Water Technology and Sciences

Included in Thomson Reuters Science Citation Index® (ISI) • Expanded Thomson Reuters Research Alert® (ISI) • EBSCO • ProQuest • Elsevier • Redalyc

Vol. VI, No. 2, March-April, 2015

Water Technology and Sciences

©***Water Technology and Sciences.*** Vol. VI, No. 2, March-April, 2015, is a bimonthly publication edited by the Instituto Mexicano de Tecnología del Agua, Paseo Cuauhnáhuac 8532, Colonia Progreso, Jiutepec, Morelos, C.P. 62550, telephone +52 (777) 3 29 36 00, extension 474, www.imta.gob.mx/tyca, fsalinas@tlaloc.imta.mx. Responsible editor, Nahún Hamed García Villanueva; Copyright No. 04-2013-121014514100-203, granted by the Instituto Nacional de Derechos de Autor. ISSN pending. Responsible for the latest update of this issue: Sub-Department of Dissemination and Circulation, Francisco José Salinas Estrada, Paseo Cuauhnáhuac 8532, Colonia Progreso, Jiutepec, Morelos, C.P. 62550.

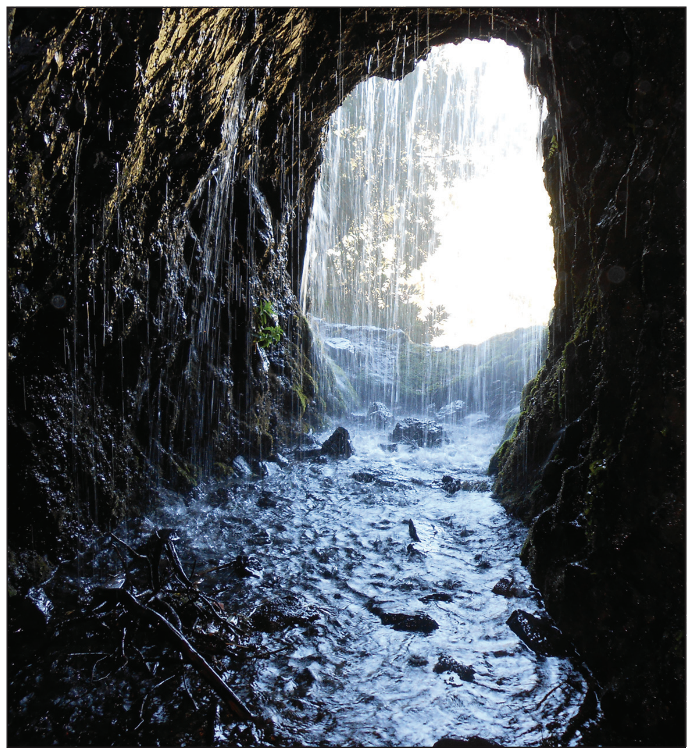
Water Technology and Sciences is the traslation of *Tecnología y Ciencias del Agua*, which is the continuation of the following journals: *Irrigación en México* (1930-1946); *Ingeniería hidráulica en México* (1947-1971); *Recursos hidráulicos* (1972-1978), and *Ingeniería hidráulica en México*, second period (1985-2009).

Water Technology and Sciences

Vol. VI, No. 2, March-April, 2015

Coordination for editorial comments, click here give

For subscriptions, click here



Cover: Channel in the Marcos and Cordero Springs, San Andres y Sauces, Canary Islands, Spain.

Though the idea of water as an economic good is not new, it has expanded since the Dublin Conference (1992). Two approaches or interpretations can be identified: water as a production input in an economic system or according to a second less narrow economic interpretation. Treating water as an economic resource does not imply the use of one specific set of economic tools. Prices, markets and private property, etcetera, are tools belonging to one toolbox, but there are other ways to manage water in a socially, economically and ecologically sustainable manner. See article “Return to Dublin: Do Traditional Communities Manage Water as an Economic Resource?” by José Antonio Batista-Medina (pp. 99-109).

Photo: .José A. Batista Medina.

Lower section of the Ebro River, Mora d´Ebre, Spain. Helley-Smith Sampler, 29 kg with a 76 mm nozzle for bed load. Gravel can be seen inside the bag after 5 minutes of sampling.

Photo: Ramon J. Batalla.

Contents

Contenido

Technical articles

Artículos técnicos

Assessment of Bed Load Transport Formula for an Armoured Gravel-Bed River

• Raúl López* • Damià Vericat • Ramon J. Batalla •
Universidad de Lleida, Lleida, España
*Corresponding Author

Abstract

López, R., Vericat, D., & Batalla, R. J. (March-April, 2015). Assessment of Bed Load Transport Formula for an Armoured Gravel-Bed River. *Water Technology and Sciences* (in Spanish), 6(2), 5-20.

The lower Ebro River (NE Iberian peninsula) has a gravel bed which flows downstream from a reservoir complex. In this section of the river, the armoured surface of the bed undergoes cycles of breaking and reestablishment as a result of natural and control floods. The objective of the present work is two-fold. First, to evaluate the capacity of three formulas to predict bed load transport under conditions in which the armour is broken or disturbed. Second, to analyze the ability of the formulas to predict the breakage or disturbance threshold of the armour. This was all based on a comparison between predictions and measurements of the bed load transport in the study section for two hydrological years. Based on the characteristics of the study section, the formulas which were finally selected were the equations developed by Parker, Klingeman and McLean (1982) (P-K-M), Bathurst (2007) (B) and Recking (2010) (R). Given the results, the P-K-M and R formulas are recommended to predict bed load transport when there is breakage or disturbance of the amour, and not formula B because of its considerable tendency to underestimate. Formulas B and R are recommended to predict the breakage or disruption threshold of the armour. Nevertheless, it is worth cautioning that in this case both formulas tended to predict thresholds much lower than those measured.

Keywords: Bed load formulae, bed load transport, sediment transport, gravel bed-river, armoured bed, River Ebro.

Resumen

López, R., Vericat, D., & Batalla, R. J. (marzo-abril, 2015). Evaluación de fórmulas de transporte de fondo en un río de gravas acorazado. Tecnología y Ciencias del Agua, *6(2), 5-20.*

El curso bajo del río Ebro (NE península Ibérica) presenta un cauce con lecho de gravas que discurre aguas abajo de un complejo de embalses. En dicho tramo, el lecho experimenta ciclos de rotura y restablecimiento de la capa superficial acorazada como consecuencia tanto de avenidas naturales como de crecidas de mantenimiento. En el citado contexto, el objetivo de la presente investigación fue doble. En primer lugar, la evaluación de la capacidad predictiva del transporte de fondo de tres fórmulas seleccionadas en condiciones de coraza rota o alterada. En segundo lugar, el análisis de la capacidad de dichas fórmulas para predecir el umbral de rotura o alteración de la coraza. Todo ello se fundamentó en la comparación entre predicciones y mediciones de carga de fondo en el tramo de estudio que abarcaron dos años hidrológicos. Conforme a los condicionantes del tramo de estudio, las fórmulas finalmente seleccionadas fueron las ecuaciones desarrolladas por Parker, Klingeman y McLean (1982) (P-K-M), Bathurst (2007) (B) y Recking (2010) (R). De acuerdo con los resultados, se recomiendan las fórmulas P-K-M y R para la predicción de la carga de fondo cuando se rompa o altere la coraza, y se desaconseja la fórmula B por su marcada tendencia a la infrapredicción. En cambio, para la predicción del umbral de rotura o alteración de la coraza se recomiendan las fórmulas B y R. Sin embargo, cabe advertir que en este caso ambas fórmulas tendieron a predecir umbrales bastante inferiores a los medidos.

Palabras clave*: fórmulas de transporte de fondo, transporte de fondo, carga de fondo, transporte de sedimentos, río de gravas, lecho acorazado, río Ebro.*

Received: 30/09/2013
Accepted: 31/10/2014

Introduction and Objectives

Predicting bed load transport is particularly relevant to several disciplines: river engineering, river morphology, river ecology, reservoir management, environmental engineering, dispersion of pollution and prediction of natural disasters (for example, Martín- Vide, 2013; Re, Kazimierski, & Menéndez, 2014). Dams present a discontinuity in the transfer of sediment through a drainage network and modify the hydrological regime of rivers. If the shear stress of the flow downstream from a dam does not exceed the initial critical value of the movement of the larger bed particles but is sufficient to transport the finer grains, then the surface layer of the sediment thickens and an armour can begin to develop. The degree of armouring of a river bed affects the granulometric distribution and the magnitude of the bed load. This can occur, for example, from the reduction of the particle size and amount of sediment transported (Parker & Sutherland, 1990). In general, the armour is stable when flows are less than the formative flow but can be broken or disturbed as larger flows pass over the river bed. The armour can also remain intact even with large flows associated with the transport of particles of all sizes present in the armour layer (Wilcock & DeTemple, 2005). Sometimes the armour stabilizes (for example, critical armouring condition; Chin, Melville, & Raudkivi, 1994) and becomes static, preventing erosions from progressing. For the purpose of the present study, the term "armour" refers to the surface layer of the bed, which is semi-permanent and develops in the lower portions of the Ebro River, in a section downstream from a reservoir complex.

Some authors have found that different bed load transport phases occur in rivers with armoured beds according to the mobility or degree of disturbance of the armour (for example, Jackson & Beschta, 1982; Bathurst, 2007; Recking, 2010). When the breakage or disturbance threshold of the armour has not been reached, the transport is categorized as phase 1, in which the bed load is made up of relatively fine sediment (from sections upstream or uplifted from patches of fine sediment present in the same section) that circulates over the unmovable and undisturbed armour. Phase 2 occurs when the flow causes the armour to partially breakup or become disturbed. During this transport phase, thicker particles composing the armour can become involved and the fine sediment from underlying material or the subsurface begins to be incorporated at a rate corresponding to the degree to which the armour is disturbed. Lastly, phase 3 corresponds to when the flow capacity has reached the point of moving sediments of all sizes present in the bed (the surface of the armour as well as the underlying material). It is important to mention that not all investigators distinguish between phases 2 and 3 but rather propose a simpler model consisting of two phases: phase 1 corresponding to a flow that transports fine sediments circulating over an armour without breaking it; and phase 2 beginning when the armour has been broken and thick particles from the armour are transported along with fine material from the underlying layer. Strictly speaking, phase 3 (that is, movement of sediments of all sizes present in the bed) occurs with much less frequency, especially in mountain rivers with steep slopes and very poorly classified sediment (containing extremely thick elements, often colluvium), where it would be very difficult for flow to transport larger-sized sediment.

Most of the bed load formulas traditionally used have been partially (and totally in more than a few cases) developed based on experiments in laboratory canals using semi-uniform granulometry sediment and transport conditions in equilibrium (where the availability of sediment does not limit solid flow) (for example, Meyer-Peter & Müller, 1948; Schoklitsch, 1950). Therefore, they did not distinguish among different layers (surface, sub-surface or both) or the granulometric conditions of the material that may be present in gravel-bed rivers. Consequently, several uncertainties exist when applying these to gravel-bed rivers with armour, such as the best characteristic diameter of the sediment to use in formulas, as well as the breakup or disturbance threshold of the armour and the different transport phases. The results are also potentially limited. Thus, it has been necessary to develop formulas that explicitly take into account the effect of bed load on the armour (for example, Parker, 1990; Bathurst, 2007; Recking, 2010), and evaluate and analyze their predictive capacity when applied to a particular river.

The present investigation corresponds to the lower portion of the Ebro River in a section located downstream of a reservoir complex containing a bed with an armour subject to a cyclical process of breakage and reestablishment. The first objective was to evaluate the capacity of selected formulas to predict bed load transport with a broken or disturbed armour (that is, transport phases 2 or 3). A second objective was to analyze the capacity of the selected equations to predict the breakage or disturbance threshold of the amour. These analyses were based on comparing predictions obtained from formulas and bed load measurements in the section under study.

Materials, Methods and Database

The Section Studied and Field Measurements

Annual runoff in the Ebro River basin greatly depends on mountainous regions. Although the mountainous region covers only 30% of the total area of the Ebro River basin, it generates roughly 60% of the annual mean runoff (López & Justribó, 2010). The Ebro River basin drains 85 530 km^2 from the northeast portion of the Iberian Peninsula to its outlet in the Mediterranean Sea. The basin's annual mean precipitation is between 600 and 700 mm. Mean flow registered by the gauging station at its outlet is 450 $m^3 \cdot s^{-1}$, equal to a mean annual supply of 14 300 hm^3. Roughly 190 large dams control 67% (approximately 7 700 hm^3) of the annual runoff in the basin. The largest dam complex was completed in 1969 in the lower portion of the river and is made up of three dams: Mequinenza, Riba-Roja and Flix . The capacity of the complex is 1 750 hm^3 (equal to 13% of the mean annual water supply of the basin) (Batalla, Gomez, & Kondolf, 2004) (Figure 1).

Flow hydraulics and sediment transport were measured continuously during flood events in the Móra d'Ebre sampling section (MESS) over the period 2002-2004. This study section is located 27 km downstream from the Flix dam, where the width of the channel is 160 m (Figure 1). There is only one channel throughout this section of the river, which has low sinuosity and a mean longitudinal slope of $8.5 \cdot 10^{-4}$ $m \cdot m^{-1}$. In this section, the river channel can be described as having natural test conditions suitable for studying changes in the bed surface caused by bed load transport. The armour which has developed controls the movement of sediment and the stability of the channel. It has resulted from a limited availability of sediment from sections upstream and the frequency of competent flows.

This section presents a brief summary of the methodology used to obtain data to characterize the sediment of the river bed and to measure the bed load transport in the MESS. A more in-depth description of the methodology can be found in Vericat and Batalla (2006), Vericat, Batalla and Garcia (2006), and Vericat, Church and Batalla (2006).

The hydrological years in the study period (2002-2003 and 2003-2004) can be considered to be medium terms of annual mean flow (415 $m^3 \cdot s^{-1}$ in the first year and 465 $m^3 \cdot s^{-1}$ in the second). Bed load transport was measured for most of the floods

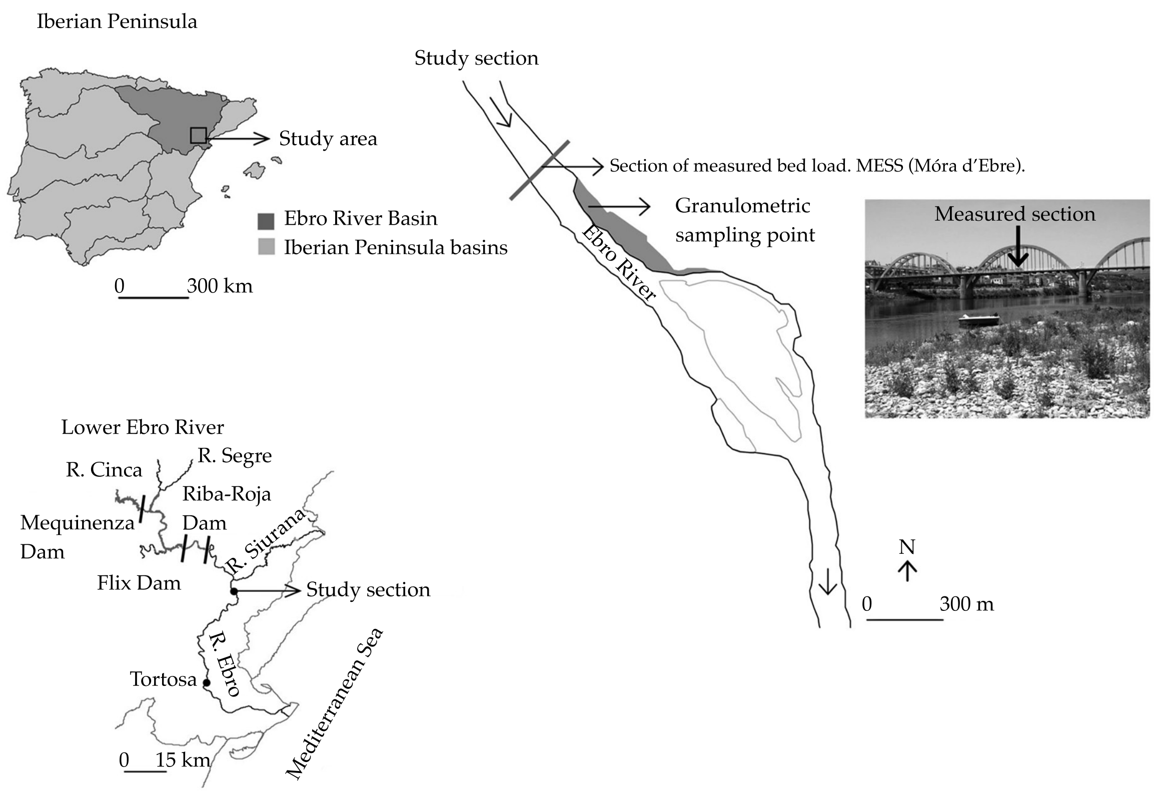


Figure 1. Location of the study zone in the lower Ebro River (NE Iberian Peninsula).

which occurred during the study period, some of which were flushing flows (Batalla & Vericat, 2009). The maximum flow registered during the period was 2 500 $m^3 \cdot s^{-1}$ (in February 2003), corresponding to a return period of 8 years and, therefore, this event was considered significant in terms of the historical distribution of the peak flows of floods.

For the purpose of this study, the granulometric distribution of the bed material (surface as well as underlying material) was used, which was obtained from an exposed bar near the MESS. This bar is 500 m downstream from the MESS (a distance equal to three times the mean width of the channel) (Figure 1). This gravel deposit is the accessible one closest to the study section and was considered fully representative of the granulometric distribution of the active sediment in the river. The inactive sediment, distinguishable by vegetation cover, was avoided since it may have little similarity with the current regime of the river. The bed material was sampled on two occasions: a) summer 2002 just before the hydrological year 2002-2003 began (bed material I, BMI) and b) summer 2003 just before hydrological year 2003-2004 began (bed material II, BMII). The data could thereby de chronologically divided according to bed material (DBM). Table 1 shows the values of the different granulometric profiles for both samples, or divisions, for surface as well as underlying material. For BMI, the thicker surface layer was characterized using the particle counting method (Wolman, 1954; Rice & Church, 1996). The area-by-weight method was used for BMII (Kellerhals & Bray, 1971) since a signifi-

Table 1. Granulometric percentages of the material on the surface and under the bed in the lower section of the Ebro River (500 m downstream from the sections where bed load was sampled).

Particle size D_i (mm)	Bed material I (BM1)[a]		Bed material II (BMII)[b]	
	Underlying	Surface	Underlying	Surface
D_{35}	10	34	12	19
D_{40}	13	39	15	23
D_{50}	19	50	21	33
D_m	26	55	26	38
D_{84}	52	88	48	70

[a] BMI: samples taken in 2002 at the beginning of the hydrological year 2002-2003.
[b] BMII: samples taken in 2003 at the beginning of the hydrological year 2003-2004.

cant portion of particles under 8mm was detected. The underlying material was sampled using the volumetric method after removal of the surface layer (Church, McLean, & Wolcott, 1987).

