 05.06''	74° 03' 01.95''	2683

Three urban rivers in the city of Bogotá were selected for the measurements: Molinos River (concrete-lined river), La Vieja Riva (natural river) and Torca River (river with both natural segments and concrete segments). The Molinos and La Vieja rivers drain into the Salitre river and the Torca river drains directly into the Bogotá river. The land use in the catchments of these rivers is predominantly residential (Fig. 1b), but there are also commercial, industrial, and institutional areas.

Possible measurement sites were identified for each river, in order of direction of flow (Fig. 2). At each site, characteristics such as flow rate and water depth were measured, since these characteristics could have very small values and may not meet the criteria

for use in the equations. Based on the above criteria, five sites were determined for Torca River, four sites for Molinos River, and four for La Vieja. These locations are described in Table 1.

2.2. Reaeration equations

We conducted a thorough literature review and created a compilation of the empirical and semi-empirical equations that predict the reaeration rate in rivers. The review produced over 30 equations, but only 20 equations were selected (Table 2). These selections were made based on the ability to apply the equations according to the operating conditions, and on the applicability of the equations as recommended

by each author, such as maximum and minimum depths, flow and velocity of the water. The equations are adapted for a temperature of 20°C, therefore the reaeration rate was adjusted for environmental temperature (Eq. 1):

$$k_{a,c} (d^{-1}) = k_{a,20} * 1.024^{(T-20)} \quad (1)$$

where: $k_{a,c}$: corrected reaeration rate value; $k_{a,20}$: empirical reaeration rate value; T : stream temperature (C°).

An initial equation was assigned to each measurement site. Equations were divided into four groups according the paper to Haider et al. (2013), in which group 1 was based on equations where the only variables were water depth and velocity. The second group contains equations that include the variables for slope, water depth, and velocity, and the third group includes travel time or dispersion coefficient. The last group includes equations that include the Froude number. Finally, an analysis by the river was developed. The reaeration rates were evaluated through a principal component analysis (PCA), and the resulting values were used to develop a hierarchical analysis with dendrograms.

2.3. Measured

Bogotá has two rainfall periods, which were taken into account for sample collection and analysis.

Measurements were recorded in April and May as well as in January and February to represent the rainy season. For the transition period, measurements were also recorded in the month of March. Two samples were collected for every site, and were averaged for use in the analyses.

Depth, slope, velocity, flow, and width of the river were measured at each location. A solutes transport model (advection-dispersion transport model) was used for the equations that use dispersion coefficients. The solutes transport model and the aggregated dead zone model, developed by Beer and Young in 1983, were used for equations that require travel time (Beer and Young, 1983; Young and Wallis, 1986). The mixing length was determined for these models and expressed as (Eq. 2):

$$L_m = 0.1v \frac{B^2}{E_{lat}} \quad (2)$$

where, L_m is mixing length in meters, v is flow velocity (m/s), B is channel width (m) and E_{lat} is the lateral dispersion coefficient (m²/s), which was estimated (Eq. 3) by:

$$E_{lat} = 0.6H \sqrt{gHS} \quad (3)$$

where H is the water depth (m), g is gravity (m²/s) and S is the slope (m/m).

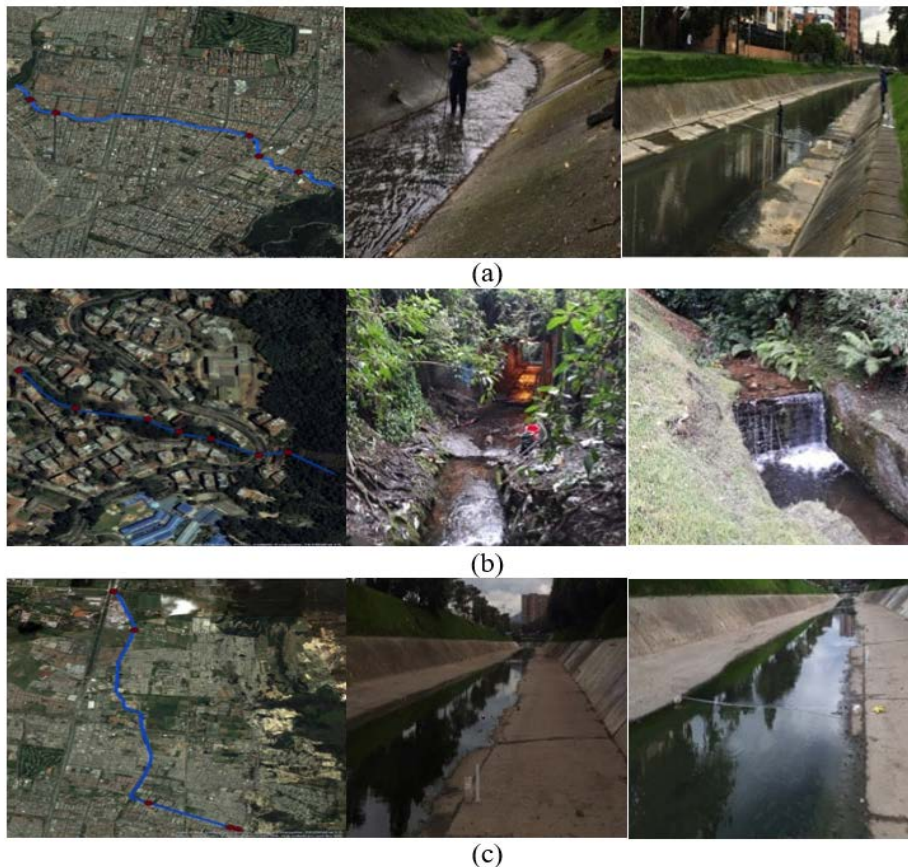


Fig. 2. Images of the geographic locations along rivers where measurements were collected: (a) Molinos River, (b) La Vieja River, (c) Torca River

