

DOI: 10.24850/j-tyca-2019-02-09

Note

**Measurement of sediment oxygen demand rates for
benthic demand of Tercero (Ctalamochita) River,
Córdoba province, Argentina**

**Cuantificación de la constante de desoxigenación por
demanda bentónica del río Tercero (Ctalamochita),
provincia de Córdoba, Argentina**

María Laura Chalimond¹

Marina Ferreyra²

Ana María Cossavella³

¹Secretaría de Recursos Hídricos y Coordinación, Córdoba, Argentina,
mlaura.chali@gmail.com

²Secretaría de Recursos Hídricos y Coordinación, Córdoba, Argentina,
marinaferreyra69@gmail.com

³Secretaría de Recursos Hídricos y Coordinación, Córdoba, Argentina.
Universidad Tecnológica Nacional, Facultad Regional Córdoba.
Universidad Nacional de Córdoba, Facultad de Ciencias Exactas Físicas y
Naturales, acosav@gmail.com

Correspondence author: María Laura Chalimond,
mlaura.chali@gmail.com

Abstract

Modeling of dissolved oxygen technique in rivers is a valuable tool for assessing water quality. Hence, assessment of different processes is of great importance, like benthic demand, that is to say, oxygen consumption of the water column in the water-sediment interface. At the moment there are no previous studies related to this field for the Tercero (Ctalamochita) River (Córdoba, Argentina). This study aimed to

measure the benthic demand of Tercero (Ctalamochita) River from sediment samples that were taken at eight sites in five campaigns during one year (June, 2013 to June, 2014), using individual respirometers. Taking into account the variation of the dissolved oxygen as regards time, water volume, sediment area and characteristics of respirometers, benthic demand was estimated using the equation of Nolan and Johnson, (1979) proposed by the USEPA. Since there is no previous data, it was impossible to compare the acquired results. However, the range values found at 20 °C was between 0.040 and 0.484 gO₂/m²d, being similar to those reported by the USEPA for mineral and sandy river sediments (0.05-1.00 gO₂/m²d). These results allow us to understand the behavior of benthic sediment and its influence on the dissolved oxygen.

Keywords: Sediment oxygen demand, individual respirometers, dissolved oxygen, Tercero (Ctalamochita) River.

Resumen

La modelación del oxígeno disuelto de un río constituye una valiosa herramienta en la evaluación de su calidad. De allí la importancia de valorar los distintos procesos involucrados, entre ellos la demanda bentónica, es decir, el consumo de oxígeno de la columna de agua en la interfaz agua-sedimento. Considerando que no se dispone de ningún estudio experimental referido a este tema para el río Tercero (Ctalamochita), Córdoba, Argentina, este trabajo tiene como objetivo cuantificar en nivel de laboratorio su demanda bentónica en ocho sitios a lo largo de su cauce, a partir de muestras de sedimento tomadas en cinco campañas efectuadas entre junio de 2013 y junio de 2014, empleando respirómetros individuales. Teniendo en cuenta la variabilidad del oxígeno disuelto en función del tiempo, el volumen de agua confinada, la superficie del sedimento y las características de los respirómetros, se calculó la demanda bentónica, aplicando la ecuación utilizada por Nolan y Johnson (1979), propuesta por USEPA. La falta de antecedentes para el río en estudio imposibilitó comparar los resultados obtenidos; sin embargo, el intervalo de valores hallados a 20 °C estuvo comprendido entre 0.040 y 0.484 gO₂/m²d, siendo similares a los reportados por USEPA para sedimentos minerales y arenosos de ríos (0.05-1.00 gO₂/m²d). Los resultados obtenidos permiten comprender el

comportamiento del sedimento béntico y su influencia en el oxígeno disuelto del cuerpo hídrico en estudio.

Palabras clave: Demanda bentónica, respirómetros individuales, oxígeno disuelto, río Tercero (Ctalamochita).