A total of 172 bed load transport samples were obtained that were usable for the purpose of this study (123 from the year 2002-2003 and 49 from the year 2003-2004) (see table 2). Approximately 96% of the circulated flow interval was sampled during the study period to analyze bed load transport. The bed load was measured using a Helley-Smith sampler with a 152 mm nozzle, operated with a crane.

Cyclical Armouring and the Division and Management of the Database

The detailed analysis of the characteristics and dynamics of the armouring of the Ebro River in the study section was described in Vericat *et al* (2006a). The river bed in this section undergoes a cyclical process of incision and armouring according to the magnitude of the flow. The granulometric analysis of the bed load along with field observations for the study period showed: a) the armour remained intact after the first flood in December 2002; b) the floods in February and March of 2003 disturbed or broke the armour; and c) the armour could be considered to have been reestablished during the floods of November and December 2003 (see Table 2). The data were divided chronologically into three sets according to the conditions or states of the armour (DSA) described above (Table 2): 1) unbroken armour (UA), 2) broken or disturbed armour (BA) and 3) reestablished armour (RA). As a result, a hypothesis was adopted about the association between each one of the three sets and the bed load transport phase. That is, phase 1 was

Table 2. Classification of the measured bed load transport by date of flood, division of bed material (DBM), division of state of armour (DSA) and bed load trasnport phase.

Floods	*Nb*[a]	*Na*[b]	DBM	DSA	Transport Phase
December, 2002	40	9	BMI	UA	Phase 1
February-March, 2003	83	15	BMI	BA	Phase 2 or 3
November-December, 2003	49	17	BMII	RA	Phase 1

[a]Total number of bed load trasnport measurements corresponding the period indicated..
[b]Total number of bed load transport data resulting from grouping measurements by liquid flow class and corresponding to the period indicated

considered representative of sets UA and RA, and phases 2 or 3 representative of BA (Table 2). In addition, the resulting relationships among the members of the DSA and DBM divisions were noted (Table 2).

Figure 2a shows the relationship between the liquid flow (*Q*) and bed load transport (q_s, expressed in weight units) measurements for the three sets that define the state of the armour (DSA). Table 2 indicates the number of data included in each one of the three sets. Figure 2a shows a large dispersion among the data. That is, value q_s is observed to have a wide variation interval (as much as several orders of magnitude) for a given value *Q*. A high temporal fluctuation in bed load has been commonly described, even with constant flow conditions (mean). This is caused by stochasticity, bedform migration, granulometric classification, hysteresis and limitation in sediment availability (for example, Recking, Liébault, Peteuil, & Jolimet, 2012). In Figure 2a, the regression curves corresponding to sets BA and UA runs from one end to the other, representing different supply conditions related to solid bed material or transport phases. For a given flow value, a higher bed load is expected for conditions BA than for UA, since the former would represent transport phase 1 and the latter phase 2 or 3. The regression curve for the RA extends from one end to the other, representing an intermediate situation. All these observations should be carefully interpreted considering the low determination coefficient (R^2) of the regression curves, especially for BA. One of the techniques used to smooth the effect of the fluctuation in bed load and the corresponding dispersion of the data is to group the data related to the independent variable (in this case, *Q*) into classes. The present study grouped the data from the three sets into classes with an interval amplitude of 40 $m^3 \cdot s^{-1}$ m, assigning a unique value to each class according to the arithmetic average of the data in the class. Table 2 shows the number of data in each set according to the grouping described. In Figure 2b, a significant reduction in the dispersion can be seen as a result of the grouping by classes and, consequently, the R^2 values of the regression curves of the three sets increased notably (especially for BA). The relative positions of the three curves are

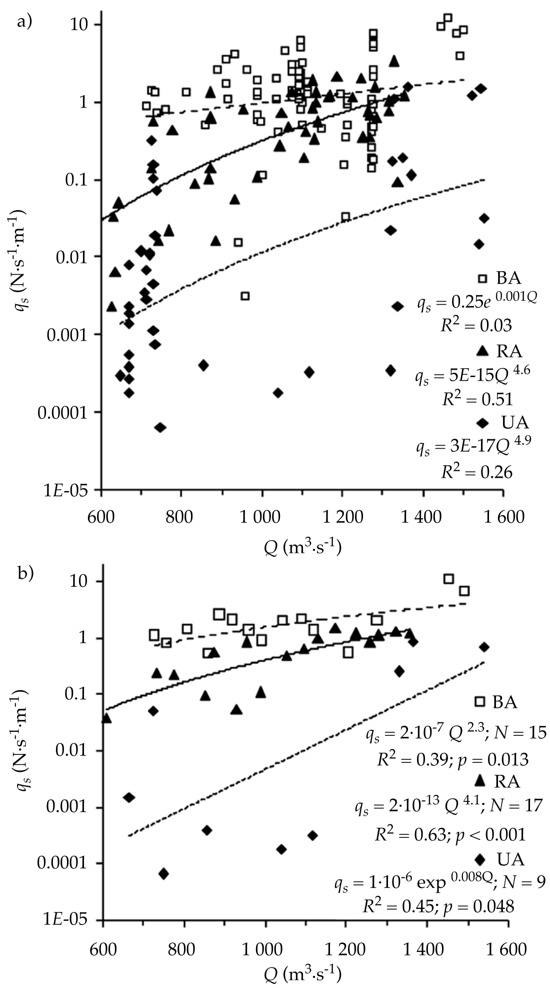


Figure 2. Relation between liquid flow measurements (*Q*) and bed load transport (q_s) for the different armour conditions: broken armour (BA), unbroken armour (UA), and restablished armour (RA). Figure 2a - complete database; Figure 2b - databases grouped by liquid flow classes (*Q*).

seen to remain the same with respect to Figure 2a.

Selection of Bed Load Transport Formulas for Armour Layers

The key requirement for the selection of the formulas evaluated herein to predict bed transport in gravel-bed rivers was that they be developed *ex profeso* by explicitly taking into account the effect of bed armouring. These formulas should at least enable calculating bed load for transport phase 2 or 3, that is, when flow is capable of disturbing or breaking the armour. Another requirement imposed was the use of a method to calculate the threshold for the breakage or disturbance of the armour (that is, the beginning of phase 2 or 3). Meanwhile, the prediction of bed load transport for phase 1 was considered to be inaccurate and therefore was not required for the objectives of the present investigation. Therefore, the formulas selected were applied only to broken armour conditions (BA) involving the complete subset (N = 83, see Table 2) as well as the grouped subset (N = 15, see Tables 2 and 3). An additional requirement was to expressly discard formulas that calculate bed load based on granulometric fractions (for example, Parker, 1990). In practice, it is difficult to apply this type of equation because, for example, complete granulometric data is often not available, it requires more calculation effort and a higher number of variables needs to be measured in the field (Recking, 2010).

Given the criteria described, the formulas which were finally selected for evaluation were those developed by Parker *et al*. (1982), Bathurst (2007) and Recking (2010) (hereafter PKM, B and R, respectively). Table 4 summarizes the variables required and the experimental or application interval for the equations (note that in three cases the empirical base includes river data). Both the mean slope of the channel and the size of the sediment particles in the

Table 3. Values of the hydraulic variables for the grouped set of data (according to liquid flow classes and for the broken armour condition (BA). (See Table 2).

Datum	Q ($m^3 \cdot s^{-1}$)	T (m)	y^a (m)	q_{sm} ($N \cdot s^{-1} \cdot m^{-1}$)
A1	727	144	3.43	1.09
A2	759	145	3.50	0.81
A3	810	146	3.62	1.37
A4	861	147	3.74	0.51
A5	888	147	3.80	2.57
A6	921	148	3.88	2.04
A7	962	149	3.97	1.33
A8	993	149	4.05	0.88
A9	1 044	150	4.17	1.99
A10	1 092	151	4.28	2.15
A11	1 121	152	4.35	1.34
A12	1 208	154	4.55	0.54
A13	1 278	155	4.71	2.00
A14	1 454	158	5.13	10.68
A15	1 493	159	5.22	6.66

[a] The study section can be considered to be hydraulically wide (the value of the hydraulic radius tends toward the mean weight).
Q is the liquid flow of the current, T the surface width of the flow, y the depth of the flow, y q_{sm} the measured unit bed load.

Table 4. Selection of bed load transport formulas applied to gravel-bed rivers with armour.

Reference	Acronym	Variables required[a]	N[b]	Empirical application	Empirical or application interval
Parker *et al.* (1982)	P-K-M	S, g, ρ, ρ_s, y, D_{50s}	—	River	$D_{50s} < 28$ mm
Bathurst (2007)	B	S, g, ρ, q, D_{84}, D_{50}, D_{50s}	≈ 600	River	$12 < D_{50}$ (mm) < 146 $30 < D_{84}$ (mm) < 540 $1.52 < D_{50}/D_{50s} < 11$
Recking (2010)	R	S, g, ρ, ρ_s, R, D_{84}, D_{50}	≈ 7 600	River and Laboratory	$0.02 < S(\%) < 8$ $0.9 < D_{84}$ (mm) < 558

[a]Variables required to calculate bed load for transport phases 2 or 3.
[b]Number of data involved in developing the formula.
S is the longitudinal slope of the channel; g, the acceleration of gravity constant; ρ and ρ_s the density of water and of the sediment particles, respectively; y the mean depth of the flow in the channel's cross-section; R the hydraulic radius of the cross-section of the channel; D_{84} and D_{50} the size of the particle on the bed's surface layer for which 84 and 50% of the sediment sample is smaller, respectively; D_{50s} is the size of the particle in the material below or under the surface of the bed for which 50% of the sediment sample is smaller.

study section are observed to comply with the experimental intervals of the formulas evaluated. Formula *R* can be used to determine which of the three theoretical phases produces bed load transport (that is, phase 1, 2 or 3) and to predict the corresponding value of the solid flow. Meanwhile, formula B only predicts bed load in the case of breakage or disturbance of the armour (without explicitly distinguishing between phases 2 and 3). Lastly, formula P-K-M predicts bed load transport only in the case of disturbance of the armour and assuming that the movement of particles of all sizes begins simultaneously when the critical condition of a disturbance or breakage is met (a concept that is most closely related to the definition of transport phase 3).

Statistical Evaluation of the Predictive Capacity of the Formulas

The predictive capacity of the formulas studied was evaluated by comparing measured (q_{sm}) and predicted (q_{sp}) values of unit bed load (sediment flow expressed by weight and unit width, in $N \cdot s^{-1} \cdot m^{-1}$). Different statistical indices and graphic methods were used to evaluate that capacity. The indices used were based on the discrepancy ratio (r), defined as the quotient of the predicted and the measured values ($r = q_{sp}/q_{sm}$). The interval of this ratio is (0, + ∞). In studies of bed transport in gravel-bed rivers, r can have a wide interval, often two or more orders of magnitude (for example, Duan, Chen, & Scott, 2006; Recking, 2010). Therefore, the statistical comparison between predicted and measured values must include logarithmic transformation and indices that are less sensitive to extreme values.

The statistical indices used to evaluate the fit between predicted and measured bed load are described next. First, the percentage of data with an r (q_{sp}/q_{sm}) that did not exceed a proportion of 2 ($0.5 < r < 2$), 5 ($0.2 < r < 5$) and 10 ($0.1 < r < 10$) was calculated. The arithmetic mean of r (mr) was also used:

$$mr = (1/N)\sum_{i=1}^{N} r_i \tag{1}$$

where r_i is the i-*th* value of r and N the number of data. This index varies in the interval (0, + ∞), indicating less discrepancy when its value is closer to 1. The arithmetic mean of the log of r(mlr) was also used:

$$mlr = (1/N)\sum_{i=1}^{N} \log r_i \tag{2}$$

where r_i is the i-*th* value of r and N the number of data. This index varies in the interval (– ∞, + ∞), indicating less discrepancy when the value is nearer to 0. In addition, a modification of the geometric mean of r (gr) was used (Habersack & Laronne, 2002):

$$gr = (r_1 r_2 \cdots r_i \cdots r_N)^{1/N} \tag{3}$$

where the inverse value of r_i was taken when $r_i < 1$ to ensure that $gr \geq 1$. Defined this way, the index varies in the interval (1, + ∞), indicating less discrepancy when the value is closer to 1. A weighted variation of the index gr(gpr) was also used (Habersack & Laronne, 2002):

$$gpr = (rp_1 rp_2 \cdots rp_i \cdots rp_N)^{1/N} \tag{4}$$

denotando rp un valor de r ponderado por la potencia del caudal sólido de fondo medido where rp is a value of r weighted by the power of the measured solid bed flow ($rp = r^{q_{sm}}$) and the inverse value of rp_i was taken when $rp_i < 1$ to ensure $gpr \geq 1$. Defined this way, the index varies in the interval (1, + ∞), indicating less discrepancy when the value is closer to 1.

In addition to the statistical indices described, graphic representations of the divergence between predicted and measured values were also used, which helped to create a visual interpretation of the performance of the formulas. The predicted value (q_{sp}) was represented on logarithmic coordinates in function of the measured value (q_{sm}) for each of the bed load data (dispersion diagram). The distribution of the discrepancy ratio (r) was also analyzed using a box plot represented on a logarithmic scale.

Classifying formulas according to their performance can vary depending on the statistical properties of the index used as the classifying criterion. Previous investigations (for example, Barry, Buffington, & King, 2007) found that given the frequency with which the indices present bias errors, a perfect index for a statistical evaluation of the performance of the equations does not exist. Therefore, a suitable combination of various indices is recommended, as used in this work. Regardless, to correctly interpret the results the main limitations of the indices used must be taken into account. For example, the mr index is more sensitive to values of r over 1 (for example, a value of r = 10 has much more weight in the calculation of mr than a value of 0.1, even though they both represent a deviation of 1 with respect to the axis of symmetry r = 1). On the other hand, for the mlr index, errors with the same magnitude have the same weight regardless of the relative position with respect to the axis of symmetry, $\log r = 0$ (for example, r = 10 and r = 0.1). Nevertheless, one of the greatest disadvantages is that values of $logr$ having equal magnitudes and opposite signs compensate each other and result in mlr = 0, in which case there is more sensitivity to small deviations without symmetry (for example, if r_1 = 1.5 and r_2 = 2, then mlr = 0.24) than to large deviations with symmetry (for example, if r_1 = 0.01 and r_2 = 100 then mlr = 0). Lastly, the gpr index, by definition, is more sensitive to errors when predicting higher measured bed load values (q_{sm}).

Results and Discussion

Tables 5 and 6 show the values of the statistical indices for the three formulas evaluated with the broken armour condition (BA), which involves the complete subset (N = 83, see Table 2) and the grouped subsets (N = 15, see Table 2). Figure 3 shows the relationship for each datum between predicted and measured bed load transport (according to the three formulas evaluated) with

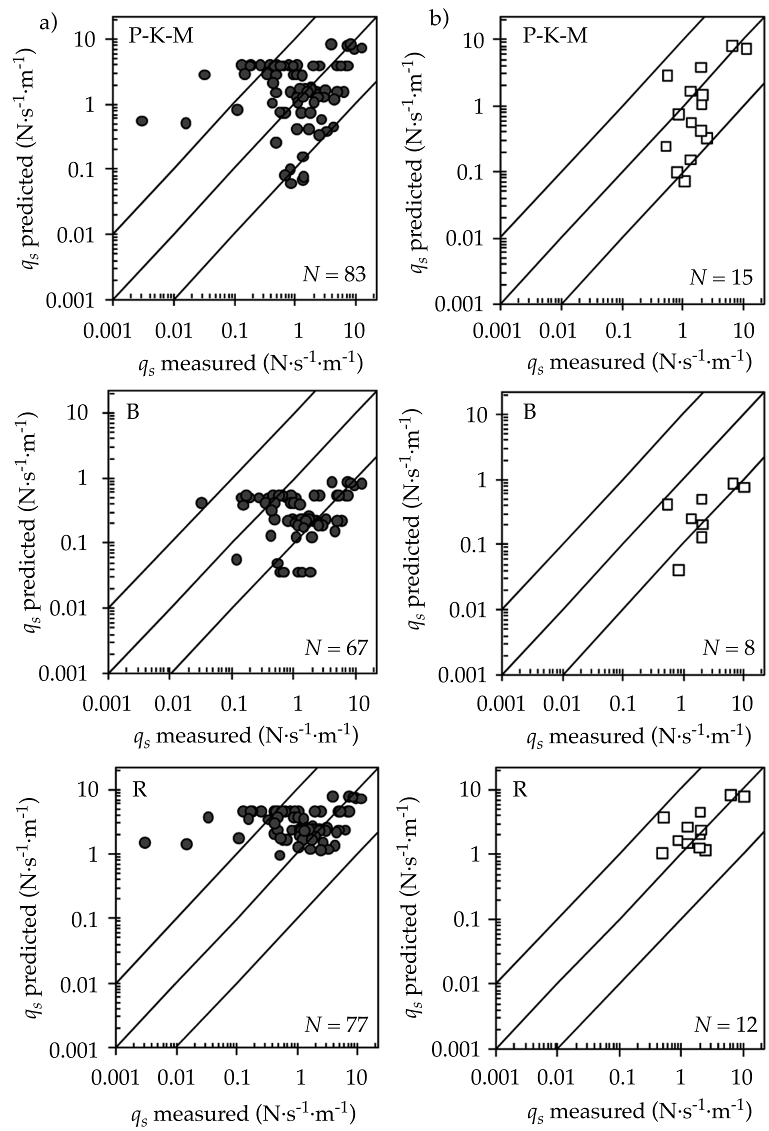


Figure 3. Representation of bed load transport predicted by the formulas evaluated versus measured bed load transport. Figure 3a: complete database; Figure 3b: database gropued by liquid flow classes (*Q*). Only data predicting bed load transport phases 2 or 3 are presented. The lines parallel to the perfect fit line (r=1) correspond to *r* = 0.1 and *r* = 10.

BA conditions, for the complete (Figure 3a) and grouped subsets (Figure 3b). In Figure 4, box plots of the distribution of the discrepancy ratio (*r*) are presented for each formula and subset of data corresponding to the BA condition (that is, complete and grouped subsets).