Table 2. Selected reaeration equations

Author(s)	$k_{a,20} (d^{-1})$	Abbreviation	Group
O’connor and Dobbins (1958)	$k_a = 3.93 \frac{U^{0.5}}{H^{1.5}}$	OD	G1
Churchill et al. (1962)	$k_a = 3.93 \frac{U^{0.969}}{H^{1.673}}$	CH	G1
Owens et al. (1964)	$k_a = 5.34 \frac{U^{0.67}}{H^{1.85}}$	OG	G1
Owens et al. (1964)	$k_a = 6.935 \frac{U^{0.73}}{H^{1.75}}$	OW	G1
Langbein and Durum (1967)	$k_a = 5.135 \frac{U}{H^{1.33}}$	LD	G1
Isaac and Gaudy (1968)	$k_a = 4.74 \frac{U}{H^{1.5}}$	IG	G1
Negulescu and Rojanski (1969)	$k_a = 10.9 \left(\frac{U}{H} \right)^{0.85}$	NR	G1
Negulescu and Rojanski (1969)	$k_a = 0.0153 D_L \left(\frac{U}{H} \right)^{1.63}$	NR-DL	G3
Padden and Gloyna (1971)	$k_a = 4.547 \frac{U^{0.703}}{H^{1.408}}$	PG	G1
Bennett and Rathbun (1971)	$k_a = 4.547 \frac{U^{0.703}}{H^{1.408}}$	BR-S	G2
Bennett and Rathbun (1971)	$k_a = 5.585 \frac{U^{0.607}}{H^{1.689}}$	BR	G1
Tsivoglou and Wallace (1972)	$k_a = 0.1573 \frac{H}{t}$	TW	G3
Parkhurst and Pomeroy (1972)	$k_a = 23.04 \frac{10.17 F^2 S U^{3/8}}{H}$	PP	G4
Bansal (1973)	$k_a = 1.83 \frac{U^{0.6}}{H^{1.4}}$	B	G1
Grant (1976)	$k_a = 0.262 \frac{H}{t}$	G	G3
Tsivoglou and Neal (1976)	$k_a = 0.3609 \frac{H}{t}$	TN	G3
	$k_a = 0.1772 \frac{H}{t}$		
Long (1984)	$k_a = 1.923 \frac{U^{0.273}}{H^{0.42}}$	L	G1
Thyssen et al. (1987)	$k_a = 8784 \frac{U^{0.734} S^{0.93}}{H^{0.42}}$	TH	G2
Moog and Jirka (1999)	$k_a = 1740 U^{0.46} S^{0.79} H^{0.74}$	MJ	G2
Thackston and Dawson (2001)	$k_a = 0.00002519 F^{1/4} \frac{u_*}{H}$	TD	G4

$F = \frac{U}{\sqrt{gH}}$ = Froude number	S = Slope (m/m)
D_L = Longitudinal dispersion coefficient (cm ² /s)	U = Average velocity (m/s)
t = Time travel (d)	g = Acceleration due to gravity
H = average water depth (m)	$u_* = \sqrt{gRS}$ = Shear velocity (m/s)
	R = Hydraulic radius (m)

2.4. Statistical analyses

First, histograms were used to evaluate the frequency of the magnitudes obtained from equations that were applied to each site along each river. Next, a principal component analysis (PCA) was performed. This step reduced the dimensionality of the data set, which is useful for identifying variables that contain or represent all or most of the information in the data set, and thus makes it possible to perform different

exploratory analyses (Abdi and Williams, 2010). The first two components from the PCA were used since they explained more than 60% of the total variance. To evaluate the representation of the variables by the two selected components, the variable squared cosine (cos²) is used.

Following the PCA, we performed a hierarchical cluster analysis using Ward's method, which uses the minimum variability between clusters and seeks to make each cluster as homogeneous as

possible (Peña-Guzmán et al., 2019). This method allows for the generation of dendrograms that enable us to identify similarities between equations. To interpret the dendrogram, it is necessary to focus on the height at which the equations are joined, since the smaller this height, the more similar the equations are

3. Results and discussion

3.1. Performance analyses of the reaeration equations in rivers

Tables 3 and 4 show the average measurements obtained according to location and river, while Table 5 presents the results obtained by each equation for each site along the three rivers.

As shown in Table 5, the magnitude of the reaeration rates differs according to the river, measurement site, and equation. The varied rates underscore the difficulty in identifying a representative reaeration value for each of the evaluated sites.

Analyses of the reaeration rate magnitudes according to river and measurement site are shown below. At site 1 in the La Vieja River, reaeration values between 2.33 d⁻¹ and 26.85 d⁻¹ were calculated, with an average of 9.37 d⁻¹. The coefficients at site 2 were between 1.46 d⁻¹ and 28.76 d⁻¹ with an average of 7.70 d⁻¹, and were between 2.10 d⁻¹ and 32.59 d⁻¹ with an average of 10.36 d⁻¹ for site 3.

Finally at site 4, the values were between 1.37

d⁻¹ and 24.36 d⁻¹ with an average of 5.58 d⁻¹, and exhibited the lowest standard deviation (5.15). The small discrepancy in the rates between sites is mainly due to the small difference in hydraulic magnitudes between sections of the river. It is important to mention that there is no incoming or outgoing water along this river, resulting in nearly constant flow.