Received: 07/07/2015

Accepted: 30/07/2018

Introduction

When assessing the quality of a river, modeling of dissolved oxygen (DO) is relevant since different processes that provide and consume oxygen are considered. Among these, we can find sediment oxygen demand (SOD), defined as dissolved oxygen consumption of the water column given through the combination of biological, biochemical and chemical processes in the water-sediment interface (Lee & Jones-Lee, 2000).

Aims

- Propose a methodological guideline to determine benthic demand using individual respirometers.
- Measure the sediment oxygen demand of Tercero (Ctalamochita) River, upstream and downstream from sewage discharge.

Study area

Tercero (Ctalamochita) River, one of the most important rivers of the Province of Córdoba, springs in the Reservoir Piedras Moras. It flows about 300 km of territory west-east along the province and is indirect tributary of Paraná River, which belongs to the Plata River basin. Throughout its course this river is used for the supply of drinking water, to water land, as well as for industrial and hydroelectric use. Its main pollution source derives from the urbanization close to its riverbed, and because the river is an effluent receptor of several industries, apart from sewage disposal of four treatment plants. They come from the City of Río Tercero, Villa María, Bell Ville and Monte Buey and a rain channel that crosses an agricultural and cattle basin (Bell Ville derivation channel) (Cossavella *et al.*, 2013).

Materials and methods

Monitoring sites and sampling

Eight sites were selected (Figure 1) for sediment sampling based on the physical features of the place, water flow speed, the possibilities to access safely to the river banks and uses of the river and mainly on wastewater disposal:

1. Station one: Balneario Almafuerte (BA) (S 32°10'11" W 64°15'59") this place receives water directly from Reservoir Piedras Moras.

2. Station two: Balneario Río III (BIII) (S 32°09'36" W 64°06'40") after an effluent dumping from an important industry development zone.
3. Station three: Bridge Los Potreros (PLP) (S 32°09'29" W 64°01'39") downstream from the Río Tercero City sewage discharge.
4. Station four: Bridge Andino (PA) (S 32°25'12" W 63°18'11"), a place located far away from an effluent dumping.
5. Station five: Downstream from the Villa María City sewage discharge (BOSN) (S 32°27'48" W 63°11'00") 130 km from the Reservoir Piedras Moras.
6. Station six: Ballesteros (AB) (S 32°34'54" W 63°00'20") upstream from the Bell Ville City sewage discharge.
7. Station seven: Downstream from the Bell Ville City sewage discharge (AACCBV) (S 32°36'55" W 62°37'47") 236 km from the Reservoir Piedras Moras.
8. Station eight: Saladillo (MB) (S 32°54'50" W 62°19'33") downstream from the Monte Buey City sewage discharge, located 294 km from the Reservoir Piedras Moras, a few meters from the confluence with Saladillo River.