First, the capacity of the formulas to predict the breakage or disturbance of the armour was analyzed. To this end, the values of the *dc* and *ndc* indices shown in Tables 5 and 6 were used. The *dc* index was defined as the percentage of data in the BA subset (broken armour) for which the formula predicted breakage or transport phases 2 or 3. Tables 5 and 6 show that the P-K-M formula performs best, with 100% for both subsets (complete and grouped). Formula R

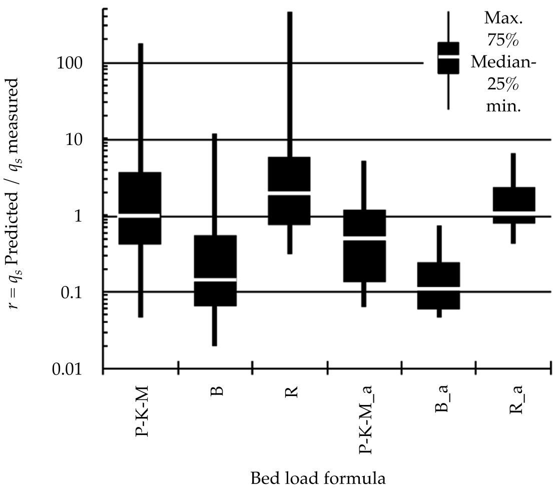


Figure 4. Box plots of the distribution of the discrepancy ratio between predicted and measured bed load (r). The distinction (_a) indicates data set grouped by classes of Q.

also resulted in high percentages— 80 and 93%— depending on the subset. Lastly, the result from formula B was more sensitive to the grouped data, with a percentages of 81 to 53%. Meanwhile, the *ndc* index was defined as the percentage of data from the sum of subsets UA and RA for which the formula did not predict breakage of the armour or predicted transport phase 1. In this case, the performance of the formulas was poorer than those analyzed earlier. In effect, formulas B and R, which obtained similar results, did not exceed 30% in the best of cases, while formula P-K-M barely exceeded 1%. Therefore, in general terms, the formulas evaluated predicted thresholds for breakage or disturbance of the armour below the threshold observed in the section studied. That is, they predicted the beginning of phase 2 or 3 transport before it actually occurred. Considering the results obtained from the study section, for practical purposes the joint use of formulas B and R is most recommendable (in all cases avoiding the use of formula P-K-M) to predict the breakage or disturbance threshold of armour and the beginning of bed load transport phase 2. Nevertheless, this should take into account that the resulting threshold will very likely be too low.

Second, the capacity of the formulas evaluated to predict the magnitude of bed load was analyzed using the data in the BA set with both the complete and grouped subsets. It is important to mention that the value of the statistics shown in Tables 5 and 6 was obtained using only the data

Table 5. Predictive capacity of the formulas evaluated with respect to the broken armour (BA) and complete subset (83 data). The values in bold and underlined correspond to the first and second best classified, respectively, according to each statistical index.

Formula	*dc*[a] (%)	*ndc*[b] (%)	*r* (0.5-2)[c] (%)	*r* (0.2-5)[d] (%)	*r* (0.1-10)[e] (%)	*mr*[f] (-)	*mlr* (-)	*gr* (-)	*gpr* (-)
P-K-M	**100**	1.2	43	70	87	6.27	**0.083**	3.4	5.3
B	81	**30**	16	39	64	**0.62**	-0.685	6.1	170
R	93	27	**47**	**77**	**87**	12.45	0.388	**3.2**	**3.2**

[a] Percentage of data corresponding to the broken armour condition (BA) for teh formula to predict transport in phase 2 or 3.
[b] Percentage of data corresponding to unbroken armour conditions (UA) and restablished armour (RA) for the formula to predict trasnport in phase 1.
[c] $0.5 < r < 2$, percentage of data whose quotient between predicted and measured (r) bed load transport does not exceed a factor of 2.
[d] $0.2 < r < 5$, percentage of data whose quotient between predicted and measured (r) bed load transport does not exceed a factor of 5.
[e] $0.1 < r < 10$, percentage of data whose quotient between predicted and measured (r) bed load transport does not exceed a factor of 10.
[f] For purposes of comparison and classification of predictive capacity of formulas, the values of mr in the interval (0,1) were considered according to their reciprocol ($1/mr$).

Table 6. Predictive capacity of the formulas evaluated with respect to broken armour (BA) and grouped subset (15 data). The values in bold and underlined correspond to the first and second best classified, respectively, according to each statistical index.

Formula	*dc*[a] (%)	*ndc*[b] (%)	*r* (0.5-2)[c] (%)	*r* (0.2-5)[d] (%)	*r* (0.1-10)[e] (%)	*mr*[f] (-)	*mlr* (-)	*gr* (-)	*gpr* (-)
P-K-M	**100**	0	47	67	93	**0.90**	-0.33	3.1	6.6
B	53	**19**	13	25	50	0.20	-0.88	7.6	1 842
R	80	15	**75**	**92**	**100**	1.73	**0.12**	**1.7**	**2.9**

[a] Percentage of data corresponding to the broken armour condition (BA) for teh formula to predict transport in phase 2 or 3.
[b] Percentage of data corresponding to unbroken armour conditions (UA) and restablished armour (RA) for the formula to predict trasnport in phase 1.
[c] $0.5 < r < 2$, percentage of data whose quotient between predicted and measured (r)bed load transport does not exceed a factor of 2.
[d] $0.2 < r < 5$, percentage of data whose quotient between predicted and measured (r)bed load transport does not exceed a factor of 5.
[e] $0.1 < r < 10$, percentage of data whose quotient between predicted and measured (r)bed load transport does not exceed a factor of 10.
[f] For purposes of comparison and classification of predictive capacity of formulas, the values of mr in the interval (0,1) were considered according to their reciprocol (1/*mr*).

for which the formulas predicted breakage or disturbance of the armour, that is, for the percentage of data specified in statistic *dc*. The above also applies to the graphs in Figures 3 and 4. This should be taken into account when comparing the predictive capacity of the three formulas, since the set of data were not exactly the same. In addition, as was mentioned in the methods section, the classification of the formulas' performances can vary according to the reference statistic used.

In general terms, the predictive capacity of the formulas evaluated was relatively low. For the three (the BA set without groupings) the means of the percentage of data with a deviation under 2 ($0.5 < r < 2$), 5 ($0.2 < r < 5$) and 10 ($0.1 < r < 10$), with respect to predicted versus measured bed loads, were 35, 62 and 79%, respectively. Although the degree of divergence may seem high, it is of the same order and often lower than values reported by previous investigations about the performance of bed load formulas in gravel-bed rivers. For example, Martin (2003) found average values of 19, 44 and 75% for deviations under 2, 5 and 10, while Martin and Ham (2005) found values of 11, 25 and 47% and Recking (2010) of 13, 27 and 34%, respectively. In addition, it is important to take into account that the bed load measurements in the study section were semi-instantaneous (that is, short duration with respect to the total duration of the flood event) and it has been found that the longer the duration of a measured period the better the performance of the formulas evaluated (Recking *et al*., 2012).

Figure 4 shows the box plot of the distribution of the discrepancy ratio corresponding to the predicted versus measured (r) bed load values for each formula, for the complete and the grouped subsets. The comparison of the diagrams of the two subsets (complete and grouped), per formula, shows that eliminating the fluctuations by classes (by grouping the data) notably reduces the dispersion of the discrepancy ratio (*r*) values of the three. This was accompanied by a decrease in the median of the distribution of the three formulas since the reduction in the dispersion was not symmetric but rather much larger for values of *r* over 1.

In general terms, Tables 5 and 6 show that formula B has the best predictive capacity for the complete subset (Table 5) as well as for the grouped subset (Table 6). The only exception was the *mr* index with the complete subset (Table 5). In this case, formula B performed best because of the bias of the *mr* index when *r* is much larger than 1, which is much more frequent in the case of the P-K-M and R formulas (Figure 4). Formula 4 presented the best fit between prediction and measurements, with only a few exceptions. Two of these exceptions occurred with index *mr* (Tables 5 and 6) due to that statistic being more sensitive to values of *r* much larger than 1, as mentioned above. Another exception occurred with the complete subset in relation to the value of the *mlr* index (Table 5), which was attributed to the low sensitivity of that statistic when deviations are symmetric (as shown in Figure 3a, when comparing the dispersion diagrams of formulas R and P-K-M, the best equation in this case). Formula P-K-M was classified as second in most cases, although it was statistically much more similar to formula R than to B (Figures 3 and 4). In addition, the prediction errors in formulas P-K-M and R were much lower with higher bed load measurements, and much higher with low bed load transport measurements (Figure 3).

In addition to the specific degree of fit between measurements and predictions, it is of interest to know whether a formula tends to over-predict or under-predict bed load transport. Figures 3 and 4 show that formula B tends to predict lower bed load values than those measured. Formula P-K-M also showed this tendency but to a much lesser degree. Lastly, formula R tends to overestimate bed load measurements, but also with a comparatively small bias. The tendencies described are general, that is, covering and including the entire range of the measured bed load interval. Nevertheless, it is also useful to know whether the tendencies varied according to the magnitude of other variables that are correlated with bed load, for example, liquid flow. To this end, Figure 5 presents the data in the BA set (grouped subset) in function of measured liquid flow (Q), as well as its regression curve and the regression curves of the three formulas evaluated. This figure clearly indicates that formula B consistently under-predicts for the entire flow range, and formula R was the best fit for flows under roughly 1 100 m^3/s, whereas little differences between the predictions by formulas P-K-M and R were found for flows over that value.

It is important to note that when the Recking (2010) formula was developed , 46 data belonging to the RA subset (table 2) were included, taken from Vericat *et al*. (2006b). Nevertheless, since they were only used (along with over 3 000 data) to verify the performance of the formula and not for fitting or calibration purposes, this does not compromise the independence of the database used by the present study with respect to formula R. It is also important to mention that the results from the present investigation may be sensitive to the sampling period (two years), and the bed load

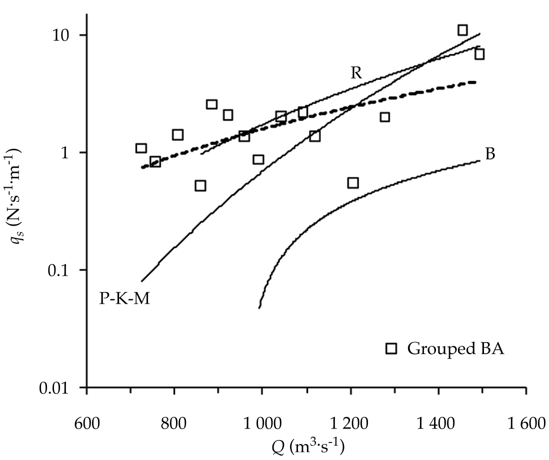


Figure 5. Ratio between measured liquid flow (Q) and bed load transport (q_s) for the broken armour set (BA) and its regression curve (dashed line) represnted along with the regression cruves for the P-K-M and R formulas for the same set of data.

measurements were limited to a single section of the river. A longer sampling period would have showed differences in the distribution of the measured bed load, affecting the performance of the formulas evaluated. Nevertheless, since the specific years registered represent medium hydrologic years, the different stages in the bed armouring cycle can be clearly seen, which is rare in rivers of this size. Said stages range from a more stabilized bed because of a well developed armour to a more mobile bed from the effect of breakage or disturbance of the armour.

Conclusions

This investigation is considered to be a direct and practical application in the study section (for example, for designs of flushing flow or gravel injection), while the methodology and even the results themselves could be extrapolated to armoured gravel-bed rivers with similar hydraulic, sedimentary and geomorphological characteristics.

In general terms, the formulas evaluated predicted armour breakage or disturbance thresholds below those observed; that is, they predicted the beginning of phase 2 or 3 before they actually occurred. Nevertheless, significant differences were found among the three equations, which have practical implications. In effect, because of the better results obtained, equations B and R are recommended to predict the breakage threshold of the armour in the study section and the use of equation P-K-M is not advisable.

Formulas P-K-M and R are recommended to predict bed load for transport phases 2 or 3 after calculating the breakage of disturbance threshold of the armour according to the recommendations described previously. Nevertheless, the tendency of formula P-K-M towards under-predictions and the bias of formula R towards over-predictions should be taken into account. The use of formula B is not recommended because of it significantly under-predicts. Regardless, it is important to highlight that this study found the performance of the formulas to be within the order of magnitude, and even higher, than performances reported by previous investigations.

Acknowledgements

The present investigation was performed as part of the following projects: REN2001-0840-C02-01/HID, CGL2005-06989-C02-02/HID, CGL2006-11679-C02-01/HID, CGL2009-09770 (subprogram BTE), SCARCE Consolider Ingenio 2010 CSD2009-00065 and CGL2012- 36394, all granted by the Ministry of Science and Technology of Spain. The second author received a Juan de la Cierva grant (JCI-2008-2910) and a Ramón and Cajal grant (RYC-2010-06264) from the Ministry of Science and Technology of Spain. The hydrological data were supplied by the Hydrographic Confederation of Ebro. The Móra d'Ebre government helped with logistical support during the field and laboratory work. We thank the anonymous reviewers for their contributions to improving the article.

References

Barry, J. J., Buffington, J. M., & King, J. G. (2007). Correction to a General Power Equation for Predicting Bed Load Transport Rates in Gravel Bed Rivers. *Water Resources Research*, *43*(8), W08702, http://dx.doi.org/10.1029/2007WR006103.

Batalla, R. J., Gomez, C. M., & Kondolf, G. M. (2004). Reservoir-Induced Hydrological Changes in the Ebro River Basin (Northeastern Spain). *J. Hydrol.*, *290*(1-2), 117-136, doi: 10.1016/j.jhydrol.2003.12.002.

Batalla, R. J., & Vericat, D. (2009). Hydrological and Sediment Transport Dynamics of Flushing Flows: Implications for Management in Large Mediterranean Rivers. *River Res. Appl.*, *25*(3), 297-314, doi: 10.1002/rra.1160.

Bathurst, J. C. (2007). Effect of Coarse Surface Layer on Bed-load Transport. *J. Hydraul. Eng.*, *133*(11), 1192-1205.

Chin, C. O., Melville, B. W., & Raudkivi, A. J. (1994). Streambed Armouring. *J. Hydraul. Eng.*, *120*(8), 899-918.

Church, M., McLean, D. G., & Wolcott, J. F. (1987). River Bed Gravels: Sampling and Analysis. In C. R. Thorne, J. C. Barthurst & R. D. Hey (Eds.), *Sediment Transport in Gravel-bed Rivers* (pp. 43-88). Chichester, UK: John Wiley and Sons.

Duan, J. G., Chen, L., & Scott, S. (2006). Application of Surface-based Bed Load Transport Equations to a Desert Gravel-bed Stream. *J. Hydraul. Res.*, *44*(5), 624-630.

Habersack, H., & Laronne, J. B. (2002). Evaluation and Improvement of Bed Load Discharge Formulas Based on Helley-Smith Sampling in an Alpine Gravel Bed River. *J. Hydraul. Eng.*, *128*(5), 484-499.

Jackson, W. L., & Beschta, R. L. (1982). A Model of Two-Phase Bed-Load Transport in an Oregon Coast Range Stream. *Earth Surf. Proc. Land.*, 7(6), 517-527.

Kellerhals, R., & Bray, D. I. (1971). Sampling Procedures for Coarse Fluvial Sediments. *J. Hydraul. Div.*, *97*(8), 1165-1180.

López, R., & Justribó, C. (2010). The Hydrological Significance of Mountains: A Regional Case Study, the Ebro River Basin, Northeast Iberian Peninsula. *Hydrol. Sci. J.*, *55*(2), 223-233, doi:10.1080/02626660903546126.

Martin, Y. (2003). Evaluation of Bed Load Transport Formulae Using Field Evidence from the Vedder River, British Columbia. *Geomorphology*, *53*, 75-95.

Martin, Y., & Ham, D. (2005). Testing Bed Load Transport Formulae Using Morphologic Transport Estimates and Field Data: Lower Fraser River, British Columbia. *Earth Surf. Process. Land.*, *30*(10), 1265-1282.

Martín-Vide, J. P. (2013). Erosion, Sedimentation and Restoration of Rivers. Engineering and Research Examples. *Water Technology and Sciences*, *4*(5), 5-18.

Meyer-Peter, E., & Müller, R. (VI, 1948). Formulas for Bed-load Transport. In W. Fellenius (Presidencia), 2nd Meeting of the Int. Assoc. for Hydraulic Structures Res. IAHR, Stockholm, Sweden.

Parker, G. (1990). Surface-Based Bedload Transport Relation for Gravel Rivers. *J. Hydraul. Res.*, *28*(4), 417-436.

Parker, G., Klingeman, P. C., & McLean, D. G. (1982). Bedload and the Size Distribution of Paved Gravel-bed Streams. *J. Hydraul. Div.*, *108*(4), 544-571.

Parker, G., & Sutherland, A. J. (1990). Fluvial Armor. *J. Hydraul. Res.*, *28*(5), 529-544.

Re, M., Kazimierski, L. D., & Menéndez, A. N. (2014). Sedimentation in Navigation Channels Under the Context of Climate Change. *Water Technology and Sciences*, *5*(1), 5-21.

Recking, A. (2010). A Comparison between Flume and Field Bed Load Transport Data and Consequences for Surface Based Bed Load Transport Prediction. *Water Resources Research*, *46*(3), W03518, http://dx.doi.org/10.1029/2009WR008007.

Recking, A., Liébault, F., Peteuil, C., & Jolimet, T. (2012). Testing Several Bed Load Transport Equations with Consideration of Time Scales. *Earth Surf. Proc. Land.*, *37*(7), 774-789, http://dx.doi.org/10.1002/esp.3213.

Rice, S., & Church, M. (1996). Sampling Surficial Fluvial Gravels: the Precision of Size Distribution Percentile Estimates. *J. Sediment. Res.*, *66*(3), 654-665.

Schoklitsch, A. (1950). *Handbuch des Wasserbaues*. New York: Springer.

Vericat, D., & Batalla, R. J. (2006). Sediment Transport in a Large Impounded River: the Lower Ebro, NE Iberian Peninsula. *Geomorphology*, *79*(1-2), 72-92, doi: 10.1016/j.geomorph.2005.09.017.

Vericat, D., Batalla, R. J., & Garcia, C. (2006a). Breakup and Reestablishment of the Armour Layer in a Highly Regulated Large Gravel-bed River: The Lower Ebro. *Geomorphology*, *76*(1-2), 122-136, doi: 10.1016/j.geomorph.2005.10.005.

Vericat, D., Church, M., & Batalla, R. J. (2006b). Bed Load Bias: Comparison of Measurements Obtained Using Two (76 and 152 mm) Helley-Smith Samplers in a Gravel-bed River. *Water Resources Research*, *42*(1), W01402, http://dx.doi.org/10.1029/2005WR004025.

Wilcock, P. R., & DeTemple, B. T. (2005). Persistence of Armour Layers in Gravel-bed Streams. *Geophys. Res. Lett.*, *32*(8), L08402, doi:10.1029/2004GL021772.

Wolman, M. G. (1954). A Method of Sampling Coarse Bed Material. *Eos Trans. AGU.*, *35*(6), 951-956.