For the La Vieja River, the first interval (that includes the lowest values) of the histograms for all sites always included values generated by the equations LD, IG, B, CH, NR, PG, L, and MJ. Seven of these equations belonged to equations group 1 (77% of the equations of this group) and one belonged to equations group 2. For the other intervals, the equations varied mainly for site 3. Finally, the values calculated with the TH equation were always in the largest intervals (the last one for sites 1, 3, and 4 and the third to last interval for site 2). The histograms are presented in Fig. 3. At site 1 in the Molinos River, the lowest determined value was 2.05 k_a d⁻¹ and the highest value was 69.84 d⁻¹, resulting in an average of 21.72 k_a d⁻¹. At site 2, the reaeration rates ranged from 4.42 d⁻¹ to 96.19 d⁻¹, with an average of 21.23 k_a d⁻¹. The rates ranged from 1.74 k_a d⁻¹ to 140.96 k_a d⁻¹ with an average of 41.20 d⁻¹ for site 3, and from 1.35 k_a d⁻¹ to 248.62 k_a d⁻¹ with an average of 66.66 k_a d⁻¹ for site 4. As for sites 3 and 4, the increase in reaeration rates is mainly due to a decrease in water depth and an increase in velocity. For the equations in group 3, reaeration rates decreased between sites 3 and 4, due to the increase in travel time.

Table 3. Average values for each input parameter and La Vieja and Molinos rivers

Parameter	Unit	La Vieja				Molinos			
		S1	S2	S3	S4	S1	S2	S3	S4
Average velocity	m/s	0.060	0.056	0.068	0.047	0.061	0.138	0.205	0.239
Depth	m	0.20	0.27	0.16	0.25	0.10	0.17	0.09	0.07
Width	m	1.20	1.00	1.50	0.90	5.65	3.40	6.30	7.10
Flow	m ³ /s	0.014	0.015	0.016	0.011	0.034	0.080	0.116	0.119
Slope	m/m	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01
Length of reach	m	100	100	100	100	500	500	500	500
Longitudinal dispersion coefficient	m ² /s	0.66	0.66	0.40	0.40	0.98	0.98	0.05	0.05
Travel time	day	0.0030	0.0030	0.0106	0.0106	0.0040	0.0040	0.0072	0.0072

Note: Values for longitudinal dispersion coefficient and travel time are determined by reach

Table 4. Average values for each input parameter and Torca river

Parameter	Unit	Torca					
		S1	S2	S3	S4	S5	S6
Average velocity	m/s	1.36	1.03	0.09	0.22	0.08	0.13
Depth	m	0.07	0.09	0.15	0.19	0.22	0.40
Width	m	1.62	1.52	6.80	5.65	10.40	5.50
Flow	m ³ /s	0.154	0.140	0.098	0.235	0.184	0.285
Slope	m/m	0.20	0.17	0.01	0.01	0.01	0.01
Length of reach	m	500	500	500	500	500	500
Longitudinal dispersion coefficient	m ² /s	0.560	0.560	0.796	0.796	0.996	0.996
Travel time	day	0.0064	0.0064	0.0057	0.0057	0.0134	0.0134

Note: Values for longitudinal dispersion coefficient and travel time are determined by reach

Table 5. Calculated reaeration rates according to river

Equation	La Vieja				Molinos				Torca					
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S5	S6
OD	9.56	5.89	14.30	6.08	27.32	18.56	58.65	92.30	220.16	131.23	18.67	19.73	9.60	4.97
CH	3.94	2.23	6.55	2.14	12.79	11.96	51.24	90.85	516.88	256.55	10.25	15.66	4.51	2.68
OG	14.09	7.72	23.32	7.96	51.49	33.40	140.96	248.62	796.93	414.76	33.00	36.89	14.39	6.55
OW	13.21	7.43	21.55	7.52	45.09	32.40	131.36	228.02	811.26	425.73	30.93	37.19	13.86	6.90
LD	2.33	1.46	3.59	1.37	5.97	6.69	23.09	37.58	213.82	115.59	5.49	9.10	2.75	2.00
IG	2.83	1.68	4.53	1.60	8.17	8.36	32.16	54.63	310.83	161.01	7.02	11.16	3.29	2.16
NR	3.48	2.54	4.72	2.36	6.38	8.16	19.56	27.58	120.87	76.89	6.66	10.93	4.12	3.72
NR-DL	12.60	6.90	13.75	3.62	60.09	96.19	28.45	54.98	9652.51	4054.67	52.79	136.45	26.33	21.63
PG	3.05	2.12	4.24	2.04	6.42	6.53	16.82	24.41	82.87	52.19	5.77	8.00	3.39	2.53
BR-S	14.01	9.92	18.75	10.56	35.45	26.74	52.55	75.09	348.80	227.99	21.73	24.53	13.46	9.02
BR	13.63	7.87	21.58	8.10	44.49	29.85	110.94	186.11	534.67	294.93	29.58	32.62	13.87	6.75
TW	9.29	12.54	2.10	3.28	3.45	5.86	1.74	1.35	1.53	1.96	3.61	4.58	2.29	4.16
PP	6.34	4.57	8.34	4.97	16.56	12.18	21.49	30.44	179.69	118.35	9.29	10.42	5.92	4.07
B	2.81	1.77	4.17	1.79	7.52	5.85	18.03	28.09	79.73	47.39	5.60	6.58	2.94	1.69
G	15.47	20.88	3.50	5.47	5.74	9.77	2.90	2.25	2.54	3.27	6.02	7.62	3.81	6.93
TN	21.30	28.76	4.82	7.53	7.91	13.45	3.99	3.10	3.50	4.50	8.29	10.50	5.25	9.54
L	3.34	2.51	4.23	2.57	6.24	4.86	9.55	12.46	20.04	14.82	4.92	4.98	3.32	2.22
TH	26.85	22.50	32.59	24.36	69.48	82.43	84.13	115.38	6703.26	4219.81	34.92	64.36	26.01	32.05
MJ	3.39	4.10	3.06	3.58	2.05	4.42	3.31	2.95	6.55	6.94	3.41	5.92	4.16	8.07
TD	5.93	4.39	7.41	4.74	11.86	6.97	13.17	16.94	16.94	13.17	7.90	6.24	5.39	2.96
Average	9.37	7.89	10.36	5.58	21.72	21.23	41.20	66.66	1031.17	532.09	15.29	23.17	8.43	7.03
Standard Deviation	6.90	7.70	8.77	5.15	21.32	25.24	43.23	74.78	2503.24	1240.22	13.89	30.69	7.36	7.40

An analysis of the histograms (Fig. 4) for the Molinos River revealed that the first interval in the histograms always represents the largest number of equations, similar to the La Vieja River. However, for all sites from the Molinos River, the number of equations was greater than or equal to 10 (more than 50% of the equations).