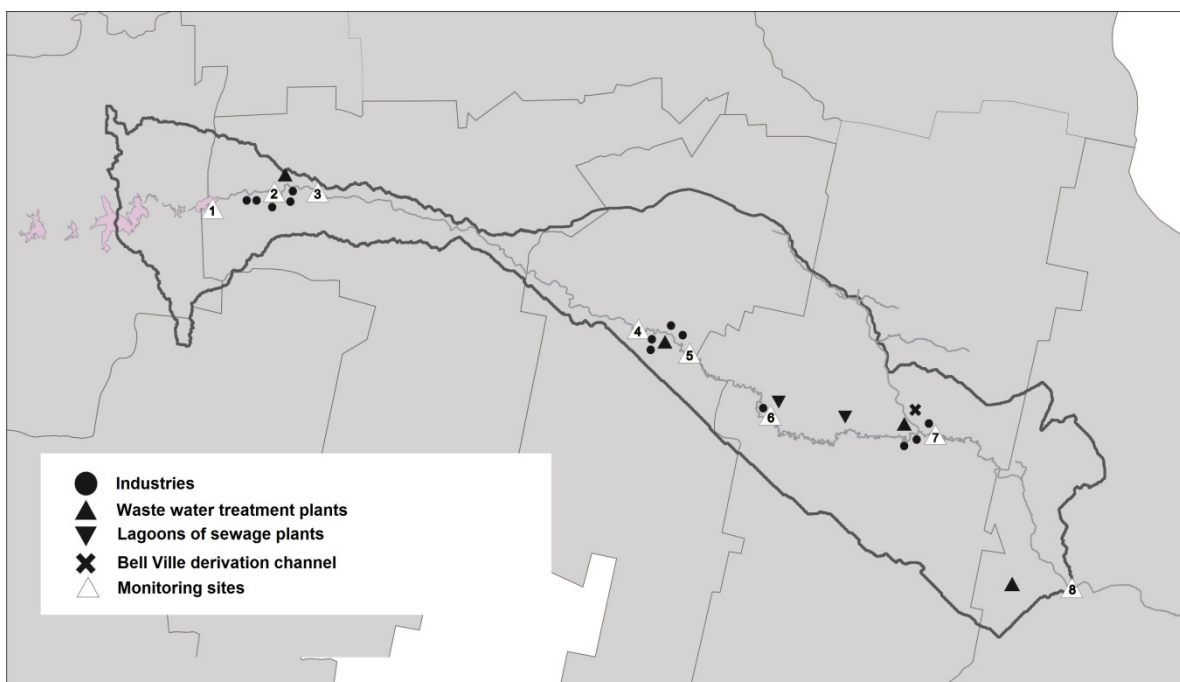


Figure 1. Sediment monitoring sites and location of sewage exit. Tercero (Ctalamochita) River.

Sediment samples were collected in June, September and November 2013 and in April and June 2014 in the eight sites. It is important to highlight that the monitoring carried out in April 2014 was performed after an extraordinary rain period in the Tercero (Ctalamochita) River basin, which took place between February and March in that year. During the campaigns, the values of middle speed of the river flow registered in the study were higher than 0.5 m/s, this is why the sampling was only carried out in the river banks (López-Martínez, Galindo-González, & Romo-Moreno, 2009). Samples of approximately 5 centimeters thick were taken under water, in zones with little turbulence, in a depth level of approximately 10-20 cm, using a shovel. These samples were placed in polythene transparent high-density bags which had been previously tagged and closed with seals, then in a black bag to prevent light input and finally refrigerated in a cooler. In the laboratory, samples were kept at 4 °C until their processing (USEPA, 2001), which was completed 14 days after extraction had been made (Lee & Jones, 1999; USEPA, 2001; Baena, Silva, & Ramirez-Callejas, 2004).

Considerations previous to the suggested methodological development

Confined Water

Benthic demand was indirectly assessed through oxygen deficit given in the water, when it contacted sediment. Dilution water (recommended by the Standard Methods for biochemical oxygen demand) was used to

perform the benthic demand. For a quality control of this water, a water blank was done every time it was prepared.

Respirometric and reaction bottles

Two types of bottles were required, with polished cap and an air-tight seal of known volumes (calibrated at 20 °C). On the one hand, those bottles where sediment sowing was done (individual respirometers of about 300 cm³). These bottles were then incubated for certain required time and others, of a lower volume (reaction bottles). In these bottles, supernatant liquid of the first bottles was transferred and the addition of reagents was carried out for the valoration of oxygen dissolved with iodine. Respirometers calibration was relevant because the suggested method for the determination of SOD demands the kinetic process to be developed in different bottles.

Sample preparation and determination of sediment sowing

Water was drained and thick materials dragged in the sample extraction which were not representative were eliminated (USEPA, 2001). To achieve a greater homogenization, a sediment mixture was manually and externally performed keeping the air-tight bag closed so as to prevent air input.

Different tests were done for each sediment, in which the only variable turned out to be the quantity of sown sample. The variability of dissolved oxygen was assessed over time. After acquiring results, it was possible to measure the volume and weight of sediment suitable to sow for each monitoring site. Furthermore, each experiment was performed from a dissolved oxygen concentration, which would make monitoring

possible along the time and would finish the assay with certain oxygen concentration.