Institutional Address of the Authors

Dr. Raúl López

Grupo de Investigación de Dinámica Fluvial-RIUS
Departamento de Ingeniería Agroforestal
Universidad de Lleida
Av. Alcalde Rovira Roure, 191
E-25198 Lleida (Cataluña), España
Teléfono: +(34) 973 70 2820
Fax +(34) 973 70 2673
rlopez@eagrof.udl.cat

Dr. Damià Vericat

Grupo de Investigación de Dinámica Fluvial-RIUS
Departamento de Medio Ambiente y Ciencias del Suelo
Universidad de Lleida
Av. Alcalde Rovira Roure, 191
E-25198 Lleida (Cataluña), España
Teléfono: +(34) 973 00 3735
Fax +(34) 973 70 2613
dvericat@macs.udl.cat

Centro Tecnológico Forestal de Cataluña
Pujada del Seminari s/n
E-25240 Solsona (Cataluña), España

Institute of Geography and Earth Sciences
Aberystwyth University
Ceredigion SY23 3DB, Wales, United Kingdom

Dr. Ramon J. Batalla

Grupo de Investigación de Dinámica Fluvial-RIUS
Departamento de Medio Ambiente y Ciencias del Suelo
Universidad de Lleida
Av. Alcalde Rovira Roure, 191
E-25198 Lleida (Cataluña), España
Teléfono: +(34) 973 70 26 76
Fax +(34) 973 70 26 13
rbatalla@macs.udl.cat

Centro Tecnológico Forestal de Cataluña
Pujada del Seminari s/n
E-25240 Solsona (Cataluña), España

Instituto Catalán de Investigación del Agua
Parc Científic i Tecnològic de la Universitat de Girona,
Edificio H2O
Emili Grahit ,101
E-17003 Girona (Cataluña), España

Mercury, Chromium and Lead Removal Using Constructed Wetlands Inoculated with Tolerant Strains

• Leonel E. Amábilis-Sosa* • Christina Siebe •
Universidad Nacional Autónoma de México
*Corresponding Author

• Gabriela Moeller-Chávez •
Universidad Politécnica del Estado de Morelos

• María del Carmen Durán-Domínguez-De-Bazúa •
Universidad Nacional Autónoma de México

Abstract

Amábilis-Sosa, L. E., Siebe, C., Moeller-Chávez, G., Durán-Domínguez-De-Bazúa, M. C. (March-April, 2015). Mercury, Chromium and Lead Removal Using Constructed Wetlands Inoculated with Tolerant Strains. *Water Technology and Sciences* (in Spanish), 6(2), 21-34.

The present investigation evaluated the performance of constructed wetlands inoculated with strains tolerant to heavy metals. The evaluation was conducted at the laboratory scale. These systems were compared to constructed wetlands having the same construction and operating conditions but containing conventional bacteria that is naturally present in the rhizosphere of the reactors. Both types of reactors were evaluated for the removal of mercury, lead and chromium in solution over 151 days of operations. By day 100, the systems inoculated with tolerant bacteria attained a stable removal percentage of roughly 50% for Hg, 57% for Pb and 45% for Cr. The reactors with conventional bacteria removed a percentage of heavy metals but the efficiency decreased as the days of operation increased and it did not reach stable values.

Keywords: Rhizospheric bacteria, tolerant strains, constructed wetlands, heavy metals.

Resumen

Amábilis-Sosa, L. E., Siebe, C., Moeller-Chávez, G., Durán-Domínguez-De-Bazúa, M. C. (marzo-abril, 2015). Remoción de mercurio, cromo y plomo por humedales artificiales inoculados con cepas tolerantes. Tecnología y Ciencias del Agua, *6(2), 21-34.*

En la presente investigación se evaluó el desempeño de humedales artificiales a escala de laboratorio, inoculados con cepas tolerantes a metales pesados. Estos sistemas fueron comparados con humedales artificiales con las mismas características constructivas y de operación, pero con bacterias convencionales que, naturalmente, se encuentran presentes en la rizosfera de los reactores. Ambos tipos de reactores fueron evaluados considerando la remoción de mercurio, plomo y cromo en solución durante 151 días de operación. A partir del día 100, los sistemas inoculados con bacterias tolerantes presentaron estabilidad en el porcentaje de remoción alrededor de 50% de Hg, 57% de Pb y 45% de Cr. Por su parte, los reactores con bacterias convencionales, a pesar de remover cierto porcentaje de metales pesados, fueron reduciendo su eficiencia en función de los días de operación, además de que no llegaron a presentar valores estables.

Palabras clave: *bacterias rizosféricas, cepas tolerantes, humedales artificiales, metales pesados.*

Received: 23/04/2014
Accepted: 12/12/2014

Introduction

Among the various environmental and public health problems that exist, those related to wastewater containing heavy metals have increased over recent years (Fu & Wang, 2011). The Pan-American Health Organization (PAHO) and the World Health

Organization (WHO) have determined these pollutants to be priorities because of their high toxicity and long persistence in the environment (CEPIS, 2001). The most dangerous are chromium (Cr), mercury (Hg) and lead (Pb), which are widely used and generated by many industries worldwide— mining, paper, leather, electroplating and battery production, among others (Fu & Wang, 2011; Khan, Ahmad, Shah, Rehman, & Khaliq, 2009). In Mexico alone, 18 states present problems from industries that use Hg, Cr or Pb as prime materials or which produced them as byproducts, as well as a combination of these heavy metals (INE, 2004; SSA, 2006). The concentrations of the total forms of these compounds vary widely depending on the type and the production capacity of the industry. Reported concentrations in discharged wastes range from 0.0005 to 2.2 mg l^{-1} for Hg (Loredo, Álvarez, & Ordóñez, 2003), 5 to 75 mg l^{-1} for Cr (Barrera, Romero, & Martínez, 2003) and 7 to 130 mg l^{-1} for Pb (Lavado, Sun, & Bendezu, 2010). Conventional wastewater treatment plants are not currently able to treat water containing heavy metals since the biological system would collapse from the toxicity of these inorganic cations or they would be discharged untreated along with the effluent. In addition, current physiochemical options— such as activated carbon, ionic exchange and chemical precipitation— always present some sort of drawback in terms of operations, finances or efficiency (Barakat, 2010; Cheng, Grosse, Karrenbrock & Thoennessen, 2002).

Meanwhile, recent studies have focused on bacteria that are resistant to the most toxic heavy metals, including Hg, Cr and Pb. For example, many cases have isolated and genetically characterized gram-positive *Bacillus* bacteria (Becerra-Castro *et al*., 2012; Çolak, Atar, Yazicioĝlu, & Olgun, 2011; Salgado-Bernal, Carballo-Valdés, Martínez-Sardiñas, Cruz- Arias, & Durán-Domínguez-de-Bazúa, 2012). These microorganisms have been found to have mechanisms that are resistant to heavy metals— such as oxygen-transport metalloproteins, along with the capacity to excrete siderophores which are chelate compounds providing extracellular protection (Schalk, Hannaver, & Braud, 2011). Another mechanism that is resistant to heavy metals, including chromium, is the genetic capacity to reduce cations with chromosome-specific genes that use reductase enzymes (He *et al*., 2011; Kumar *et al*., 2013).

Given the results reported above, authors such as Rathnayake, Megharaj, Bolan and Naidu (2010), Salgado-Bernal *et al*. (2012), and Xie, Fu, Wang and Liu (2010) have worked with heavy metal-resistant bacteria to treat soils and surface water. In a study by Salgado-Bernal *et al*. (2012), the bacterial strains are not only resistant to Hg, Cr and Pb but also present a certain removal capacity in the aqueous phase. These results, along with the problems described, suggest that constructed wetlands containing resistant bacteria may be a technically efficient for treating wastewater containing heavy metals, since these systems remove pollutants through the interaction of bacteria and vegetation. Unlike biological systems that do not contain vegetation, this interaction has enabled constructed wetlands to be used to treat water containing a certain level of heavy metals. Thus, it is suggested that heavy metal-resistant bacteria can be used in constructed wetlands to provide and improve the capacity to remove Hg, Pb and Cr, as compared to systems with conventional bacteria from wastewater. Furthermore, concentration levels characteristic of industrial discharges could be treated.

The present work evaluates the mercury, chromium and lead removal efficiency of a constructed wetland inoculated with resistant strains, and compares it to the same system without the addition of resistant bacteria. The results provide preliminary experimental data and the initial design elements for future pilot-scale studies related to the treatment of effluents containing heavy metals.

Methodology

Experimental Design

Six laboratory-scale reactors were used, containing PVC cylinders measuring 39 cm high and 20 cm in diameter, for a height/diameter ratio of 1.7:1— within the proportions recommended and widely used for this type of system (Lüderitz, 2004; Puigagut, Caselles-Osorio, Vaello, & García, 2008; Winter & Goetz, 2003; Wood, 1995). These dimensions correspond to the fill volume of the support medium, which consisted of volcanic rock called tezontle, with a particle diameter from 3.8 to 4.5 mm and a porosity of 38% (Kadlec *et al*., 2000; USEPA, 2000). The water level in each of the six wetlands was adjusted to 5 cm below the surface of the fill medium, resulting in a liquid volume of approximately 4.0 l. Three of the six systems were sterilized and inoculated with a heavy metal-resistant bacterial consortium, identified as RSR. The other three systems were not sterilized in order to contain bacteria associated with the rhizosphere of the vegetation. These are identified as conventional strain reactors (CSR).

Operating Conditions of the Constructed Wetlands

The *phragmites* species was planted in all the constructed wetlands (RSR and CSR). In the case of the three reactors inoculated with resistant strains (RSR), the rhizosphere was sterilized by applying 10% NaClO (sodium hypochlorite), followed by 70% C_2H_6O (ethanol) (De Souza, Huang, Chee, & Terry, 1999). The fill material was also washed and sterilized with moist heat at 115°C for 15 minutes using an autoclave (Black, 1999; Ramírez *et al*., 2011).

After the six wetland systems were filled and planted, the three CSR were inoculated with a bacterial consortium consisting of five heavy-metal resistant strains previously studied by Salgado-Bernal *et al*. (2012), all belonging gram-positive *Bacillus* genus — TAN117, TAN119, TAN1113, TAN1115 and TAN217. The inoculation was performed by planting each one of the resistant strains mentioned in an Erlenmeyer flask with one liter of nutrient solution. After the bacteria proliferated, the medium was diluted to a concentration of 300 mg l^{-1} of COD. This solution was then poured into each of the three RSR which, given their dimensions, exhibited an organic load of 16 $gm^{-2}d^{-1}$, a value characteristic of constructed wetland systems (Kadlec *et al*., 2000; Kadlec & Wallace, 2009).

The RSR were fed with a solution containing a $C_{12}H_{22}O_{11}$ (sucrose) content of 400 mg l^{-1} of COD (Masters & Ela, 2008) so that the organic load mentioned above would be the same in all the reactors.

For both types of reactors, the development of the microbial density was quantified as of day 3 and daily thereafter, based on unit forming colonies (UFS) by counting viable cells using the pour plate method. This quantification was performed until day 15, the point at which the six reactors were considered to be colonized, having presented an asymptotic behavior in the bacterial density over time, reaching a value of roughly 37 x 10^6 UFC ml^{-1}.

After bacterial colonization, the six reactors were operated in batch for 136 days

(151 total days from the time of inoculation), changing the water every four days. Table 1 shows the composition of the synthetic wastewater used to feed the reactors, based on studies by Orduña- Bustamante, Vaca-Mier, Escalante-Estrada and Durán-Domínguez-de-Bazúa (2011). The values shown are characteristic of typical municipal wastewater (Crites & Tchobanoglous, 2000; Masters and Ela, 2008). Heavy metal concentrations were determined using bacterial and phytotoxicity tests to ensure that the biological components of the constructed wetlands were not inhibited and that these systems could operate as wastewater treatment systems over the course of the days. In addition, the heavy metal concentrations used were characteristic of discharges from the industries previously mentioned (Barrera *et al*., 2003; Lavado *et al*., 2010; Loredo *et al*., 2003). The procedures for testing toxicity will be described next.

Phytotoxicity and Bacterial Tests

To test for phytotoxicity, a biological test was conducted with *Lactuca sativa* seeds to evaluate the effects of the heavy metal mixture of interest. The methodology used was described by Sobrero and Ronco (2004), in which the germination of the seeds as well as the development of lettuce seedlings were statistically determined based on radicle (root in the embryonic phase) and hypocotyl (stem in the embryonic phase) measurements. The different concentrations tested are described in Table 2. The germination tests were performed in triplicate for each concentration and each repetition contained 10 dispersed *L sativa* seeds. After incubating the seeds, inhibitions in germination and/or hypocotyl and root development were observed and the results were compared against the control (zero concentration of heavy metals), thereby establishing the inhibition percentages for each concentration evaluated.

The biological test to identify the effect of each heavy metal mixture on the bacterial density of the resistant bacterial consortium was performed in a similar manner as the phytotoxicity tests. The concentrations shown in Table 2 were evaluated, which according to previous studies by Salgado-Bernal *et al*. (2012) are the maximum concentrations obtained by the proliferation of the bacteria of interest. These are similar to the maximums evaluated by the present study. In general terms, the nutrient solution was prepared in triplicate for each concentration of heavy metal mixture to be tested (Table 2), followed by inoculation by roasting, extracting the inoculum from

Table 1. Composition of synthetic wastewater used to feed each of the constructed wetland systems.

Nutrient	Concentration, mg l^{-1}	Compound used
Carbon	400 (expressed as COD)	$C_{12}H_{22}O_{11}$
Nitrogen	30	$(NH_4)_2SO_4$
Phosphorus	6	Na_3PO_4
Potasium	30	KNO_3
Mercury	0.106	$HgCl_2$
Lead	26	$Pb(NO_3)_2$
Chromium	16.5	$Cr(NO_3)_6$

each agar nutrient containing the resistant bacteria. After incubating for 40 hours at 34°C, the bacteria in the consortium were quantified after the pour plate analysis to obtain the results in UFC ml^{-1} (Aquiáhuatl & Pérez, 2004; Ramírez *et al.*, 2011). Comparing these to the respective heavy metal concentrations, the lethal concentrations (LC) proportional to the degree of inhibition were calculated. That is, LC_{50} refers to a heavy metal concentration that inhibits the bacterial population by 50% with respect to the control without heavy metals, and in function of the resulting equation (kinetic behavior). In effect, LC_{50} is the variable used in studies to test toxicity, especially when the test organisms are bacteria, since even though the population is reduced by 50%, inhibition is proportional to reproduction by binary fission (duplication) (Sobrero & Ronco, 2004).

Analytical Determinations and Statistical Analyses

Samples were taken from each reactor every four days, according to the times at which water was changed, using polyethylene jars previously washed with 5% HNO_3 (nitric acid). Metals were determined with a Perkin-Elmer Optima 4 300DV atomic absorption spectrometry, using the generation of hydride for the mercury samples and the flame method for lead and chromium, according to the protocol by the USEPA 3 005A method (1996).

To compare removal efficiencies between the two types of constructed wetlands, all the heavy metal results were statistically analyzed with an analysis of variance and ANOVA using repeated measurements. Before the ANOVA analysis, the normality and homogeneity of the data were verified with the Kolmogorov-Smirnov test. Minitab 15 for Windows was used for these analyses.

Results and Discussion

The results from this investigation are presented next in the order in which the experiments were performed (rather than the order of the methodologies followed). That is, the metal concentrations required for the laboratory tests with the reactors that simulated constructed wetlands will be presented first, followed by the results from testing with the heavy metals.

Toxicity Tests of the Heavy Metal Mixture

Figure 1 shows the dose-response curves for each of the toxicity tests performed. In terms of phytotoxicity, the heavy metals did not present any lethal effects given that all the seeds germinated after incuba-

Table 2. Heavy mental concentrations in the mixtures applied during toxicity tests of the microbial consortium and the *L. sativa* seeds.

Combination of heavy metal concentrations, mg l^{-1}			
Concentration level	**Chromium**	**Lead**	**Mercury**
0	0	0	0
1	0.525	0.825	0.003
2	3.5	5.5	0.02
3	10.5	16.5	0.06
4	21	33	0.12
5	42	66	0.24
6	70	110	0.4

tion time. Nevertheless, notable inhibitory effects on plant growth were observed, as compared to the control which did not contain the heavy metals mixture, as shown in Table 3. This table also shows a close similarity among the last three values of the hypocotyl length (corresponding to the three mixtures highest in metals), and therefore the response (effect) to the high dose was virtually the same. The column showing the radicle length indicates that this decreases proportionally to the increase in the concentration of heavy metals. Such behaviors in vegetation from the effect of high doses of heavy metals coincide with reports by Di Salvatore, Carafa and Carratú (2008), and Walter, Martínez and Cala (2006), who also worked with at least three of the metals used by the present investigation. Figures 1a and 1b present the inhibition percentages corresponding to the hypocotyl and radicle lengths, respectively, in function of the concentration of metals applied. The asymptotic trend in the inhibition is characteristic of performing this type of test with photoautotrophic specimens, since inorganic toxic compounds can circulate through tissue with a saturation limit, resulting in a first-order assimilation (Nagajyoti, Lee, & Sreekanth, 2010). The curves in Figures 1a and 1b show that the concentrations resulting in a 50% inhibition in radicle and hypocotyl growth are very similar in both parts of the plants— 0.109 mg l^{-1} of Hg, 17.3 mg l^{-1} of Cr and 27.2 mg l^{-1} of Pb for the radicle, and 0.106 mg l^{-1} of mercury, 16.5 mg l^{-1} of Cr and 26 mg l^{-1} of Pb for the hypocotyl.

Figure 1c shows the bacterial inhibition in function of the concentration of heavy metals applied. The equation of the resulting curve (first-order characteristic) shows an LC_{50} for the bacterial consortium of 0.112 mg l^{-1} for Hg, 18.2 mg l_{-1} mg l^{-1} for Cr and 29.5 mg l^{-1} for Pb. These are higher than the maximum allowable values for biological

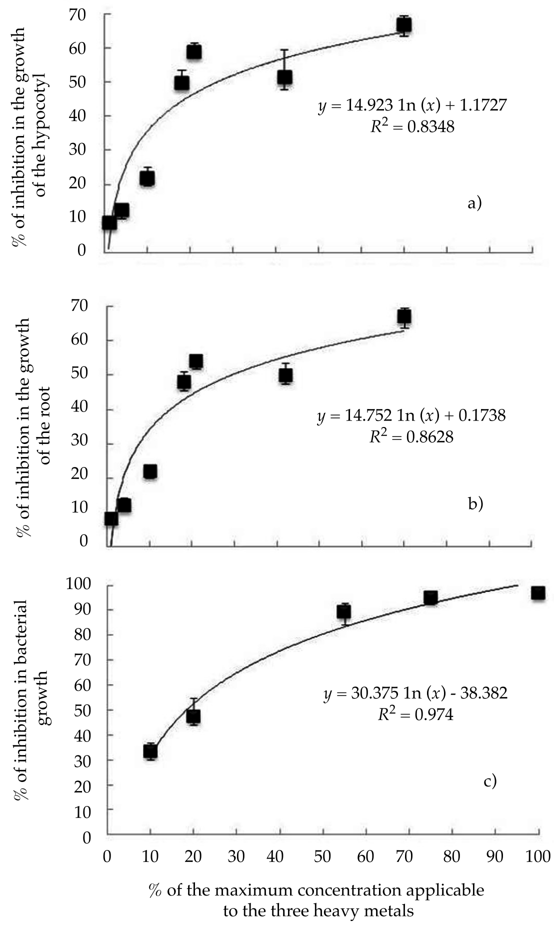


Figure 2. Results from toxicity tests from the mixtures of the three heavy metals: inhibition of growth of the hypocoltyl (Figure 1a); inhibition in root growth (Figure 1b); inhibition of bacterial development or "growth" (Figure 1c) (± standard deviation).

wastewater treatment systems (Jin, Yang, Yu, & Zheng, 2012; Karvelas, Katsoyiannis, & Samara, 2003) and very similar to those reported by Viti, Pace and Giovannetti (2002), while they are lower than the *in vitro* study by Congeevaram, Dhanaran, Park, Dexilin and Kaliannan (2007).