The first interval for all sites always included values estimated using the equations: LD, NR, PG, TW, PP, B, G, TN, L, MJ, and TD. This indicates that

the equations in group 1 were dominant among the values of smaller magnitude, since five equations from equations group 1 were represented. As for the other groups, only one equation (MJ) from equations group 2 was represented, while three equations from group 3 and two equations from group 4 were represented in the first interval. The last interval of the histograms for sites 1 and 2, equations NR-DL and TH yielded the highest values. For sites 3 and 4, equation OG yielded the highest values.

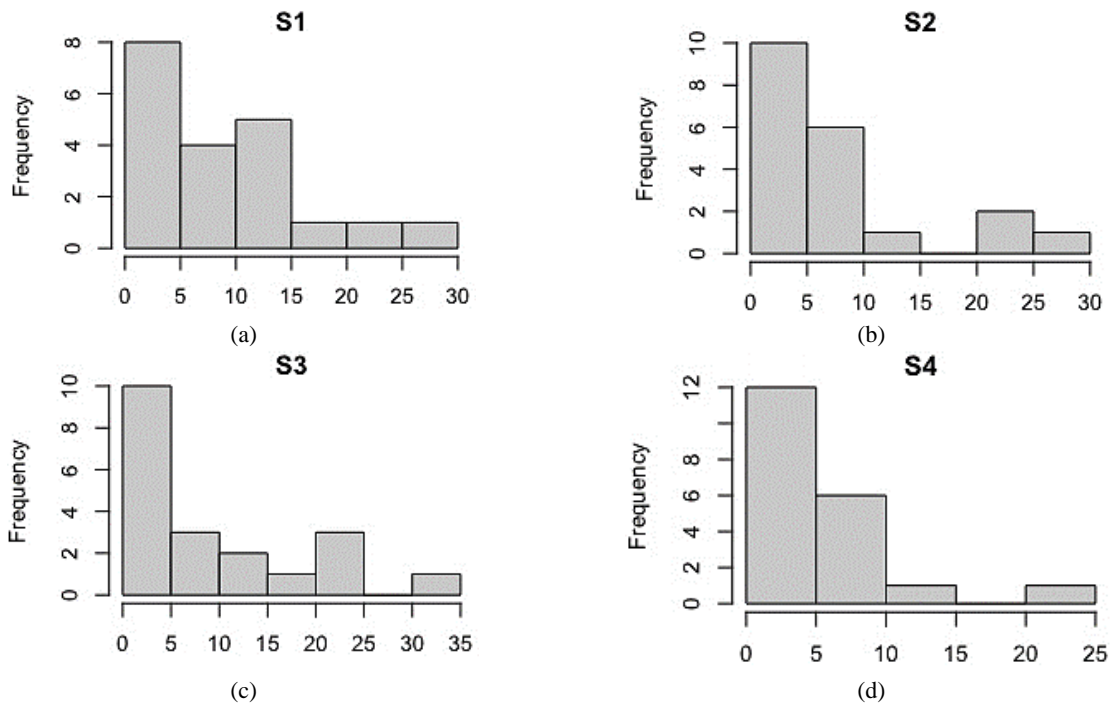


Fig. 3. Histograms of reaeration rates for La Vieja River at four sites: (a) site 1, (b) site 2, (c) site 3, (d) site 4. Rates were calculated using 20 different equations

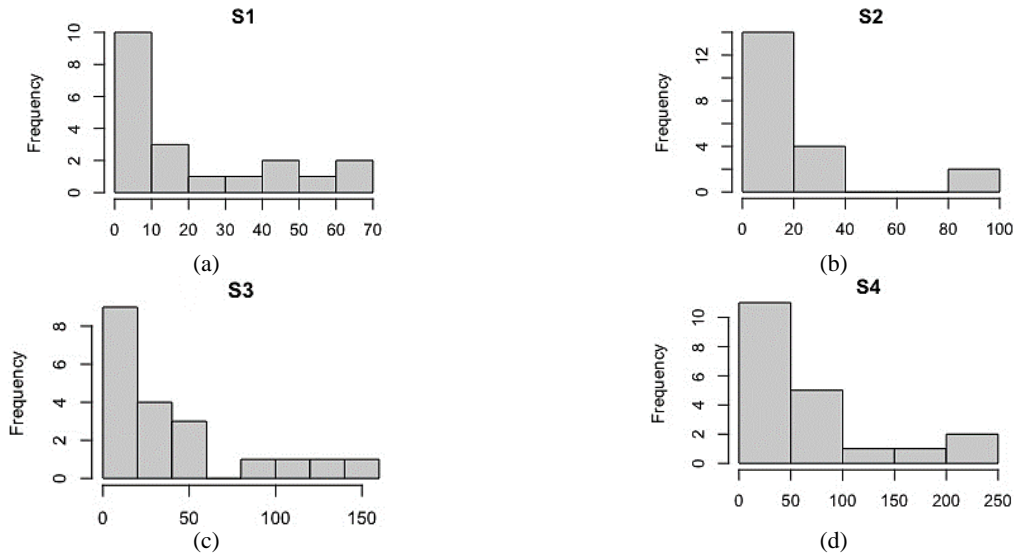


Fig. 4. Histograms of reaeration rates for Molinos River at four sites: (a) site 1, (b) site 2, (c) site 3, (d) site 4. Rates were calculated using 20 different equations