In order to achieve a homogeneous sediment surface in contact with confined water in all respirometers, a turn of each bottle was manually done after sowing and then the bottles were filled in with confined water.

Relation between confined water volume and the surface of sowing sediment

Once the best quantity of sediment to sow for the assay was established, the volume of confined water was automatically determined by the volume of each bottle. As a result, a relation between the volume of confined water and the sediment surface was defined, which corresponded to the most suitable for the determination suggested for each particular sample. It was important to preserve this constant relation in each respirometer used in the same assay.

Immediate demand of dissolved oxygen and monitoring time of dissolved oxygen

The movement caused by sowing procedure and the filling of the respirometer with water to be confined, generated an immediate oxygen demand in which, the variation of DO concentration along the time was very fast and nonlinear. Thus, it was not useful to measure the deoxygenation constant by the sediment (Nolan & Johnson, 1979; Caldwell & Doyle, 1995; Rounds & Doyle, 1997; Lee & Jones, 1999). To assess it in the working conditions, a sediment sample was sown and the concentration of dissolved oxygen was measured after 5 minutes and in intervals of 10 minutes, within the first hour of the assay. From

that moment, readings were carried out in higher intervals to assess the lineal variability of dissolved oxygen in matters of time. Most assays were completed during 26-27 hours, this interval made possible a monitoring of DO reduction as consequence of demand exerted by the sediment.

Intra-assay accuracy

To assess accuracy in the method to measure sediment oxygen demand and to know the distribution of uncertain mistakes, a repeatability assay or intra-assay accuracy was performed (ISO, 1994). Twenty determinations were completed so as to have statistical validity. Each respirometer was sown with a difference of 15 minutes and readings the dissolved oxygen were done at 16 hours. The assay was put into practice with a sediment sample taken in November 2013 downstream from the Villa María City sewage discharge.

Required instruments and reagents

Analytical balance, granataria balance, calibrated glass bottles with polished cap and air-tight seal of about 300 cm³ (individual respirometers) and about 220 cm³ (reaction bottles), a funnel, a test tube, a wash bottle, a clock, a thermometer, an incubator and equipment for sediment characterization. Reagents were required for DO valoration through the Winkler method, modified by Alsterberg, and those required for dilution water (Rice, Baird, Eaton, & Clesceri, 2012).

Procedure to measure benthic demand using individual respirometers

First, dilution water and the sample were prepared. Then, previous assays were done to determine the best quantity of sample to be sown. Once results were obtained, the methodological development started.

1. A known volume tray was filled up, using a scraper.
2. A tray was filled up to volume and its weight was immediately registered to determine not only the volume, but also the weight to sow in each bottle.
3. Sediment in the tray was transferred to the respirometrical bottle using a funnel and a scraper. Then, the instruments were washed using a wash bottle firstly and then a test tube with 50 ml of dilution water. After that, an approximate volume of 100 ml of dilution water was introduced, which slid through the bottle walls.
4. A turn of the bottle was manually done to level the sediment surface in the respirometer. The bottle volume was slowly completed with dilution water.
5. When it was filled up, the bottle was immediately sealed to avoid the remaining of air bubbles and time was also registered. Once sown, each respirometrical bottle was left in a calibrated incubator at 20 °C.
6. After the time for a determined respirometer passed, supernatant water was carefully transferred to the reaction bottle, minimizing sediment resuspension.
7. Reagents necessary for dissolved oxygen determination were immediately added through the Winkler method, modified by Alsterberg.

This process was repeated with each of the respirometers in the assay (Figure 2).



Figure 2. A: Sediment sowing; B: Respirometer filled up with dilution water; C: Sown respirometers; D: Transference of confined water to the reaction bottle; E and F: DO Titling.