Considering the lethal concentrations obtained with the three tests performed, the ones that were lowest in the feed water were used, which correspond to the hypocotyl. This ensures that the wetland systems can operate without collapsing from the presence of heavy metals. It is worth mentioning that these concentrations are within the ranges reported in the different industries that generate at least one of the heavy metals tested in this study, as mentioned in the methodology. Thus, the results obtained in this first experimental phase provide criteria for subsequent studies of heavy metal removal using this type of biological system. Specifically, concentration levels that are feasible for removal were determined, and the procedure was established to identify those levels given variations in the microorganisms or heavy metals to be evaluated.

Heavy Metal Removal

Figure 2 shows the removal of three heavy metals by the two types of reactors evaluated over the 151 days of operation. When applying the Kolmogorov-Smirnow test to determine the normality of the data, the tests with Pb and Cr resulted in a normal distribution ($P > 0.05$), whereas with mercury the distribution of the data did not fit a normal distribution ($P < 0.05$) but rather a Weibull distribution. Therefore, the Box Cox transformation method was used and an ANOVA analysis with repeated measurements was applied.

Figure 2a shows the trends in mercury removal obtained with the constructed wetlands, which was 50%, on average, with conventional bacterial strains (CSR) and 60% with the reactors containing resistant bacteria (RSR). At the beginning of operations, removal values over 90% were observed in both systems, with a decreasing trend up to day 30, at which point removal began to increase in both types of reactors until day 50. After this, it fell sharply to under 50% on day 74 of operations. The high mercury removal percentages obtained until this point are likely related to volatilization, as suggested by Ventura, Simoes, Tomaz and Costa (2005), and Schlüter (2000), in addition to the evapotranspiration of the metal by the vegetation (Han, Su, Monts, Waggoner, & Plodinec, 2006; Kabatas-Pendias & Pendias, 2001). This would explain why the behavior and removal was virtually the same for both types of reactors during the first half of the experiments. Nevertheless, after day 74 only the RSR presented stable behavior, especially over the last 30 days, period during which the removal efficiency of the CSR tended to decrease as the days of operation increased (in spite of showing little variation) and the removal efficiency did not stabilize. This difference between the RSR and CSR systems is due

Table 3. Quantitative effect of the heavy metal dose applied during phytotoxicity and bacterial toxicity tests (± standard deviation).

Chromium, mg l^{-1}	Lead, mg l^{-1}	Mercury, mg l^{-1}	Bacterial density, UFC ml^{-1} x 10^3	Root length, cm	Hypocotyl length, cm
0	0	0	30 000 ± 2 900	2.70 ± 0.08	4.50 ± 0.06
0.525	0.825	0.003	27 000 ± 3 100	2.14 ± 0.20	4.10 ± 0.46
3.5	5.5	0.02	22 000 ± 2 100	1.93 ± 0.20	3.96 ± 0.43
10.5	16.5	0.06	10 000 ± 1 400	1.41 ± 0.16	3.31 ± 0.25
21	33	0.12	3 900 ± 300	0.31 ± 0.26	1.87 ± 0.12
42	66	0.24	12 ± 1.10	0.26 ± 0.35	2.20 ± 0.51
70	110	0.4	2 ± 0.15	0.18 ± 0.23	1.60 ± 0.20

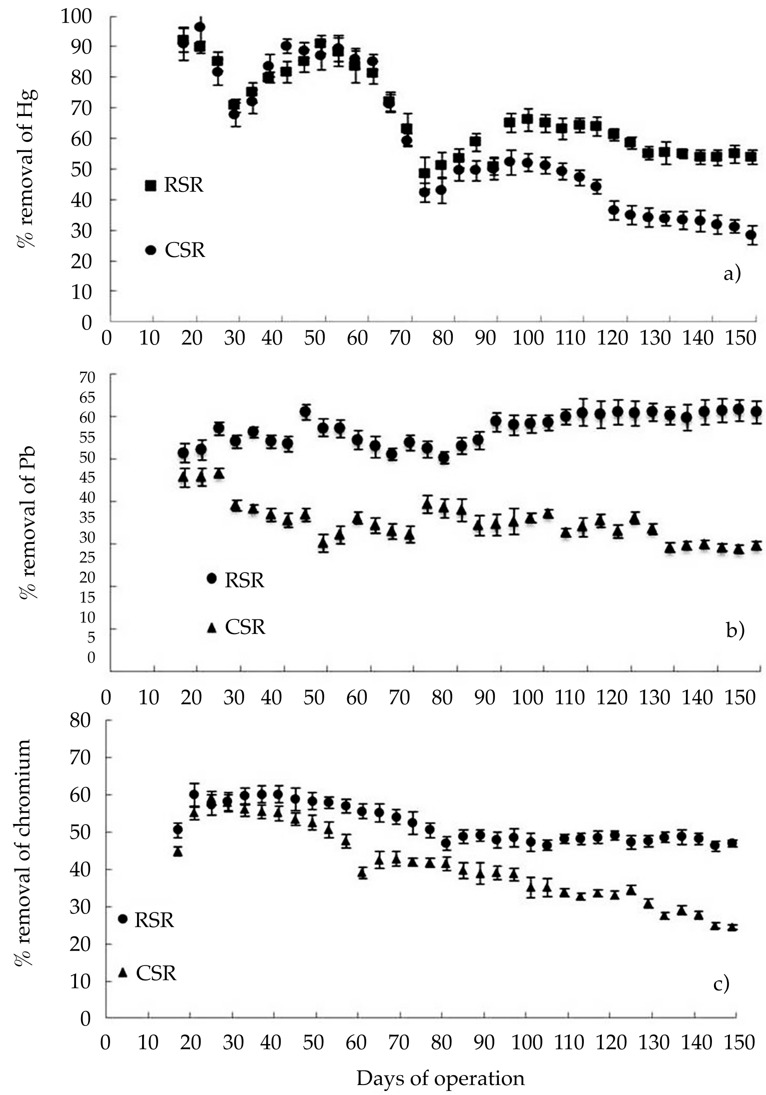


Figure 2. Results from removal of mercury (Figure 2a), lead (Figure 2b) and chromium (Figure 2c) from each one of the types of reactors studied. CSR - conventional strain reactor, RSR - resistant strain reactor (± standard deviation).

to the type of organisms with which they were inoculated since, as indicated by Salgado-Bernal *et al*. (2012), with some heavy metals concentrations generational adaptations contribute to the RSR consortium's resistance capacity and proliferation. That is, in spite of inhibition by the heavy metals, proliferation through binary fission stabilizes the bacterial population (De, Ramaiah, & Vardanyan, 2008; Xie *et al*., 2010). This difference is reflected in the statistical analysis, where significant differences ($P < 0.05$) occurred as of day 80 of operations.

The removal efficiencies in this study are below those reported by De *et al*. (2008) and Filali *et al*. (2000), although the experimental conditions are not the same, since these two investigations only performed *in* *vitro* tests without introducing the bacteria in the operating conditions of wastewater treatment systems.

In terms of removal of Pb, Figure 2b shows the removal efficiency varying around 55% in the reactors inoculated with resistant strains (RSR) from day 15 to day 80. Thereafter and until the end of operations the behavior became very stable, with variations under 5%. In effect, the trend line was asymptotic once the maximum removal was reached (55%). This is likely due to the complete adaptation of the resistant bacteria to the constructed wetland conditions, and to the interaction with the vegetation, in particular. This can be explained by evidence of the tendency of lead to accumulate in the rhizome and in the roots of aquatic plants over the first days (Deng, Ye, & Wong, 2004), which was precisely when the lead removal was relatively high, though unstable (Figure 2a). Along these same lines, a large part of the removal exhibited during the first 80 days of operations (Figure 2b) likely occurred from the rhizosphere's assimilation of the vegetation, which was greater in the RSR system. This assimilation mainly occurs from heavy metals bonded with secondary transporters (such as proteins) passing through the plasmatic membrane of the vegetation (Clemens, Plamgreen and Kramer, 2002; Guerinot, 2000). In addition, microorganisms associated with the rhizosphere foster the regeneration of proteins and other compounds which are exuded by the plants (Clemens *et al*., 2002; Williams, Pittman y Hall, 2000).

Using conventional bacterial systems (CSR) the trend is opposite to that of the RSR, with removal dropping up until day 80. Nevertheless, the variations decrease after this point and become stable over the last 20 days of operation, although the removal percentage is roughly half that of the RSR, with statistically significant differences over time ($P < 0.005$). These results indicate the ability of the bacteria to adapt to media polluted with lead and to continue performing their metabolic functions, interacting with the vegetation and removing metal, even though they are not resistant at first. This reflects an evolutionary characteristic suggested by Rathnayake *et al*. (2010), and Vacca, Wand and Kuschk (2005), which coincides with Lyer, Mody and Jha (2005) who report that the microorganisms contain natural lead detoxification mechanisms through cellular exudates which function as chelates.

Lastly, the trend for chromium removal was best with both types of systems. Figure 2c shows that the reactors inoculated with resistant strains (RSR) began with removal values of around 60%, which decreased to 47% by day 80. Thereafter and until the last day of operation, the removal stabilized at around 50%, with variations under 10%. This behavior is different than that observed with the constructed wetlands containing conventional strains (CSR), which became less efficient in removing chromium over time. Though removals of around 50% were obtained over the first days of operation, this decreased to 24% by the end of the tests and the behavior was not stable (Figure 2c). Therefore, the results from the two types of systems present statistically significant differences after day 40 of operations ($P < 0.05$). The higher removal registered in the resistant strains is likely due to the same mechanisms as with lead, in which resistant bacteria interact synergistically with the vegetation. In addition, the literature reports that a higher proportion of chromium than lead is translocated (Cheng *et al*., 2002), which could have resulted in chromium removal being more stable than lead removal, exhibiting mobility throughout the plant and not only in the roots (Khan *et al*., 2009) (Figures 2b and 2c). Furthermore, as mentioned, the heavy metal-resistant bacteria have a protection mechanism which reduces the cations through reductase enzymes (He *et al*., 2011; Kumar *et al*., 2013). In the present study, this reduction in valence turned out to be beneficial in terms of toxicity for the case of chromium.

The chromium removal percentages obtained by the present investigation coincide with reports by Kröpfelová, Vymazal, Švehla and Štíchová (2009) and by Mant, Costa, Williams and Tambourgi (2006). These authors worked with constructed wetlands and the wastewater characteristic of leather industries.

In general, the results from this last experimental portion indicate that, for the three metals, the systems with resistant bacteria (RSR) stabilized after 100 days of operation. This information is useful to pilot-scale and full-scale studies related to design, start-up, operations and removal levels to be obtained once the constructed wetlands stabilize. In effect, the design and operations of wastewater treatment systems require that variations in discharges not exceed 10% (Crites & Tchobanouglous, 2000; Masters & Ela, 2008) and the present study attained this level of stabilization, particularly for lead, which varied by 5%.

It is worth mentioning that the above contribution— with its focus on scaling to treat water containing mercury, lead and/or chromium from the industries mentioned — can be considered applicable given the results produced by the systems with resistant bacterial strains, which stabilized the removal of heavy metals.

The possible removal mechanisms found in constructed wetlands include phytoextraction, adsorption by the fill media and volatilization.

In effect, resistant strains contribute to increasing or improving the functioning of these mechanisms in these systems. In terms of adsorption in the constructed wetlands, bacteria proliferate in the form of biomass adhered to the fill media, which is known as a biofilm. This is an efficient bioadsorbent of heavy metals (Chong, Ahmad, & Lim, 2009), which are released in a suspended manner over time. Since they are resistant organisms, the biofilm grows, develops and regenerates regardless of the presence of heavy metals (Nies, 2003). Phytoextraction is another mechanism that is optimized by the resistant bacteria. In this case, metals accumulate in the vegetative organs as a result of the bonding of these cations with bacterial proteins and the selectivity of root membranes and rhizomes to these molecules, enabling them to enter. This molecular modification into metalloproteins is characteristic of heavy-metal resistant microorganisms (Schalk *et al*., 2011), resulting in significant differences between the two types of systems evaluated. The increased phytoextraction from the use of resistant bacteria is more evident in mercury removal, which can be evapotranspired through the upper organs of vegetation (Clemens, 2006) and transferred to the atmosphere (volatilization) because of its low vapor pressure (Kabatas-Pendias & Pendias, 2001; Ventura *et al*., 2005).

The results presented by the study herein demonstrate the importance of using resistant strains in constructed wetlands to remove heavy metals. In this case, the removal of the three metals was similar (roughly 50%), although the maximum allowable limits established by NOM-001-SEMARNAT-1996 (DOF, 1996) were not satisfied because of the influent concentrations mentioned in previous paragraphs. Nevertheless, it is worth highlighting that this fact is not due to the degree of efficiency but rather the high influent concentration being treated. That is, the regulations would not have been met even if removal efficiencies over 95% had been obtained. Therefore, the few systems used to treat industrial effluents containing chromium, lead and/or mercury pollutants always operate sequentially or in combination with other systems (physiochemical or electrochemical) (Fu & Wang, 2011; Khan *et al*., 2009). These systems could be substituted by constructed wetlands as a primary treatment or as a secondary polishing treatment, since they are much more economically and operationally accessible and they generate secondary benefits (Kadlec *et al*., 2000; Kadlec and Wallace, 2009).

Conclusions

The results from the removal of heavy metals by the systems studied demonstrate the contribution of resistant strains in constructed wetlands, which increased removal and, in particular, contributed to stability. This latter aspect makes it possible to implement them as systems to treat wastewater containing mercury, lead and/or chromium.

The increased removal and stability achieved by the treatment of heavy metals are likely due to improvements in the removal mechanisms in the wetlands (adsorption, phytoextraction and volatilization). It would be useful to study the role of resistant bacteria in accumulating and distributing heavy metals in constructed wetland systems, considering each one of the factors involved— vegetation, fill media, bacteria and effluent. To this end, the results from the present study provide criteria to build and operate these systems based on experimental tests.

Considering the removal efficiencies attained and the reported concentrations of mercury, chromium and lead in industrial effluents, constructed wetlands inoculated with resistant strains could be a useful alternative, necessarily in combination with physiochemical treatment in order to comply with current regulations. To corroborate this, pilot-scale studies based on the results from the present investigation will be useful, given that the heavy metal influent concentrations (according to the toxicity tests) and the operating characteristics used were adequate, as demonstrated by the subsistence and proliferation of both the bacteria and the vegetation throughout the entire operating period and the fact that the values fell within the range of those reported for effluents from industries that use and/or produce heavy metals.

Acknowledgements

The first author would like to thank the UNAM Postgraduate School for its doctoral grant, and the Mexican National Council for Science and Technology. The authors also thank Dr. Irina Salgado-Bernal, School of Biology, University of Havana, Cuba, for use of the heavy metal-resistant strains she isolated from the Almendares River in Havana, Cuba. The first measurements of lead were performed at the Autonomous University of Campeche, Mexico, with valuable help from Dr. Jorge Arturo Benitez-Torres.

References

Aquiáhuatl, M. A., & Pérez, M. L. (2004). *Manual de prácticas del laboratorio de microbiología general* (75 pp.). México, DF: Universidad Autónoma Metropolitana.

Barakat, M. A. (2010). New Trends in Removing Heavy Metals from Industrial Wastewater. *Arabian Journal of Chemistry*, *10*, 1016-1034.

Barrera, C., Romero, M., & Martínez, S. (2003). Chemical and Electrochemical Considerations on the Removal Process of Hexavalent Chromium from Aqueous Media. *Journal of Applied Electrochemistry*, *33*, 61-71.

Becerra-Castro, C., Monterroso, C., Prieto-Fernández, A., Rodríguez-Lamas, L., Loureiro-Viñas, M., Acea, M. J., & Kidd, P. S. (2012). *Pseudometallophytes colonising* Pb/Zn Mine Tailings: A Description of the Plant-Microorganism-Rhizosphere Soil System and Isolation of Metal-tolerant bacteria. *Journal of Hazardous Materials*, *217-218*, 350-359.

Black, J. G. (1999). *Microbiology: Principles and Explorations* (786 pp.). 4th edition. New York: Prentice Hall.

CEPIS (2001). *Manual de evaluación y manejo de sustancias tóxicas en aguas superficiales* (24 pp.). Washington, DC: Centro Panamericano de Ingeniería Sanitaria y Ciencias del Ambiente, Organización Panamericana de la Salud, División de Salud y Ambiente, Oficina Regional de la Organización Mundial de la Salud.

Cheng, S., Grosse, W., Karrenbrock, F., & Thoennessen, M. (2002). Efficiency of Constructed Wetlands in Decontamination of Water Polluted by Heavy Metals. *Ecological Engineering*, *18*, 317-325.

Chong, H. L. H., Ahmad, M. N., & Lim, P. E. (2009). Growth of *Thypha angustifolia* and Media Biofilm Formation in Constructed Wetlands with Different Media. *Borneo Sciences*, *25*(1), 11-21.

Clemens, S. (2006). Toxic Metal Accumulation, Responses to Exposures and Mechanisms of Tolerance in Plants. *Biochemie*, *88*, 1707-1719.

Clemens, S., Plamgren, M. G., & Kramer, U. (2002). A Long Way Ahead: Understanding and Engineering Plant Metal Accumulation. *Trends Plant Science*, *7*, 309-315.

Çolak, F., Atar, N., Yazicioĝlu, D., & Olgun, A. (2011). Biosorption of Lead from Aqueous Solutions by *Bacillus* Strains Possessing Heavy-metal Resistance. *Chemical Engineering Journal*, 173(2), 422-428.

Congeevaram, S., Dhanaran, S., Park, J., Dexilin, M., & Kaliannan, T. (July, 2007). Biosorption of Chromium and Nickel by Heavy Metal Resistant Fungal and Bacterial Isolates. *Journal of Hazardous Materials*, *146*(1-2), 270-277.

Crites, R., & Tchobanoglous, G. (2000). *Tratamiento de aguas residuales en pequeñas poblaciones* (776 pp.). Bogotá: McGraw-Hill.

De, J., Ramaiah, N., & Vardanyan, L. (2008). Detoxification of Toxic Heavy Metals by Marine Bacteria Highly Resistant to Mercury. *Marine Biotechnology*, *10*, 471-477.

Deng, H., Ye, Z. H., & Wong, M. H. (November, 2004). Accumulation of Lead, Zinc, Cooper and Cadmium by 12 Wetland Plant Species Thriving in Metal-contaminated Sites in China. *Environmental Pollution*, *132*(1), 29-40.

De Souza, M. P., Huang, C. P. A., Chee, N., & Terry, N. (August, 1999). Rizosphere Bacteria EEnhance the Accumulation of Selenium and Mercury in Wetland Plants. *Planta*, *209*(2), 259-263.

Di Salvatore, M., Carafa, A. M., & Carratú, G. (November, 2008). Assessment of Heavy Metal Phytotoxicity Using Seed Germination and Root Elongation Tests: A Comparison of Two Growth Substrates. *Chemosphere*, *73*(9), 1461-1464.