For the Torca River, the lowest value found at site 1 was 1.53 d^{-1} and the highest value was 9652.25 d^{-1} , with an average of 1031.17 d^{-1} . This site had the highest values for velocity and slope and the lowest value for water depth, making the reaeration rates at this site the highest in the Torca River. Reaeration rates ranged from 1.96 d^{-1} to 4219.81 d^{-1} with an average of 532.09 d^{-1} at site 2. The reaeration rates decreased at this site. This was mainly due to the decrease in velocity and the increase in water depth. The reaeration rates continued to decrease at site 3, with the rates ranging from 3.41 d^{-1} to 52.72 d^{-1} and an average of 15.29 d^{-1} . These results are mainly due to a decrease in velocity and an increase in depth. In addition, both sites 3 and 5 had the lowest values for slope. The rates at site 4 were slightly higher than at site 3, due to an increase in velocity. The reaeration rates at site 4 ranged from 4.58 d^{-1} to 136.45 d^{-1} with an average of 23.17 ka d^{-1} . The rates were lower still at site 5 due to the lower values for velocity and slope and higher a value for water depth, with a range of 2.29 d^{-1} to 26.33 d^{-1} and an average of 18.43 d^{-1} . Finally, more than 80% of the rates at site 6 were lower compared to the other sites, due to having the highest value for water depth. Additionally, site 6 exhibited the lowest value for standard deviation at 7.40 and a range of reaeration values, from 1.69 d^{-1} to 32.05 d^{-1} with an average of 7.03 d^{-1} . A histogram of the reaeration rates is shown in Fig. 5.

For all sites along the Torca River, between 50% and 90% of the equations produced values that were in the interval. For sites 1, 2, 4, and 6, equations NR-DL and TH produced the highest reaeration values compared to the other equations. The previous analyses have shown that velocity and depth greatly affect the rates of reaeration. This indicates that reaeration rates exhibit a very high sensitivity to these two variables, especially water depth.

3.2. Statistical analysis of the performance of the reaeration equations in rivers

According to the principal component analysis, for the La Vieja River, all equations were represented by two components (PC1 and PC2). This is due to small differences in the hydraulic conditions in the La Vieja River. PCA shows that the equations that are most represented by the first component (PC1), with \cos^2 values between 0.9 and 0.99, are CH, LD, IG, NR, PG, B, L, TH, MJ, and TD. Equations NR-DL, BR-S, and PP are represented to a lesser extent with \cos^2 values between 0.8 and 0.89. It is important to mention that equations TH and NR-DL account for the greatest amount of variance to PC1, as shown by their large values. Equations OD, TW, G, and TN contribute the most to the second component (PC2), and the remaining equations OW and OG contribute similarly to both components. Of note, equations TW, G, and TN exhibit inverse relationships with the other equations (Fig. 6a). The dendrograms for the La Vieja River (Fig. 6b) generated four clusters. These include two main clusters. The first cluster includes equations LD, PG, IG, B, MJ, CH, L, NR, seven of which are from group 1 and one is from group 2. The second cluster is composed of equations BR-S, OG, OW, and BR, of which three equations are in group 1 and one is from group 2.

For the Molinos River, there was an increase in the variance between equations due to differences in hydraulic variables, as described above. The contributions of the equations to the two components and their \cos^2 values (Fig. 7a) were examined. Those that contributed most to PC1, with values from 0.99 to 0.9, were equations LD, NR, PG, TW, PP, B, G, TN, L, MJ, and TD. Other equations that contributed to a slightly smaller degree, with \cos^2 values between 0.8 and 0.89, were OG, OW, and BR.