To measure the deoxygenation rate constant by benthic demand, the equation used by Nolan and Johnson (1979), suggested by the USEPA:

$$SOD = \frac{\{(OD_i - OD_f) - (Bi - Bf)\} V}{(T_f - T_i) S} \quad (1)$$

Where SOD is the benthic demand ($\text{gO}_2/\text{m}^2\text{d}$); DO_i is the dissolved oxygen in the first respirometrical bottle (g/m^3); DO_f is the oxygen dissolved in the last respirometrical bottle (g/m^3); Bi and Bf represent the initial and final dissolved oxygen respectively of confined water when river water is used (g/m^3); V is the confined water volume (m^3); S is the sediment area (m^2); T_f is the reading time of the last respirometrical bottle (days) and T_i is the reading time of the first respirometrical bottle (days). In this project, dilution water (recommended by the Standard Methods for biochemical oxygen demand) was used to perform the benthic demand. After making a water blank every time it was prepared, it was confirmed that the dilution water did not require dissolved oxygen in the time passed in each assay. Therefore, the term $Bi - Bf$ was disregarded.

Once sown, all the respirometers were taken to an incubator at 20 °C, so it was not necessary to make temperature corrections as regards the benthic demand estimated values.

The volume of confined water in the respirometers was acquired by the difference between the volume of each respirometer and the volume of sown sediment. The guideline adopted was measurement of the average of confined water volumes of all bottles used in each assay, standardizing data of dissolved oxygen referring them to that volume, and using this value in the Equation 1. It was the only way to ensure that the kinetic process developed was the same in each bottle. This allowed the report of a right and comparable DO concentration in each respirometer.

Sediment characterization

When SOD measurements finished, the sediment samples were characterized as regards aspect, color, smell, density, pH, humidity, total, fixed and volatile solids, based on these, an approximate value of organic matter was acquired.

Results

Immediate oxygen demand took place approximately within the first 45 minutes. Consequently, data to measure benthic demand was collected after 60 minutes.

From the repeatability assay, it was possible to observe that the average and the medium coincided. Thus, the value appearing with higher frequency was that one which occupied the center of distribution.

Accuracy in measurement results, expressed as a standard deviation obtained under repeatability conditions, was of 0.05 mg/L.

Results acquired from the benthic deoxygenation rate constant in the eight sites of Tercero (Ctalamochita) River measured between June 2013 and June 2014 are shown in Figure 3. Except the campaign of April 2014 where samples under altered conditions were collected, the highest values were found in BIII and BOSN, downstream an industrial development zone and of a sewage collector, respectively. The lowest values were measured in PA, place where anthropic activities feature little influence on the river.

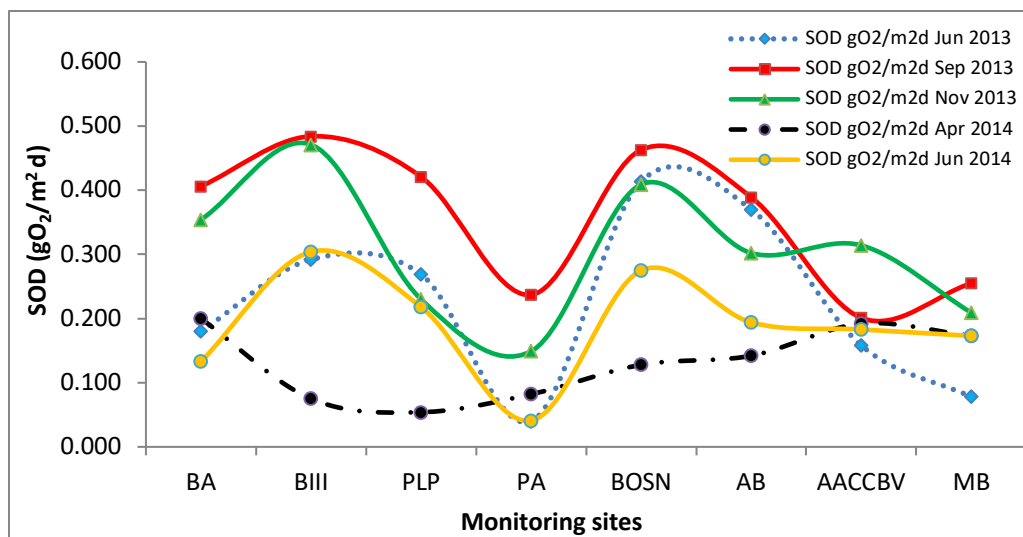


Figure 3. Spatial and temporal benthic demand variability.