DOF (1996). Norma Oficial Mexicana NOM-001-SEMARNAT-1996 Que establece los límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales. *Diario Oficial de la Federación*. México, DF: Poder Ejecutivo Federal.

Filali, B. K., Taoufik, J., Zeroval, Y., Dzairi, F.Z., Talbi, M., & Blaghhen, M. (2000). Waste Water Bacterial Isolate Resistant to Heavy Metal and Antibiotics. *Current Microbiology*, *41*, 151-156.

Fu, F., & Wang, Q. (2011). Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environmental Management*, *92*, 407-418.

Guerinot, M. L. (May, 2000). The ZIP Family of Metal Transporters. *Biochemica et Biophysica Acta (BBA)-Biomembranes*, *1465*(1-2), 190-198.

Han, F. X., Su, Y., Monts, D. L., Waggoner, C. A., & Plodinec, M. J. (September, 2006). Binding, Distribution, and Plant Uptake of Mercury in a Soil from Oak Ridge, Tennessee, USA. *Science of the Total Environment*, *368*(2-3), 753-768.

He, M., Li, X., Liu, H., Miller, S.J., Wang, G., & Rensing, C. (2011). Characterization and Genomic Analysis of a Highly Chromate Resistant and Reducing Bacterial Strain *Lysinibacillus fusiformis ZC1*. *Journal of Hazardous Materials*, *185*(2-3), 682-688.

INE (2004). Instituto Nacional de Ecología. La contaminación por mercurio en México. *Gaceta Ecológica*, *72*, 21-34.

Jin, R. C., Yang, G. F., Yu, J. J., & Zheng, P. (2012). The Inhibition of the Anammox Process: A Review. *Chemical Engineering Journal*, *197*, 67-79.

Kabatas-Pendias, A., & Pendias, H. (2001). *Trace Elements in Soils and Plants* (412 pp.). 3th edition. Florida, USA: CRC Press.

Kadlec, R. H., Knight, R., Vymazal, J., Brix, H., Cooper, P., & Haberl, R. (2000)., *Constructed Wetlands for Pollution Control. Processes, Performance, Design and Operation*. London: IWA Publishing, 156 pp.

Kadlec, R. H., & Wallace, S. (2009)., *Treatment Wetlands* (1016 pp.). 2nd edition. Florida, USA: CRC Press.

Karvelas, M., Katsoyiannis, A., & Samara, C. (2003). Occurrence and Fate of Heavy Metals in the Wastewater Treatment Process. *Chemosphere*, *53*(10), 201-1210.

Khan, S., Ahmad, I., Shah, M. T., Rehman, S., & Khaliq, A. (2009). Use of Constructed Wetlands for the Removal of Heavy Metals from Industrial Wastewater. *Journal of Environmental Management*, *90*, 3451-3457.

Kröpfelová, L., Vymazal, J., Švehla, J. Y., & Štíchová J. (April, 2009). Removal of Trace Elements in Three Horizontal Sub-surface Flow Constructed Wetlands in the Czech Republic. *Environmental Pollution*, *157*(4), 1186-1194.

Kumar, M., Kaur, N., Gautam, K., Pathak, R. K., Khasa, Y. P., & Gupta, L. R. (2013). Reporting Heavy Metal Resistance Bacterial Strains from Industrially Polluted Sites of Northern India Using Fatty Acid Methyl Ether (FAME) Analysis and Plasma Atomic Emission Spectroscopy (ICP-AES). *Advanced Science Letters*, *19*(11), 3311-3314.

Lavado, C., Sun, M. R., & Bendezu, S. (2010). Adsorción de plomo de efluentes industriales usando carbones activados con H_3PO_4. *Revista de la Sociedad Química del Perú*, *76*(2), 1810-1836.

Loredo, J., Álvarez, R., & Ordóñez, A. (2003). Release of Toxic Metals and Metalloids from Los Rueldos Mercury

Mine (Asturias, Spain). *Science of the Total Environment*, *340*, 247-260.

Lüderitz, V. (2004). Towards Sustainable Water Resources Management: A Case Study from Saxony-Anhalt, Germany. *Management of Environmental Quality: An International Journal*, *15*(1), 17-24.

Lyer, A., Mody, K., & Jha, B. (March, 2005). Biosorption of Heavy Metals by a Marine Bacterium. *Marine Pollution Bulletin*, *50*, 340-343.

Mant, C., Costa, S., Williams, J., & Tambourgi, E. (October, 2006). Phytorremediation of Chromium by Model Constructed Wetland. *Bioresource Technology*, *97*(15), 1767-1772.

Masters, G., & Ela, W. (2008)., *Introduction to Environmental Engineering* (708 pp.). 3th edition. New York: Prentice Hall.

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy Metals, Ocurrence and Toxicity for Plants: A Review. *Environmental Chemical Letters*, *8*, 199-216.

Nies, D. H. (June, 2003). Efflux Mediated Heavy Metals Resistance in Prokaryotes. *FEMS Microbiology Reviews*, *27*(2-3), 313-339.

Orduña-Bustamante, M. A., Vaca-Mier, M., Escalante-Estrada, J. A., & Durán-Domínguez-De-Bazúa, M. C. (2011). Nitrogen and Potassium Variation on Contaminant Removal for a Vertical Subsurface Flow Lab Scale Constructed Wetland. *Bioresource Technololy*, *102*, 7745-7754.

Puigagut, J., Caselles-Osorio, A., Vaello, N., & García, J. (2008). Fractionation Biodegradability and Particle-size Distribution of Organic Matter in Horizontal Subsurface-Flow Constructed Wetland (pp. 289-297). In J. Vymazal (Ed.). *Wastewater Treatment, Plant Dynamics and Managemente in Constructed and Natural Wetlands*. ed. Czech Republic: Springer Netherlands.

Ramírez, R. M., Luna, B., Velázquez, O., Hernández, L., Müggenburg, I., Camacho, A., & Urzúa, M. C. (2011)., *Manual de prácticas de microbiología general* (159 pp.) Sexta edición. México, DF: Facultad de Química de la Universidad Nacional Autónoma de México.

Rathnayake, I. V. N., Megharaj, M., Bolan, N., & Naidu, R. (2010). Tolerance of Heavy Metals by Gram Positive Soil Bacteria. *International Journal of Civil and Environmental Engineering and Technology*, *2*(4), 191-195.

Salgado-Bernal, I., Carballo-Valdés, M. E., Martínez-Sardiñas, A., Cruz-Arias, M. & Durán-Domínguez-De-Bazúa, M. C. (julio-septiembre, 2012). Interacción de aislados bacterianos rizosféricos con metales de importancia ambientalRhizosphere Bacterial Isolates Environmentally Significant Metals. *Tecnología y Ciencias del Agua*, 3(3), 83-95.

Schalk, I. J., Hannaver, M., & Braud, A. (2011). New Roles for Bacterial Siderophores in Metal Transport and Tolerance. *Environmental Microbiology*, *13*(11), 2844-2854.

Schlüter, K. (January, 2000). Review: Evaporation of Mercury from Soils. An Integration and Synthesis of Current Knowledge. *Environmental Geology*, *39*(3-4), 249-271.

Sobrero, M. C., & Ronco, A. (2004). Ensayo de toxicidad aguda con semillas de lechuga (*Lactuca sativa* L.) (pp. 71-79). En G. Castillo (Ed.). *Ensayos toxicológicos y métodos de evaluación de calidad de aguas. Estandarización, intercalibración, resultados y aplicaciones*ed. G. . Ottawa: Centro Internacional de Investigaciones para el Desarrollo e Instituto Mexicano de Tecnología del Agua.

SSA (2006). *Programa de Acción: Salud Ambiental* (210 pp.). México, DF: Secretaría de Salud, Programa Secretarial.

USEPA (1996). *Method 3005A. Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy* (5 pp.). Cincinnati, Ohio: Environmental Protection Agency.

USEPA (2000). *Constructed Wetlands Treatment of Municipal Wastewaters* (165 pp).. Cincinnati, Ohio: United States Environmental Protection Agency.

Vacca, G., Wand, H., & Kuschk, P. (April, 2005). Effect of Plants and Filter Materials on Bacteria Removal in Pilot Scale Constructed Wetlands. *Water Research*, *39*(7), 1361-1373.

Ventura, D. F., Simoes, A. L., Tomaz, S., & Costa, M. F. (2005). Colour Vision and Contrast Sensitivity Losses of Mercury Intoxicated Industry Workers in Brazil. *Environmental Research*, 77(2), 173-177.

Viti, C., Pace, A., & Giovannetti, L. (2003). Characterization of Cr(VI)-resistant Bacteria Isolated for Chromium-contaminated Soil by Tannery Activity. *Current Micriobiology*, *46*, 1-5.

Walter, I., Martínez, F., & Cala, V. (February, 2006). Heavy Metal Speciation and Phytotoxicity Effects of Three Representative Sewage Sludge for Agricultural Uses. *Environmental Pollution*, *139*(3), 507-514.

Williams, L. E., Pittman, J. K., & Hall, J. L. (May, 2000). Emerging Mechanisms for Heavy Metal Transport in Plants. *Biochimica et Biophysica Acta (BBA)-Biomembranes*, *1465*(1-2), 104-126.

Winter, K. J., & Goetz, D. (2003). The Impact of Sewage Composition on the Soil Clogging Phenomena of Vertical Flow Constructed Wetlands. *Water Science and Technology*, *48*(5), 9-14.

Wood, A. (1995). Constructed Wetlands in Water Pollution Control: Fundamentals to their Understanding. *Water Science and Technology*, *32*(3), 21-29.

Xie, X., Fu, J., Wang, H., & Liu, J. (June, 2010). Heavy Metal Resistance by Two Bacteria Strains Isolated from a Copper Mine Tailing in China. *African Journal of Biotechnology*, *9*(26), 4056-4066.

Institutional Address of the Authors

M.I. Leonel E. Amábilis-Sosa
Dra. María del Carmen Durán-Domínguez-De-Bazúa

Facultad de Química
Universidad Nacional Autónoma de México
Conjunto E, Ciudad Universitaria s/n
Delegación Coyoacán
04510 México, D.F., MÉXICO
Teléfono: 52 (55) 5622 5300 al 04
leoamabilis@yahoo.com.mx
mcduran@unam.mx

Dra. Christina Siebe

Instituto de Geología
Universidad Nacional Autónoma de México
Ciudad Universitaria s/n
Delegación Coyoacán
04510 México, D.F., MÉXICO
Teléfono: 52 (55) 5622 4265, extensión 155
siebe@unam.mx

Dra. Gabriela Moeller-Chávez

Universidad Politécnica del Estado de Morelos
Paseo Cuauhnáhuac 566, Colonia Lomas del Texcal
62550 Jiutepec, Morelos, MÉXICO
Teléfono: 52 (777) 2293533
gabriela.moeller@gmail.com

Evaluation of Different Sources of Organic Fecal Matter as Inoculum for Methane Production

• Olivia García-Galindo • Aurelio Pedroza-Sandoval* •
• José Antonio Chávez-Rivero • Ricardo Trejo-Calzada •
Universidad Autónoma Chapingo, México
*Corresponding Author

• Ignacio Sánchez-Cohen •
Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias, México

Abstract

García-Galindo, O., Pedroza-Sandoval, A., Chávez-Rivero, J. A., Trejo-Calzada, R., & Sánchez-Cohen, I. (March-April, 2015). Evaluation of Different Sources of Organic Fecal Matter as Inoculum for Methane Production. *Water Technology and Sciences* (in Spanish), 6(2), 35-49.

The use of alternative energies is growing in light of the high costs of fossil fuels and their environmental impact. The objective of this study was to determine the best source of organic fecal matter for use as an initial inoculum in the production of methane, at different temperatures. Batch reactors of 1 000 ml were established in vitro and organic fecal matter and a microbial solution were added as an initial inoculum. A random block design with three repetitions was used. Four sources of organic matter were evaluated — human, cow, pig and goat— as well as the possible double combinations. Each treatment was subjected to temperatures of 3, 37 and 50 °C. A slightly acidic pH created a higher chemical oxygen demand (COD) and therefore a larger production of methane. According to the COD, organic matter from pigs and the combination of pigs and goats were the best treatments ($P < 0.05$) for the production of methane, primarily at a temperature of 37°C. The removal of organic matter was more efficient and thus methane production was improved during a second scaling phase of the best treatment identified in the in vitro stage, using a UASB (Upflow Anaerobic Sludge Blanket) reactor, with a pH stabilized near neutral and slightly acidic at the end of the experiment.

Keywords: Alternative energy, methane gas, biogas, environmental impact.

Resumen

García-Galindo, O., Pedroza-Sandoval, A., Chávez-Rivero, J. A., Trejo-Calzada, R., & Sánchez-Cohen, I. (marzo-abril, 2015). Evaluación de fuentes de materia orgánica fecal como inóculo en la producción de metano. Tecnología y Ciencias del Agua, *6(2), 35-49.*

Las energías alternativas están tomando auge ante los altos costos de los hidrocarburos fósiles y el impacto ambiental. El objetivo de este estudio fue determinar la mejor fuente de materia orgánica fecal como inóculo inicial a diferentes temperaturas en la producción de metano. Se establecieron reactores Batch de 1 000 ml en condiciones in vitro, a los cuales se les adicionó materia orgánica fecal y una solución microbiana como inóculo inicial. Se usó un diseño en bloques al azar con tres repeticiones. Se evaluaron cuatro fuentes de materia orgánica: humano, vaca, cerdo, cabra, más las combinaciones dobles posibles; cada tratamiento se sometió a temperaturas de 3, 37 y 50 °C. El pH con ligera tendencia hacia la acidez propició una mayor demanda química de oxígeno (DQO) y, por ende, mayor producción de metano. De acuerdo con la DQO, las fuentes orgánicas de cerdo y la combinación de cabra y cerdo fueron los mejores tratamientos ($P < 0.05$) en la producción de metano, principalmente a una temperatura de 37 °C. En una segunda fase de escalamiento del mejor tratamiento identificado en la fase in vitro, mediante uso de un reactor UASB (Upflow Anaerobic Sludge Blanket, por sus siglas en inglés), el pH se estabilizó hacia el valor neutro, con ligera tendencia al final hacia la acidez, haciendo más eficiente la remoción de la materia orgánica y, por tanto, la producción de metano.

***Palabras clave**: energía alternativa, gas metano, biogás, impacto ambiental.*

Received: 22/01/2014
Accepted: 01/12/2014

Introduction

From an ecological perspective, the lack of water and the environmental impact from the use of fossil fuels are some among the most common problems on the planet, particularly in arid zones where water is most limited. Producing methane gas with anaerobic digestion and reusing it to treat wastewater is a viable alternative in which biogas production and the efficient use of water contribute to addressing the problem on a regional level (Fang, Ke, & Shang, 2004). In terms of biogas production, the main gases that contribute to the greenhouse effect (GE) are carbon dioxide, methane, nitrogen oxides and chlorofluorocarbons, among others with lesser effects. Carbon dioxide is among those having the most impact. It is released into the atmosphere as a result of human activity such as burning fossil fuels and felling forests, which reduce the biological fixation of CO_2 (Carmona, Bolívar, & Giraldo, 2005). Methane contributes to 15% of global warming and is one of the gases with the greatest capacity to create a greenhouse effect, 23 times more than CO_2. Fortunately, large quantities do not exist in the atmosphere, but it is important to prevent it from increasing (Moss & Givens, 2000). Animal production is one of the sources of methane generation, particularly ruminants such as cattle, goats, sheep, buffalo and camelids. These animals digest food through a process called "enteric fermentation" where the microorganisms in the digestive system (rumen) ferment the food. The fermentation releases methane into the atmosphere as a byproduct. In non-ruminants, fermentation occurs in the large intestine and the bacteria have a much lower capacity to generate methane (McCaughey, Wittenberg, & Corrigan, 1999).

Thus, the amount of methane released depends on the type of animal, the type and digestibility of the food and the level of production. In addition, manure creates methane and nitrous oxide emissions, and the manure generated by confined animals who are fed high energy foods has twice the methane emissions capacity as manure from animals consuming large amounts by foraging (Orrico-Junior, Orrico, & Júnio, 2011).

From an anthropocentric perspective the production of food from animal origins— and particularly ruminants— is a necessity. Nevertheless, this should not be a reason to continue to ignore the problem. Given the complexity of the problem, alternative solutions need to be analyzed in order to mitigate the negative impact from this type of activity, as opposed to trying to eradicate it. From the ecological perspective, one option is to determine how to use this type of waste based on its potential to contribute to greenhouse gas emissions (GGE), such as the case of methane; on the one hand, using it as a source of prime material, and on the other as alternative energies such as biofuels to meet domestic and even industrial needs demanded by today's society. Biofuels represent an important alternative to satisfy current energy demand nationally as well as internationally, since they can be used as an energy source for various purposes, thereby mitigating the greenhouse effect and contributing to the sustainability of natural processes (Carere, Sparling, Cicek, & Levin, 2008). In particular, methane production from organic waste is a viable and increasingly pertinent alternative. In rural regions in developing countries, many cellulose biomasses are abundantly available and have good potential to satisfy energy demands, especially domestic (Shanta & Ramakant, 2010). Therefore, biogas production through anaerobic digestion using ASBR (Anaerobic Sequencing Batch Reactor) is increasingly common because of the advantages they provide: ease in operation, effective treatment of compounds that are poorly degraded (such as phenol) and stability of the process under changes in temperature (Guieysse, Wikströnm, Forsman, & Mattiasson, 2001; Bermúdez, Rodríguez, Martínez, & Terry, 2003; Chen, Cheng, & Creamer, 2008). In addition, the results obtained with this type of reactor support decisions about the design and construction of treatment systems used in biogas production, which should be based on: 1) maximum protection of public and environmental health and 2) minimum construction and operating costs (Lorenzo & Obaya, 2006). Given this scenario, the efficiency of UASB (Upflow Anaerobic Sludge Blanket) reactors to treat wastewater needs to be analyzed for their ability to produce biogas and to treat wastewater for reuse in regions where water is limited but where high amounts of organic matter (manure) are also produced, such as the study area for the present investigation.

UASB reactors provide a series of advantages over conventional aerobic systems, primarily: lower implementation and maintenance costs; lower production of excess sludge; less electric energy consumption; and simple functioning (Ramírez & Koetz, 1998). Thus, anaerobic filters are relatively small, easy to build and present good organic matter removal efficiencies (Castillo, Solano, & Rangel, 2006). They improve water treatment for subsequent stages, since they have a higher concentration of bacteria than other systems which enables operating with higher organic loading rates. They also reduce clogging from solids and the possibility of short circuits.

Considering the above, the study's objective was to identify the best sources of fecal organic matter, or combinations thereof, for the production of methane gas, at different temperatures, using anaerobic degradation and with batch reactors. A second experimental stage was to test the best treatment identified in the first stage using a UASB reactor to produce biogas.