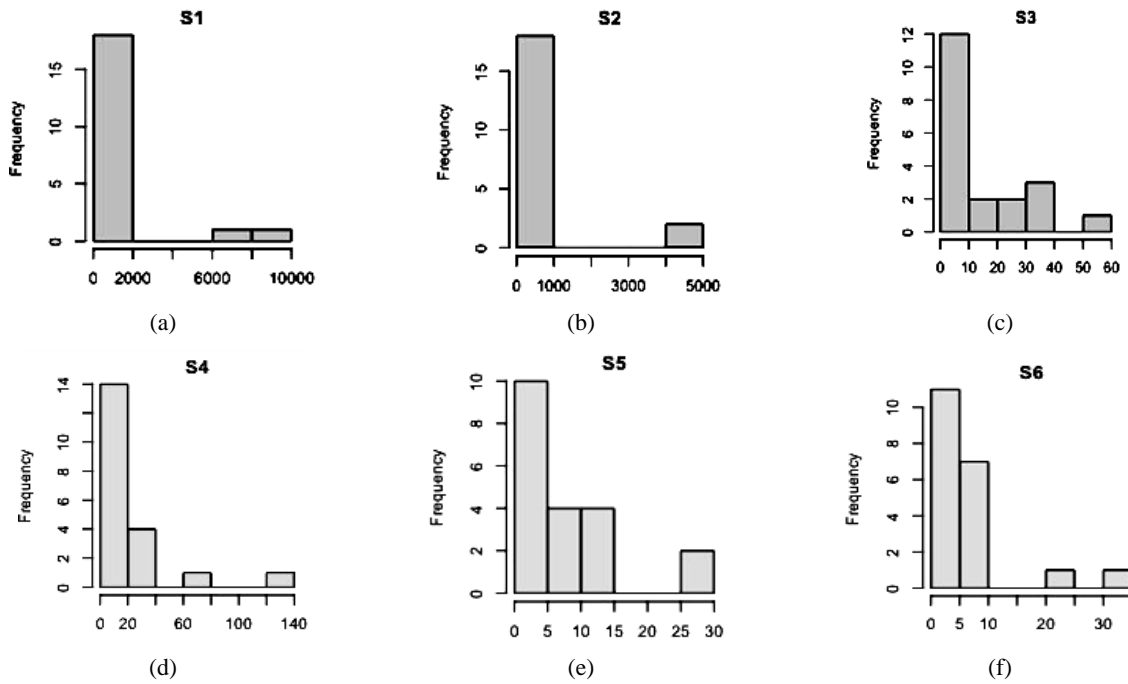


Fig. 5. Histograms of reaeration rates for Torca River at six sites: (a) site 1, (b) site 2, (c) site 3, (d) site 4, (e) site 5, (f) site 6. Rates were calculated using 20 different equations

However, because of the location of these equations on the graph (Fig. 7a), they also contribute less to PC2. Equations CH and to a lesser extent, NR-DL are the main equations that contribute to PC2. Equations OD, IG, BR-S, and TH contribute to both PC1 and PC2, but with a slightly bigger contribution to PC1. PCA reveals an inverse relationship between equations NR-DL, TW, G, and TN.

A dendrogram of the Molinos River (Fig. 7b) revealed four clusters. Of these four clusters, one was defined by the shortest distances and included equations OD (from group 1) and BR-S (from group 2). A second cluster contained equations OW, OG and BR, all from group 1. Within the largest cluster (in yellow in Fig. 7b) there were two subclusters: subcluster 1, composed of MJ, TW and G (from group 3) and TN (from group 2); and subcluster 2, composed of LD, PG, B, NR, L, and IG (from group 1) and TD and PP (from group 4).

We performed a PCA of the Torca River (Fig. 8a.) data which revealed a high degree of variance between the equations. This is due to the wide range of values for velocity and depth. Equations that contribute most to PC1 are NR, NR-DL, PG, TW, PP, B, L, TH, and TD. Equations CH, LD, IG, and G contributed slightly less with \cos^2 values between 0.8 and 0.89. Equations OD, BR, OG, and OW contribute the most to PC2, but they also contribute to PC1 to a lesser extent. Equations OG, OW, BR-S, and BR contribute to both components PC1 and PC2, due to their sensitivity to depth, producing the highest values (with the exception of NR-DL, which uses travel time as reference) for this river. PCA revealed an inverse relationship for equations TW, G, and TN. The dendrogram for the Torca River (Fig. 8b) shows three

large subclusters within the larger yellow cluster, based on distance: the first subcluster includes equations TN and G (from equations group 3) and MJ (from equations group 2); the second subcluster includes equations TW (from group 3) and LD, PG, L, and B (from group 1); and the third subcluster includes PP, CH, TD, IG, and NR (from group 1) and PP and TD (from group 4). In addition, there are two subclusters within the grey cluster: the first subcluster includes equations BR, OW, and OG (from group 1); and the second cluster contains equations OD (from group 1) and BR-S (from group 2).

Finally, we analyzed the dominant clusters that were obtained from heights generated in the dendrograms of the three the rivers (Table 5). Table 6 shows that for the three rivers, equations LD, PG, L, and B were consistently in cluster the most dominant cluster and were all from group 1. The average standard deviation was calculated for the results obtained for only this group of equations for each river. We found that the standard deviation was 0.42 for the La Vieja River, 4.37 for the Molinos River, and 21.11 for the Torca River. This shows that the analyses using PCA and dendrograms allowed us to identify equations with smaller differences, mainly in the Vieja and Molinos Rivers. This information could provide some evidence for ecommending these equations for application in rivers with low flow and water depth. The second dominant cluster is composed of equations OW and OG, both from group 1. The average standard deviations for each river was 0.50 for the La Vieja River, 13.22 for the Molinos River, and 38.83 for the Torca River, showing a greater standard deviation between the three rivers despite having fewer equations.