Regarding samples characterization, it has been possible to prove that, in most cases, high values of benthic demand belonged to sediments with higher percentage of volatile solids and vice versa, following the same guideline throughout sampling sites, with an exception on the results of the campaign in April 2014 (Figure 4).

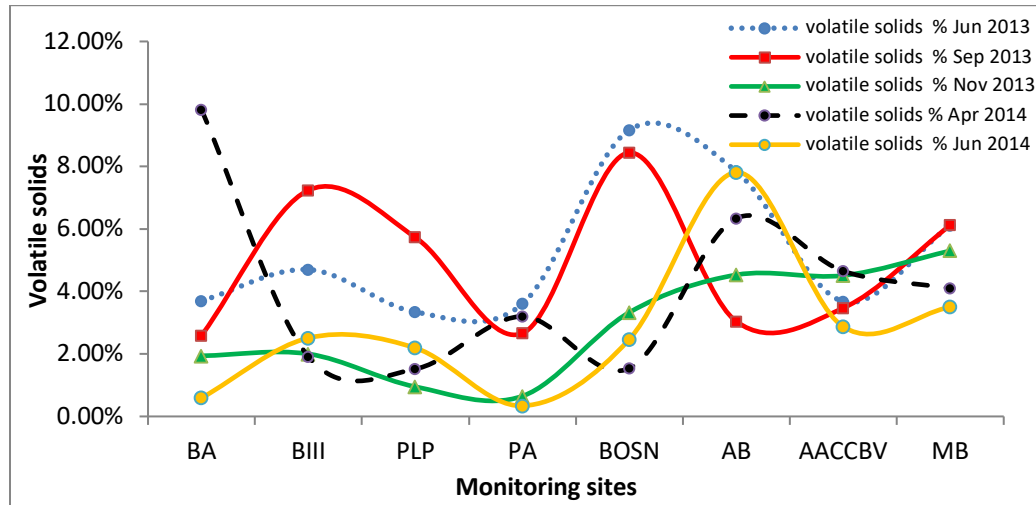


Figure 4. Spatial and temporal variability of volatile solids.

As expected, in most cases an opposing behavior between the oxygen demand produced by sediment and the quantified dissolved oxygen of water in each monitoring site was observed. Besides, a similar behaviour between benthic demand and biochemical demand of water oxygen was noticed. These results would confirm what was reported by different authors about the important role of sediment in oxygen consumption of the water column (USEPA, 1985; Caldwell & Doyle, 1995; Baena *et al.*, 2004; Mateus-García, 2011).

Discussion

The highest values of benthic demand were measured downstream the dumping of a sewage treatment plant and downstream an effluent dumping deriving from an industry development zone. By contrast, the lowest value was obtained in a remote place from the sewage dumping. Results demonstrated the influence of anthropic activities in oxygen consumption produced by the sediment in the studied river.

The lack of reports about benthic demand in Tercero (Ctalamochita) River makes it impossible to make a comparison with current findings. However, the interval of values of SOD acquired at 20 °C was between 0.040 and 0.484 gO₂/m²d, being similar to those reported by EPA for mineral and sandy river sediments (USEPA, 1985). Differences found in various sites at distinct times are based on several factors such as each sediment features, diverse seasonal and hydrological features where samples were taken, including flow rate, water speed, temperature, heterogeneity of each sediment, as well as the influence of wastewater disposal.

The methodology suggested, with its controls and considerations, helps to assess natural waters quality, contributing to the modeling of dissolved oxygen.