Materials and Methods

Geographic Location

The study was performed under *in vitro* conditions in the laboratory at the Regional Arid Zones University Unit (URUZA, Spanish acronym), at the Autonomous University of Chapingo (UACH, Spanish acronym) in Bermegillo, Mapimi, Durango, Mexico. This region is located at coordinates 104° 36″ 36′ and 103° 33″ 36′ west longitude and 26° 5″ 24′ and 25° 28″ 48′ north latitude. In addition, support was provided by the Research and Advanced Studies Center of the National Polytechnic Institute, located at 9.6 kilometers on the Libramiento Norte, Irapuato-Leon highway, 36821 Irapuato, Guanajuato, Mexico, located at coordinates 20° 43″ 8′ north and 101° 19″ 43′ west (García, 1973).

Sample Collection

The different organic materials used as inocula to produce methane were obtained from different sites in the area of influence of the URUZA. Human organic matter was obtained from the sewer sump pump collector. Pig, goat and bovine matter was collected from the university's livestock farm. The samples were collected in 1-liter clear plastic jars which were closed after collecting the samples and transported to the laboratory.

Establishment and Operations of the Batch Reactor

The study was performed with 1 000 ml batch reactors according to Guieysse *et al*. (2001). After applying the fecal organic matter and microbial inoculum, 10 g of plastic bottle pieces were placed in the reactors as an inert support to foster the formation of the bacterial biofilm. The bacterial consortium applied inside the reactors consisted of 50 ml of solution containing various anaerobic bacteria, particularly *Pseudomonas* spp. and *Brevibacillus* sp., among others. These degrade the organic matter through an anaerobic process. The consortium used was provided by the Lerdo municipal wastewater treatment plant, in the state of Durango. Four grams of fecal matter were used for each source of inoculum, diluted in 700 ml of water in each of the stationary reactors, also called batch ASBR (Anaerobic Sequencing Batch Reactor) (Guieysse *et al*., 2001). This proportion was determined according to the average organic load in most of the wastewater in the study region so that the information generated, if positive, could be used to produce biogas while also obtaining treated wastewater. After the organic matter was introduced, the reactors were closed and air was extracted until reaching anaerobic conditions (Figure 1). Then, a sample of gas was taken with a needle and a Vacutainer tube. The sample was stored for later quantification. In order to determine the methane production during different growth phases of the bacterial consortium, this procedure was performed every week between November and December 2011 until the experiment was completed. Thus, the hydraulic retention time was 30 days, considering only 28 for practical experimental reasons.

Experimental Design

A random block design was used with three repetitions. One factor that was varied was the source of fecal organic matter (FOM)— cow (C), human (H), goat (G) and pig (P)— and the different simple combinations: C-H, C-G, C-P, H-G, H-P, G-P, plus the control. The other factor that was varied was the temperature. Each treatment was subjected to temperatures of 3, 37 and 50°C using an incubator for temperatures 37 and 50°C and refrigeration for 3°C. There was a total of 33 treatments, the product of 11 x 3.

Variables Evaluated

Potential of hydrogen (pH) was measured with a Conductronic PC45 potentiometer. Chemical oxygen demand (COD),

Figura 1. Preparation and mounting of batch reactors in the laboratory.

was measured with HACH DR/890 colorimetry to determine organic matter removal. Methane gas production (CH_4) was obtained using gas chromatography (GC) with Agilent Technologies model 7890 equipment. The pH and COD were measured at the beginning and end of the experiment, on November 24 and December 15, 2011, respectively. This was in accordance with the analysis of water-determination times based on the chemical oxygen demand for natural water, wastewater, and treated wastewater, according to the NMX-AA-154-SCFI-2011 guidelines referring to the determination of total chemical oxygen demand and potential of hydrogen (Semarnat, 2011). Methane was measured four times (once per week) over the course of the project and quantified using gas chromatography.

For the scaling phase, a 1 000 liter capacity UASB reactor was designed and mounted. Pig and goat organic matter were collected based on the best treatment results from the *in vitro* phase. Four kilograms of organic matter (2 kg of pig and 2 kg of goat), 10 kg of inert support (plastic bottle pieces) and 50 l of the bacterial consortium were used. This was determined according to the weight-volume proportion used in the *in vitro* phase. After the reactor was mounted and the film had formed, the organic matter to be treated was added and temperature, pH and COD were monitored. The monitoring was performed every third day for a period of 33 days, allowing for a hydraulic retention time of 24 hours per 1 000 l load. According to these determinations, the production of methane gas was calculated using the equation by Cámara, Hernández and Paz (s/f):

$$VCH_4 = (0.3516)\,[(So - S)\,(1/1\,000)\,1.42Px]$$

Where:

VCH_4 = methane volume (m^3).
So = Last influent COD (mg l^{-1}).
S = Last effluent COD (mg l^{-1}).
Px = Net mass of the cellular tissue produced daily (kg day^{-1}).

Results and Discussion

According to the statistical analysis performed ($P \leq 0.05$), no interaction effect was identified between the sources of the fecal organic matter and the temperatures. Therefore, each variable was analyzed separately.

Potential of hydrogen

The potential of hydrogen (pH) varied significantly ($P \leq 0.05$) at the beginning of the experiment in relation to the source of organic matter. The highest values exceeded 8, corresponding to H, P, H-P, H-G and P-G organic matter. A pH under 7 was registered for the remaining matter. The final pH indicated a higher normalization around neutral (7.2), which is more favorable to microbial development (Table 1). The pH is a critical parameter for the growth of microorganisms, since each microorganism can grow only in a narrow pH range, outside of which the growth of its population decreases. During their population growth stage, the microorganisms modify the pH of the medium containing them, generally towards acidic conditions. This can be caused by several factors, one of which is the release of products from metabolic reactions. Van Haandel and Britz (1994) indicate that the value and stability of the pH in a reactor is important since the methanogenic activity is much more vulnerable than the other populations present to changes in pH. Methanogenesis decreases significantly when the pH is lower than 6.3 or higher than 7.8. With low pH values, acidic fermentation overtakes methanogenic fermentation, resulting in

Table 1. Effect of the source of fecal organic matter (FOM) on initial and final potential of hydrogen.

FOM	pHi	Phf
No FOM	7.0 k	7.1 ab
C	7.5 i	7.2 ab
H	8.5 a	7.2 ab
G	7.4 j	6.9 b
P	8.0 e	7.3 a
H-C	7.9 f	7.2 ab
H-G	8.3 c	7.2 ab
H-P	8.4 b	7.4 a
C-G	7.7 h	7.3 a
C-P	7.9 g	7.3 a
P-G	8.2 d	7.2 ab
Average	7.8	7.2

Tukey test ($P \leq 0.05$). Data with different letters in the same column are statistically different; pHi = initial potential of hydrogen; pHf = final potential of hydrogen.

the acidification of the contents of the reactor.

The above reports are similar to those by Martínez, Maldonado, Ríos and Garza (2008), who worked with complex waters using treatment systems with biofilms. They observed pH values varying between 6 and 9, with an average near neutral. These conditions indicate that the microbial activity behaves efficiently. Van Kessel and Russell (1995) also reported that methanogens are sensitive to low pH and inhibition of methanogenesis is caused by the toxicity of acids from the fermentation produced under these conditions.

Chemical Oxygen Demand

With respect to organic matter removal efficiency, the COD indicates that the fecal matter with the best efficiencies were cow and cow-human and cow-goat combinations (74.7, 88.4 and 82.01%, respectively), and the human-goat combination (83.92%) ($P < 0.05$). This may occur from the bacterial consortium adapting more easily to these fecal inocula combinations, as compared to the pig and pig-human and pig-cow combinations (with lower efficiencies of 56.4, 58.5 and 49.22%, respectively). Based on these results, it can be inferred that the bacterial consortium required more time to adapt to the pig manure because it is a more complex fecal matter, and the higher degradation activity required more time for the bacterial consortium to adapt. The control registered virtually null COD values, which is congruent with the absence of organic matter (Table 2). Thus, COD is directly related to the degradation of organic matter and the production of methane, since anaerobic digestion is a process that transforms rather than destroys organic matter. Given that no oxidant is present in the process, the electron transfer capacity of the organic matter remains intact in the methane produced. Since there is no oxidation, the theoretical COD of the methane corresponds to most of the COD of the digested organic matter (90 to 97%), and very little is converted to sludge (3 to 10%). In the biochemical reactions that occur in the anaerobic digestions, only a small part of the free energy is released, while most of that energy remains as chemical energy in the methane produced (Rodríguez, s/f).

Table 2. Effect of different sources of fecal organic matter (FOM) on initial chemical oxygen demand (CODI) and final chemical oxygen demand (CODF).

FOM	CODI (mg l^{-1})	CODF (mg l^{-1})
No FOM	0.00 h	6.1 f
c	916.5 e	232.3 cde
H	564.0 g	183.0 def
g	1 500.0 b	364.0 bcd
p	1 516.6 a	660.5 a
H-C	744.0 f	86.3 ef
H-G	1 500.0 b	241.1 cde
H-P	1 005.8 d	416.8 bc
C-G	1 500.0 b	269.8 cde
C-P	1 074.0 c	545.3 ab
P-G	1 500.0 b	561.6 ab

Tukey test ($P \leq 0.05$). Data with different letters in the same column are statistically different.

In addition, the initial COD was statistically higher at 37°C (1 077.6 mg l^{-1}) than at the extreme temperatures of 3 and 50°C (1 073.1 mg l^{-1}), between which there is no statistical difference. In terms of the final COD, this was significantly higher at 3°C, followed by 50°C and lastly 37°C (Figure 2). The apparent differences between CODI and CODF may be due to the speed of degradation, where the highest activity occurred at 37°C, to the extent that by the end there was not enough organic matter to degrade, which is when the fourth phase begins— bacterial growth kinetics, known as the bacterial death phase. This may indicate that most of the microorganisms in the bacterial consortium may be mesophiles; that is, they adapted to optimal temperature ranges between 20 and 40°C, when most of the degradation activity of the organic matter occurs. This is reflected in the COD values.

Methane Gas Production

The behavior of methane gas over time — with the two prototype treatments (COD and methane production with P and P-G)— demonstrates an exponential growth phase beginning 7 days after the start of the experiment (DASE) and lasting up to 14 DASE. This is reflected by a high degradation of the organic matter and high chemical oxygen demand, resulting in higher methane production. From 14 to 21 DASE, a stabilization phase occurs and the methane production begins to decrease, possibly associated with the phase corresponding to a decrease in the organic load providing nutrients for the microbial population and also with the change in the enzymatic activity in which the substrate is consumed only for maintenance. Between 21 and 17 DASE, the phase corresponding to the death of the microorganisms occurs, reflected in a lower methane production rate associated with a lack of fecal organic matter (Figure 3). This process is similar to that reported by Sanz (2011), and Behling, Caldera, Marín, Rincón and Fernández (2005), who indicated the existence of low methane production during the first 5 days of the adaptation phase, exponential production between 5 and 15 days, a stabiliza-

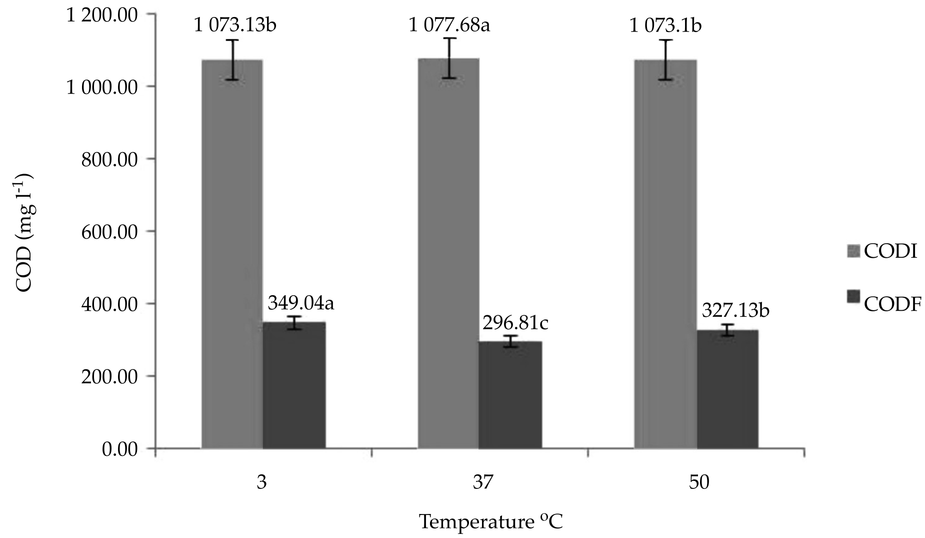


Figure 2. Effect of temperature (*T*) on average COD values obtained from the treatments with fecal organic matter.Tukey Test ($P < 0.05$). Data with different letters on top of the even bars are statistically different. CODI = initial chemical oxygen demand. CODF = final chemical oxygen demand.

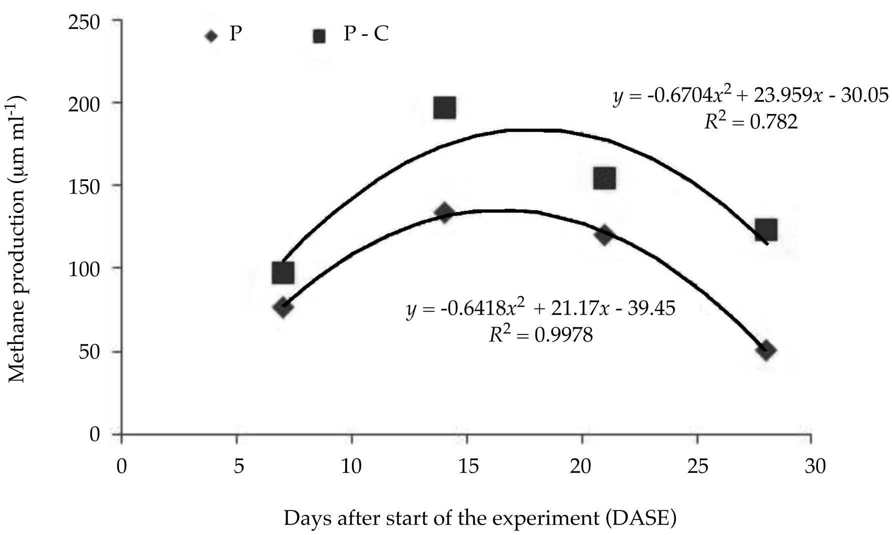


Figure 3. Temporal behavior of methane production on days 7, 14, 21 and 28 after the start of the experiment.

tion phase between days 15 and 20 and a decrease during the death phase from days 20 to 25.

The best treatments for the production of methane were fecal organic matter from pig (P) and the combination of pig-goat (P-G) and cow-pig (C-P), with values of 133.2, 197.4 and 154.9 μm ml^{-1} on day 14 after the start of the experiment, respectively. This phase resulted in the highest methane production with most of the treatments. The values for the rest of the treatments are lower than those cited above, without a very large statistical variation among them. The human organic matter (H) and the cow-human (C-H) combination had the least effect on the production of methane, with no statistical difference compared to the control (Table 3), which is consistent with the results from the statistical analysis of COD.

With regard to temperature, methane production was significantly higher at 37 and 50°C, except for the first and third evaluations at 50°C. This is consistent with the expectation that the degradation of organic matter accelerates at higher temperatures and, therefore, more biogas is produced. The most consistent temperature over the study period was 37°C, and extreme temperatures tended to inhibit this process (Figure 4).

This is relevant since 37°C is the most frequent temperature during the spring-summer period in the study region, which would enable obtaining good methane production using organic matter from pig or the combination of pig and goat, both highly available in the area of influence where the study was performed, an area notable for intensive productive activities with this type of livestock (Sagarpa-Cei-egdrs, 2003). The above results coincide with that reported by Martínez *et al*. (2008), who indicate that the optimal temperature conditions for treating wastewater are between 30 and 40°C, since temperatures lower than 15°C and higher than 45°C inhibit bacterial growth, causing the removal efficiency of COD to decrease.

In terms of the correlation among the variables, a significant correlation was observed between pH and COD— the higher the pH the higher the COD, and vice versa. This is identifiable by the initial COD (P = 0.0014) and the final COD (P = 0.003). The results from the first part were also corroborated— there is a significant positive correlation between COD and methane (CH_4) production, where the correlation between initial COD and methane production are highly significant (P = 0.0001) and final COD is significant (P = 0.0146). In terms of the relationship between pH and methane production, initial pH was found to have no effect on methane pro-

Table 3. Effect of the fecal organic matter (FOM) source on methane production.

FOM	P.CH_4 (μm ml^{-1}) 7 DASE	P.CH_4 (μm ml^{-1}) 14 DASE	P.CH_4 (μm ml^{-1}) 21 DASE	P.CH_4 (μm ml^{-1}) 28 DASE
No FOM	0.24 d	0.2 d	0.2 d	0.2 b
C	18.0 cd	48.46 cd	38.7 bcd	33.1 ab
H	0.74 d	0.3 d	0.4 d	0.4 b
G	54.2 abc	72.7 bcd	103.2 abc	37.7 ab
P	76.6 ab	133.2 abc	120.0 ab	50.8 ab
H-C	4.3 cd	6.4 d	3.5 d	4.1 b
H-G	14.5 cd	22.1 d	8.0 cd	20.9 ab
H-P	46.2 bcd	83.2 bcd	40.7 bcd	92.7 ab
C-G	31.3 dcd	42.0 cd	16.7 cd	47.0 ab
C-P	80.0 ab	154.9 ab	85.8 abcd	127.1 a
P-G	97.0 a	197.4 a	154.0 a	123.2 a

Tukey Test ($P < 0.05$). Data with different letters in the same column are statistically different. CODI = initial chemical oxygen demand. CODF = final chemical oxygen demand. P.CH_4 = methane gas production. DASE = days after start of experiment.

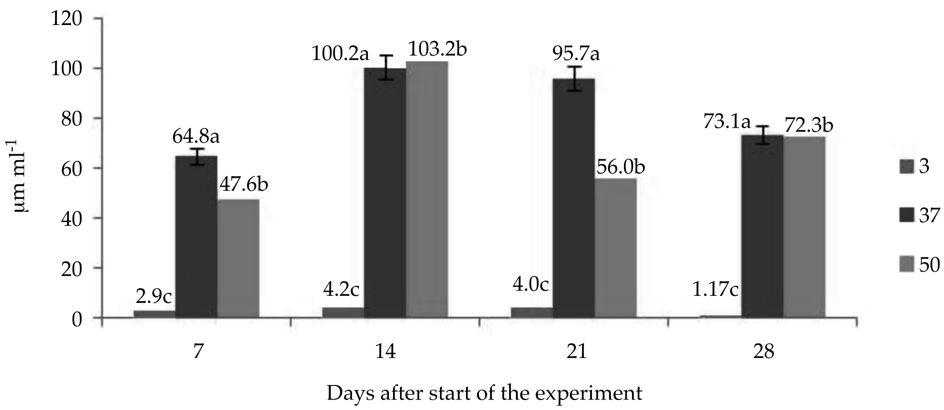


Figure 4. Effect of final temperature on chemical oxygen demand and methane gas production based on the average of the different fecal organic matter. Tukey Test ($P < 0.05$). Data with different letters in each block of columns are statistically different.