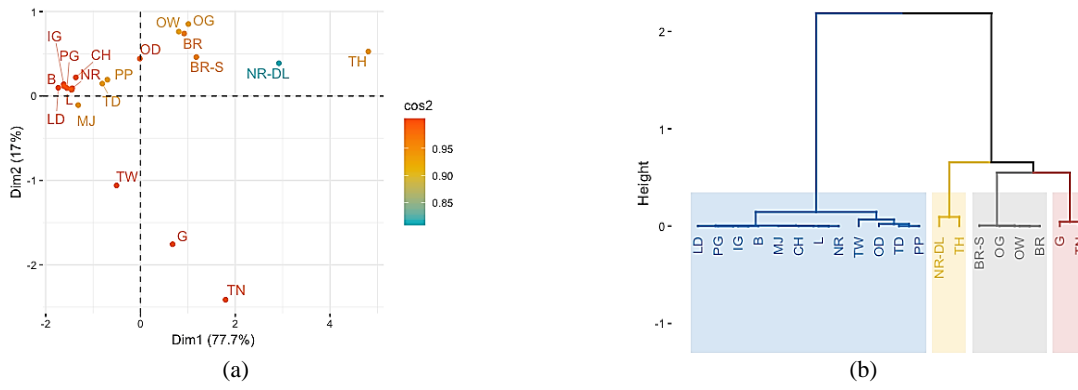


Fig. 6. (a) PCA of the La Vieja River. (b) Dendrogram obtained from PCA

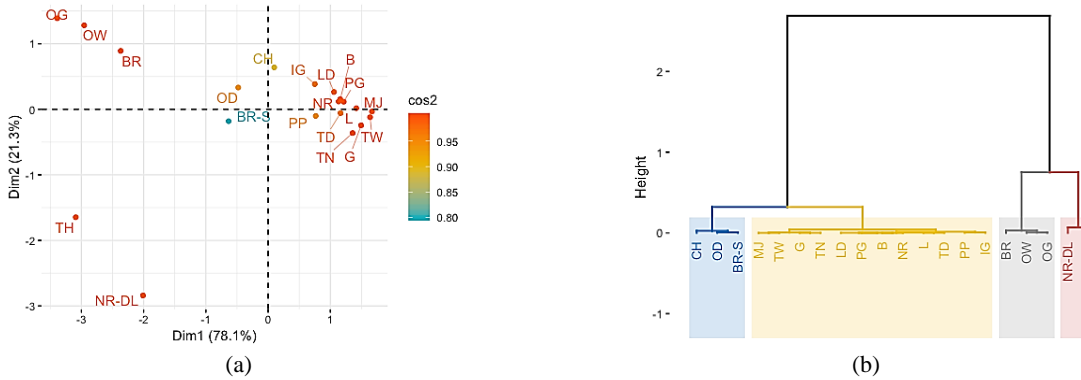


Fig. 7. (a) PCA of the Molinos River. (b) Dendrogram obtained from PCA

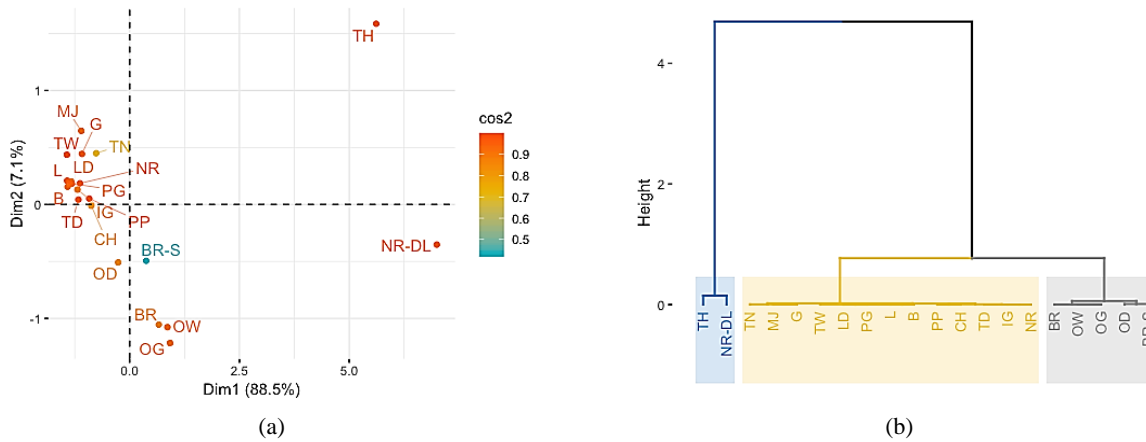


Fig. 8. (a) PCA of the Torca River. (b) Dendrogram obtained from PCA

Table 6. Dominant clusters by river

River	Cluster 1	Cluster 2	Cluster 3
La Vieja	LD (G1)	OW (G1)	
	PG (G1)	OG (G1)	
	L (G1)	BR (G1)	
	B (G1)		
Molinos	LD (G1)	OW (G1)	TN (G3)
	PG (G1)	OG (G1)	MJ (G2)
	L (G1)	BR (G1)	G (G3)
	B (G1)		
Torca	LD (G1)	OW (G1)	TN (G3)
	PG (G1)	OG (G1)	MJ (G2)
	L (G1)	BR (G1)	G (G3)
	B (G1)		

On the other hand, two subgroups were identified for only two rivers, the first subgroup is composed of equation MJ from group 2 and TN and G from group 3 for the Molinos and Torca Rivers. The average standard deviation was 2.12 for the Molinos River and 1.80 for the Torca River, indicating that this group of equations is well-suited for large rivers with stronger flow. In addition, their standard deviation values did not vary much despite the differences in water depth and velocity. This could be due to the fact that the equations in group 3 apply the travel time variable, which can accurately describe the hydrodynamic characteristics of the rivers. Accurate characteristics are recorded through tracers that travel as a solute in the water, allowing us to characterize the different conditions of water flow in the river.

3.3. Recommendations for the evaluation of reaeration rates

The main objective of this paper was to identify and highlight the variations and patterns and determine groups of equations based on their reaeration rates magnitudes. However, determining an equation that represents the true conditions for reaeration in rivers was difficult, due to hydrodynamic variability and geomorphology. We have therefore decided to establish some recommendations that may be helpful to readers for the evaluation and application of these equations, based on the literature and laboratory-scale experimentation.

The previous analyses clearly show that there are large differences in the magnitude of values generated by each of the equations that were evaluated. These differences must be independent of the variables within them, since we observed groupings of equations that are based on different variables. On the other hand, as is evidenced by velocity and water depth and the sensitivity of these variables, the equations show a range of conditions and their results can vary dramatically.

First, we recommend trying to determine reaeration rates by using in situ techniques, such as tracers and dissolved oxygen balances, as the hydraulic and hydrodynamic characteristics of rivers can rapidly change over short distances. These results can then be compared with the empirical equations and the appropriate equation can be selected based on these comparisons. Once an equation is identified or defined, it can be used to analyze water quality in situations of climate change, geomorphological alterations and hydraulic variability, to which urban rivers are especially vulnerable.