Conclusions

- The methodology used allowed to measure the oxygen demand by sediment using individual respirometers, without the need of confined water shaking.
- Except for the campaign in April 2014, the lowest benthic demand was acquired in a remote place from the effluent dumping, and the highest measured values were estimated downstream an industry development zone and a sewage collector. The findings have proved the influence of anthropic activities on oxygen demand that sediment produces.
- The experimental determination of the benthic deoxygenation rate constant of Tercero (Ctalamochita) River performed became a first consideration for dissolved oxygen balance.
- The proposed methodology, duly monitored, becomes considerably appropriate for most laboratories, since basic instruments are needed to measure benthic demand. Therefore, it might be easily applied in different water bodies, aiming at calibrating models with true data.

Acknowledgments

The authors would like to thank the Center of Studies and Technology of Water (CETA, by its Spanish acronym) of the National University of Córdoba (UNC by its Spanish acronym), Hidromediterránea and the Secretary of Sciences and Technology, UNC.

References

- Baena, L. M., Silva, J. P., & Ramirez-Callejas, C. (2004). Estudio experimental para la determinación de las constantes bénticas en el río Cauca. *Ingeniería de Recursos Naturales y del Ambiente*, 1(1), 12-17.
- Caldwell, J. M., & Doyle, M. C. (1995). *Sediment oxygen demand in the lower Willamette River, Oregon, 1994* (Report 95-4196). U.S. Geological Survey Water-Resources Investigations, Oregon, United States.
- Cossavella, A., Carranza, P., Oroná, C., Monarde, F., Larrosa, N., Nadal, F., Roqué, M., Nuño, C., Hunziker, M., Ferreyra, M., Brito, R., Saldaño, V., Melián, J., Bresciano, J., & Diaz, A. (octubre, 2013). Gestión de efluentes líquidos en la cuenca del río Tercero (Ctalamochita). En Simposio llevado a cabo en el XXIVº Congreso Nacional del Agua, San Juan, Argentina.
- ISO, International Organization for Standardization. (1994). *ISO 5725-1:1994. International standard. Accuracy (trueness and precision) of measurement methods and results. Part 1: General principles and definitions*. Geneva, Switzerland: International Organization for Standardization
- Lee, G. F., & Jones, R. A. (1999). Oxygen demand of US Waterway Sediments. Report. El Macero, USA: Fred Lee & Associates.
- Lee, G. F., & Jones-Lee, A. (2000). *Issues in developing the San Joaquin River. Deep water ship channel DO TMDL. Report to San Joaquin River Dissolved Oxygen Total Maximum Daily Load Steering Committee and the Central Valley Regional Water Quality Control Board Sacramento, USA*. Report. El Macero, USA: Fred Lee & Associates.

- López-Martínez, M. L., Galindo-González, D. F.- & Romo-Moreno, G. D. (2009). Determinación de la constante de desoxigenación por demanda béntica en el río Pasto. *Criterios*, (23), 59-73.
- Mateus-García, S. I. (2011). *Determinación de la influencia de los factores hidrodinámicos y de calidad del agua en la demanda béntica de la cuenca alta del río Bogotá* (tesis de maestría). Universidad Nacional de Colombia, Bogotá, Colombia.
- Nolan, P. M., & Johnson, A. F. (1979). *A method for measuring sediment oxygen demand using a bench model benthic respirometer*. United States Environmental Protection Agency. Region I. Boston, USA: Library JFK Federal BLDG.
- Rice, E. W., Baird, R. B., Eaton, A. D., & Clesceri, L. S. (2012). *Standard Methods for the Examination of Water and Wastewater*. (22nd ed.). Washington, DC, USA: American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF).
- Rounds, S. A., & Doyle, M. C. (1997). *Sediment oxygen demand in the Tualatin River Basin, Oregon 1992-96* (Report 97-4103). Oregon, USA: US Geological Survey Water Resources Investigations.
- USEPA, United States Environmental Protection Agency. (1985). *Rates, constants and kinetics formulation in surface water quality modeling* (2nd ed.) (PA 600/3-85/040). Athens, USA: Environmental Research Laboratory Office of Research and Development.
- USEPA, United States Environmental Protection Agency. (2001). *Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: Technical Manual* (EPA 823-B-01-002). Washington, DC, USA: Office of Water, United States Environmental Protection Agency.