We also recommend the use of both gas and dye tracers to define river characteristics such as hydraulic, hydrodynamic, dispersion and dilution properties. These tracers are advantageous because they are water soluble and can accurately depict the characteristics of river water. The gaseous tracers that are mainly used are sulfur hexafluoride (SF₆), xenon

(Xe), krypton (Kr), and propane, which are solubilized in conservative tracers such as Rhodamine WT (de Souza Ferreira et al., 2020; Jin et al., 2012; Knapp et al., 2019, 2015; Reid et al., 2007; Soares et al., 2013). These gases are added to the water and then measured downstream, and the loss of tracer to the atmosphere is used as a proxy for gas exchange, allowing for the calculation of the reaeration rate (Benson et al., 2014). A disadvantage of this technique is the need for specialized equipment, mainly gas chromatographs, which can be costly (Gonçalves et al., 2018; Morse et al., 2007).

Mass balance models can be used to measure the metabolism of oxygen consumption in the source surface water, and water quality variables such as dissolved oxygen and biochemical oxygen. The variables are measured at site of interest, such as upstream, downstream, and at tributary inputs, and the rates of photosynthesis and respiration are also measured (Arora and Keshari, 2018; Jha et al., 2004, 2001; Kalburgi et al., 2015). The main advantage of this method is the ease of collecting DO and BOD measurements, for which there are numerous techniques.

Authors such as Moog and Jirka (1999), Jha et al. (2001), Omole et al. (2013), Palumbo and Brown, (2014), Kalburgi et al. (2015), and Arora and Keshari (2018), among others, have proposed the use of statistical analyses of absolute and relative error and performance coefficients to compare reaeration rates measured in the field with those determined using equations. Some of these equations are shown in Table 7.

4. Conclusions

Reaeration equations are fundamental to determining the quality of bodies of water. However, the characteristics of these equations and their variables reveal differences that are at times significant, suggesting the over- or underestimation of reaeration rates. According to Gualtieri et al. (2002), no one equation can be applied to all hydrodynamic conditions; on the contrary, each equation is specific to a particular stream or river, and this was clearly observed in our results. We determined that each of the three rivers as well as each segment of the rivers (except for the La Vieja River) had different conditions and drastically varied values.

The variables that most significantly influenced reaeration rates in our study were velocity and depth. Velocity showed a linear increase, and depth showed an accelerated decrease with the increase in velocity. This however, does not occur with equations TW, G, and TN, which demonstrated an inverse relationship. For the La Vieja River, the equations that yielded the lowest values at all sites were LD, IG, B, CH, NR, PG, L, and MJ, most of which belong to group 1 (one is from group 2). The equation with the highest value was TH.

Table 7. Equations for measured error

Name	Equation	Optimal value
Mean multiplicative error (MME)	$MME = \exp \left[\frac{\sum_{i=1}^n \ln \left(\frac{k_{a,M}}{k_{a,P}} \right)_i}{n} \right]$	Optimal value 0
Bias factor (BF)	$BF = \exp \left[\frac{\sum_{i=1}^n \ln k_{a,M} - \ln k_{a,P}}{n} \right]$	Optimal value 0
Standard error (SE)	$SE = \exp \left[\sum_{i=1}^n \frac{(k_{a,P} - k_{a,M})^2}{n} \right]^{1/2}$	Optimal value 0
Normalized mean error (NME)	$NME = \frac{100\%}{n} \sum_{i=1}^n \left(\frac{k_{a,P} - k_{a,M}}{k_{a,M}} \right)_i$	Optimal value 0
Nash–Sutcliffe model efficiency coefficient (NSE)	$NSE = 1 - \frac{\sum_{i=1}^n (k_{a,M} - k_{a,P})^2}{\sum_{i=1}^n (k_{a,M} - \overline{k_{a,M}})^2}$	Optimal value 1
Coefficient of determination (R2)	$R^2 = \frac{\sum_{i=1}^n (k_{a,P} - k_{a,M})^2}{\sum_{i=1}^n (k_{a,P} - \overline{k_{a,P}})^2}$	Optimal value 1
Root mean square error (RMSE)	$RMSE = \sqrt{\frac{\sum_{i=1}^n (k_{a,P} - k_{a,M})^2}{n}}$	Optimal value 0

where: $k_{a,M}$: Reaeration rate measured (d⁻¹); $k_{a,P}$: Reaeration rate predicted (d⁻¹); $\overline{k_{a,P}}$: Mean of reaeration rate predicted (d⁻¹); $\overline{k_{a,M}}$: Mean of reaeration rate measured (d⁻¹); n : Number measured

For the Molinos River, the equations with the lowest reaeration rate values were LD, NR, PG, B, and L from group 1, MJ from group 2, TW, G and TN from group 3 and PP and TD from group 4. For the Torca River, the high values generated by equation NR-DL resulted in between 50% and 90% of the other equations, with relatively low values, being represented in the first interval of the histogram. Based on this information, we can conclude that differences in hydraulic characteristics at different locations along the same river achieves the grouping of equations from all groups.

We performed PCA for the three rivers and found that equations NR, PG, B, and L from group 1 and TD from group 4 had cos2 values between 0.99 and 0.9 for the first component, PC1. Equation OD consistently contributed to the second component, PC2.

Equations TH and NR-DL did not generate a reliable cluster as they exhibited the greatest distances in the dendrograms. This is because they yielded large magnitude values compared to the other equations.

Inverse relationships were observed between equations TW, G, and TN, all of which belong to group 3. This is consistent with the principles of travel time, since increasing the distance between sites also increases the travel time, thus decreases the reaeration

rate. However, it is important to note that in rivers with dramatic changes in hydrodynamics due to the river segments selected, the reaeration rate may not be accurate.

For decision-making and the management of urban basins, particularly those that are in the process of decontamination, the rapid changes in the materials, slope, flow, level of pollutants and land use associated with these basins make it necessary to have reliable data. For this reason, we demonstrate the differences in the rates of reaeration as determined by empirical or semi-empirical equations, providing guidance for their application. However, we recommend the use of in situ methods and analyses to more reliably determine the rate of reaeration for decision-making purposes.

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