Table 4. Analysis of the Pearson Correlation among potential of hydrogen (pH), chemical oxygen demand (COD and methane production (CH_4).

	PHI	CODI	PICH$_4$	PHF	CODF	PFCH$_4$
PHI	1.00000	0.31625 0.0014	0.10176 0.3162	0.22235 0.0270	0.29541 0.0030	0.12638 0.2126
CODI		1.00000	0.41026 < 0.0001	0.04887 0.06310	0.58003 < 0.0001	0.24470 0.0146
PICH$_4$			1.00000	0.27543 0.0058	0.36984 0.0002	0.69855 < 0.001
PHF				1.00000	0.05959 0.5579	0.33051 0.0008
CODF					1.00000	0.29200 0.0034
PICH$_4$						1.00000

PHI = initial pH; PHF = final pH; CODI = initial chemical oxygen demand; CODF = final chemical oxygen demand; PICH$_4$ = initial methane gas production; PFCH$_4$= final methane gas production.

duction while final pH did have an effect ($P = 0.0008$) (Table 4). This confirms that the microbial activity is better with a neutral pH than with an alkaline pH (Van Kessel & Russell, 1995).

In terms of the scaling phase with the best treatment identified in the *in vitro* phase (pig-goat fecal matter), the effect of sampling days (in DASE) on pH, temperature and COD was found to be statistically significant ($P \leq 0.05$), which indicates the variability of the process over time (Table 5).

At the beginning of the experiment, pH was significantly more alkaline, near values of 8, while it remained around neutral during the rest of the period, with values of 7, until ending with an acidic pH with a value of 6.3. This is due to the release of products from the secondary reactions of the bacteria in the bacterial consortium. The pH in this study phase ranged from an initial value of 8.0 to a final value of 6.3, which was directly related with the parameters established by Van Haandel and Britz (1994)— reflected in the production

Table 5. Effect of time on potential of hydrogen, temperature and chemical oxygen demand.

DASE	pH	*T* (°C)	COD (mg l^{-1})
1	8.00 a	22 a	1 650 a
3	7.00 b	22 a	1 067 b
5	7.00 b	21 b	846 c
7	7.00 b	21 b	836 c
9	7.00 b	20 c	785 d
11	7.00 b	19 d	792 d
13	7.00 b	19 d	668 e
15	7.00 b	19 d	644 f
17	7.00 b	18 e	582 g
19	6.66 bc	18 e	500 i
21	7.00 b	19 d	565 h
23	7.00 b	19 d	419 j
25	7.00 b	18 e	413 j
27	7.00 b	18 e	395 j
29	7.00 b	18 e	384 k
31	7.00 b	18 e	380 k
33	6.33 cd	18 e	170 l

Tukey Test ($P < 0.05$). Data with the same letter in the same column are statistically equal. DASE = days after the start of the experiment; pH = potential of hydrogen; *T* = temperature; COD = chemical oxygen demand.

of methane gas when the pH values during the experiment were 7.0 (Table 5).

In terms of temperature, 9 DASE was statistically different than the rest of the days ($P \leq 0.05$), with a value of 20°C, whereas the other sampling dates registered an initial temperature of 22°C and a final temperature of 18°C (the lowest during the experiment). Since anaerobic biological digestion processes strongly depend on temperature, it can generally be said that the optimal growth rate of the bacteria occurs within a limited temperature range, even though survival can occur in a wide range (30 to 40°C). Although this activity is possible at low temperatures (10°C), the efficiency of the anaerobic treatment system decreases significantly as the temperature decreases. This was not evident in the present study since the temperature during the sampling periods ranged from 18 to 22°C.

With respect to removal of organic matter as expressed by the COD, this was statistically different ($P \leq 0.05$) on most of the sampling days, except on days 5 and 7; 9 and 11; 23, 25 and 27; and 29 and 31, which were statistically equal (Table 5). The monitoring of the influent and the effluent showed that the bacterial consortium that composed the biofilm adapted to the new substrate over time. This resulted in a decrease in organic matter from day to day, expressed by an increase in the organic matter removal efficiency. This is associated with the biofilm which formed in the support being subjected to drastic changes in the type of substrate on which it fed. In addition, the degradation activity increased exponentially as the enzymatic activity of the biofilm changed— beginning with a COD of 1 650 mg l^{-1} and reaching its maximum efficiency of 90% on day 33, when the lowest COD values were registered (170 mg l^{-1}). That is, organic matter removal efficiency was favorable over time even given the temperatures registered during the sampling period, indicating other advantages and efficiencies of the anaerobic treatment system (Figure 5). This can be attributed to the change in the substrate, as mentioned by Maldonado (2008), who reported that biofilm undergoes "shock" loading, which is basically a change in the substrate. With respect to this, it is important to take into account that methanogenic bacteria are extremely sensitive to the presence of toxic compounds in the wastewater to which they were subjected during the anaerobic treatment. Nevertheless, as the process progresses over time, and if the period is sufficiently long, the microorganisms can adapt to certain concentrations of diverse toxic substances. This period is called the solid retention time (SRT) in the reactor, referring to a period of days or months, which in the latter case requires a longer period for the microorganisms to adapt to the concentrations of the toxic substances.

In terms of the production of methane gas, this increases 13 days after the start of the experiment, when according to Sanz (2011) the bacterial consortium undergoes an exponential growth process, when high substrate consumption occurs and more methane gas is thereby produced. A continual decrease in COD can also be observed, which according to Massé and Massé (2000) is indicative that the anaerobic processes are treating the organic matter, transforming it into methane and carbon dioxide. As the organic matter degrades, production increases and byproducts are released — mainly methane gas and carbon dioxide (Figure 6). A continuous increase in methane gas production was identified, especially as of 13 DASE, with approximate values of 0.345 m^3 of methane gas produced, reaching its maximum of 0.520 m^3 on day 33.

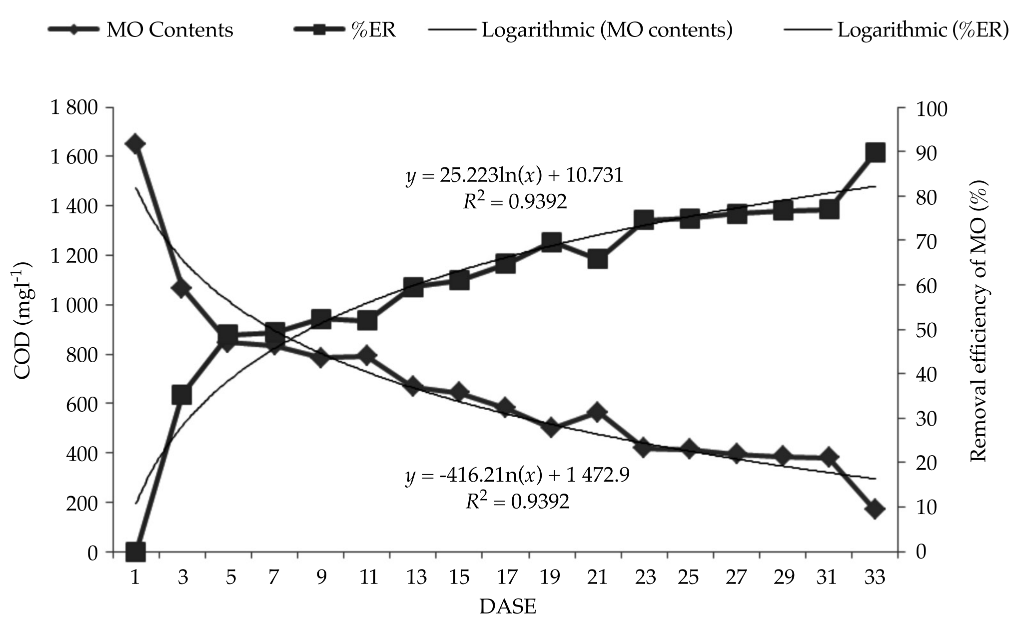


Figure 5. Behavior of COD and removal efficiency of MO over time in days after start of the experiment (DASE).

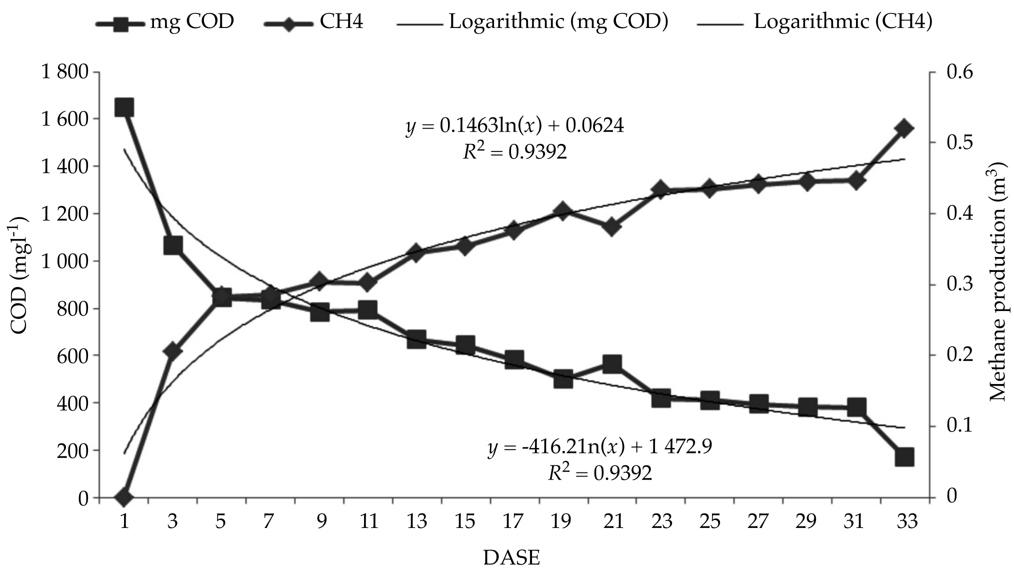


Figure 6. Chemical oxygen demand as an indicator of removal of MO and the resulting production of methane gas ($EPCH_4$).

Conclusions

For the different treatments, the pH began with slightly alkaline values and then tended towards neutral (7), which is correlated with more COD and more methane production.

COD and methane production were positively correlated and both were higher when using fecal organic matter from pig (P) or the combination of cow-pig (C-P).

The highest COD and methane production occurred 14 days after the start of the experiment in most of the treatments, particularly those subjected to 37°C.

The *in vitro* phase is consistent with the results obtained in the scaling phase, where the pH stabilized around neutral values and showed a slight acidic trend at the end, making the chemical oxygen demand removal more efficient and thereby producing more methane gas.

Acknowledgements

The authors acknowledge the Council on Science and Technology (Consejo de Ciencia y Tecnologia) of the state of Durango, the Regional University for Arid Zones (Unidad Regional Universitaria de Zonas Áridas) of the Autonomous University of Chapingo and the Research and Advanced Studies Center of the National Polytechnic Institute (Cinvestav-IPN ; Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional), Irapuato unit, for their support for the present work.

References

Behling, Q. E. H., Caldera, Y. A., Marín, J. C., Rincón, L. C., & Fernández, L. M. (2005). *Eficiencia de un reactor anaeróbico en el tratamiento del efluente de una tenería* [en línea]. Departamento de Ingeniería Sanitaria y Ambiental de la Escuela de Ingeniería Civil de la Universidad de Zulia, Venezuela. Citado el 17 de mayo de 2013. Recuperado de http://www.revistas.luz.edu.ve/index.php/bcib/article/viewFile/101/3339.

Bermúdez, R., Rodríguez, S., Martínez, M., & Terry, A. (2003). Ventajas del empleo de reactores UASB en el tratamiento de residuales líquidos para la obtención de biogás. *Tecnol. Química*, *23*, 37-44.

Cámara-Da, L., Hernández, M., & Paz, L. (s/f.). *Manual de diseño para plantas de tratamiento de aguas residuales alimenticias. Miniproyecto de Ingeniería Química*. Recuperado de http://uniciencia.ambientalex.info/infoCT/Mandisplataaguresaliar.pdf.

Carere, C. R., Sparling, R., Cicek, N., & Levin, D. (2008). Third Generation Biofuels Via Direct Cellulose Fermentation. *Genome Biology*, *9*, 242. Citado el 15 de mayo de 2013. Recuperado de http://www.vurup.sk/pc/vol49_2007/issue2/pdf/pc_2_2007_jordanov.pdf.

Carmona, J. C., Bolívar, D. M., & Giraldo, L. A. (2005). El gas metano en la producción ganadera y alternativas para medir sus emisiones y aminorar su impacto a nivel ambiental ductivo. *Revista Colombiana de Ciencias Pecuarias*, *18*(1). Citado el 24 de julio de 2013. Recuperado de http://rccp.udea.edu.co/index.php/ojs/article/view/6.

Castillo, E. F., Solano, J. K., & Rangel, M. P. (2006). Evaluación operacional de un sistema a escala laboratorio de biopelícula anaerobia soportada para el tratamiento de aguas residuales domésticas. *Revista ION*, *19*(1), 18-22. Citado el 24 de julio de 2013. Recuperado http:// www.redalyc.org/pdf/3420/342030277004.pdf.

Chen, Y., Cheng, J. J. & Creamer, K. S. (2008). Inhibition of Anaerobic Digestion Process: A Review. *Bioresurce Technology*, *99*(10), 4044-4064.

Fang, H. H. P., Ke, L. U., & Shang, S. Z. (2004). Anaerobic Degradation of Phenol in Wastewater at Ambient Temperature. *Water Science and Technology 49*, 95-102.

García, E. (1973). *Apuntes de climatología* (155 pp.). México, DF: Universidad Nacional Autónoma de México.F

Guieysse, B., Wikströnm, P., Forsman, M., & Mattiasson, B. (2001). Biomonitoring of Continuous Microbial Community Adaptation Towards More Efficient Phenol-Degradation in a Fed-Batch Bioreactor. *Applied Microbiology and Biotechnology*, *56*, 780-787.

Lorenzo, Y., & Obaya, M. C. (2006). La digestión anaerobia y los reactores UASB. *Generalidades. ICIDCA. Sobre los derivados de la caña de azúcar*, *40*(1), 13-21. Citado el 22 de julio de 2013. Recuperado de http://www.redalyc.org/articulo.oa?id=223121549002.

Maldonado, C. A. (2008). Tratamiento de agua residual del rastro, mediante biopelículas anaerobias desarrolladas en *Opuntia imbricata"* (70 pp.). Tesis inédita de maestría. Monclova, México: Universidad Autónoma de Coahuila, Facultad de Ciencias Químicas, Departamento de Biología.

Martínez, R. J., Maldonado, C. A., Ríos, G. L. J., & Garza, Y. (2008). *Tratamiento de agua residual del rastro mediante biopelículas anaerobias desarrolladas en* Opuntia imbricata *y lodo granular*. XII Congreso Nacional de Biotecnología y Bioingeniería. Citado el 20 do julio de 2013. Recuperado de *www.smbb.com.mx/congresos%20smbb/morelia07/...IV/.../CIV-75.pd*.

Massé, D. I., & Massé, L. (2000). Characterization of Wastewater from Hog Slaughterhouse in Eastern Canada and Evaluation of their In-Plant Wastewater Treatment System., *Can. Agr. Eng.*, *42*, 139-146.

McCaughey, W., Wittenberg, K., & Corrigan, D. (1999) Impact of Pasture Type on Methane Production by Lacting Beef Cows. Can. J. Sc., 79(2), 221-226.

Moss, A. R., & Givens, D. I. (2002). The Effect of Supplementing Grass Silage with Soya Bean Meal on Digestibility, in Sacco Degradability, Rumen Fermentation and Methane Production in Sheep. Animal Feed Science and Technology, 97, 127-143.

Orrico-Junior, M. A. P., Orrico. A. C. A., & Júnio, J. L. (April, 2011). Animal Production and Environment: A Comparison between Potential of Methane Emission from Waste and Quantity of Produced Food. *Journal Engenharia Agrícola*, 31(2). Citado el 20 de julio de 2013. Recuperado de http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-69162011000200020&lng=pt&nrm=iso&tlng=pt.

Ramírez, O., Koetz, P. (1998). *Evaluación de un reactor UASB para el tratamiento de efluentes de la industria de aceite de arroz*. VTtaller y Seminario Latinoamericano de Tratamiento Anaerobio de Aguas Residuales. Viña del Mar, Chile,.

Rodríguez, V. J. A. (s./f.). *Tratamiento anaerobio de aguas residuales*. Universidad el Valle de Cali, Colombia. Citado el 20 de agosto de 2013. Recuperado de http://www.ingenieroambiental.com/4014/tratamiento545.pdf

Semarnat (2011). Normas Mexicanas en Materia de Agua. Citado el 20 de junio de 2013. Recuperado de http://www.semarnat.gob.mx/leyes-y-normas/nmx-agua.

Sagarpa-Ceiegdrs (2003). Anuario estadístico de la producción agropecuaria de la Región Lagunera Durango-Coahuila (163 pp.). Ciudad Lerdo, México: Delegación en la Región Lagunera Durango-Coahuila. Subdelegación de Planeación y Desarrollo Social.

Sanz, J. L. (2011). *Microbiología ambiental*. Taller práctico. México, DF: Universidad Autónoma Metropolitana. Citado el 25 do mayo de 2013. Recuperado de http://www.cbm.uam.es/imagweb/Memoria.../04bvirologiaymicrobiologia.pdf.

Shanta, S., & Ramakant, S. (2010). Biogas Production Enhancement by Soya Sludge Amendment in Cattle Dung Digesters. *Biomass and Bionergy*, *34*, 278-1282.

Van Haandel, M. M., & Britz, T. J. (1994). Characterization and Numerical Analysis of the Microbial Community in Raw Baker's Yeast Factory Effluent. *Water SA.*, *20*(2). Citado el 15 do junio de 2013. Recuperado de http://www.wrc.org.za/downloads/watersa/1994/April/0784%20abstract.pdf.

Van Kessell, J. S., & Russell, B. (November, 1995). *The Effect of pH in Vitro Methane Production from Ruminal Bacteria* (Abstract # 2). In 23rd Biennial Conference on Rumen Function, Chicago, Illinois, USA, *23*, 14-16.

Institutional Address of the Authors

M.C. Olivia García Galindo

Estudiante de la maestría en Recursos Naturales y Medio Ambiente en Zonas Áridas
Unidad Regional Universitaria de Zonas Áridas (URUZA)
Universidad Autónoma Chapingo
Km. 35 Carretera Gómez Palacio-Ciudad Juárez
35230 Bermejillo, Durango, México
Teléfono: +52 (872) 7760 160
oly_ggalindo@hotmail.com

Dr. Aurelio Pedroza Sandoval

Subdirector de Investigación de la Unidad Regional Universitaria de Zonas Áridas (URUZA)
Universidad Autónoma Chapingo
Km. 35 Carretera Gómez Palacio-Ciudad Juárez
35230 Bermejillo, Durango, México
Teléfono: +52 (872) 7760 160
apedroza@chapingo.uruza.edu.mx

M.C. José Antonio Chávez-Rivero

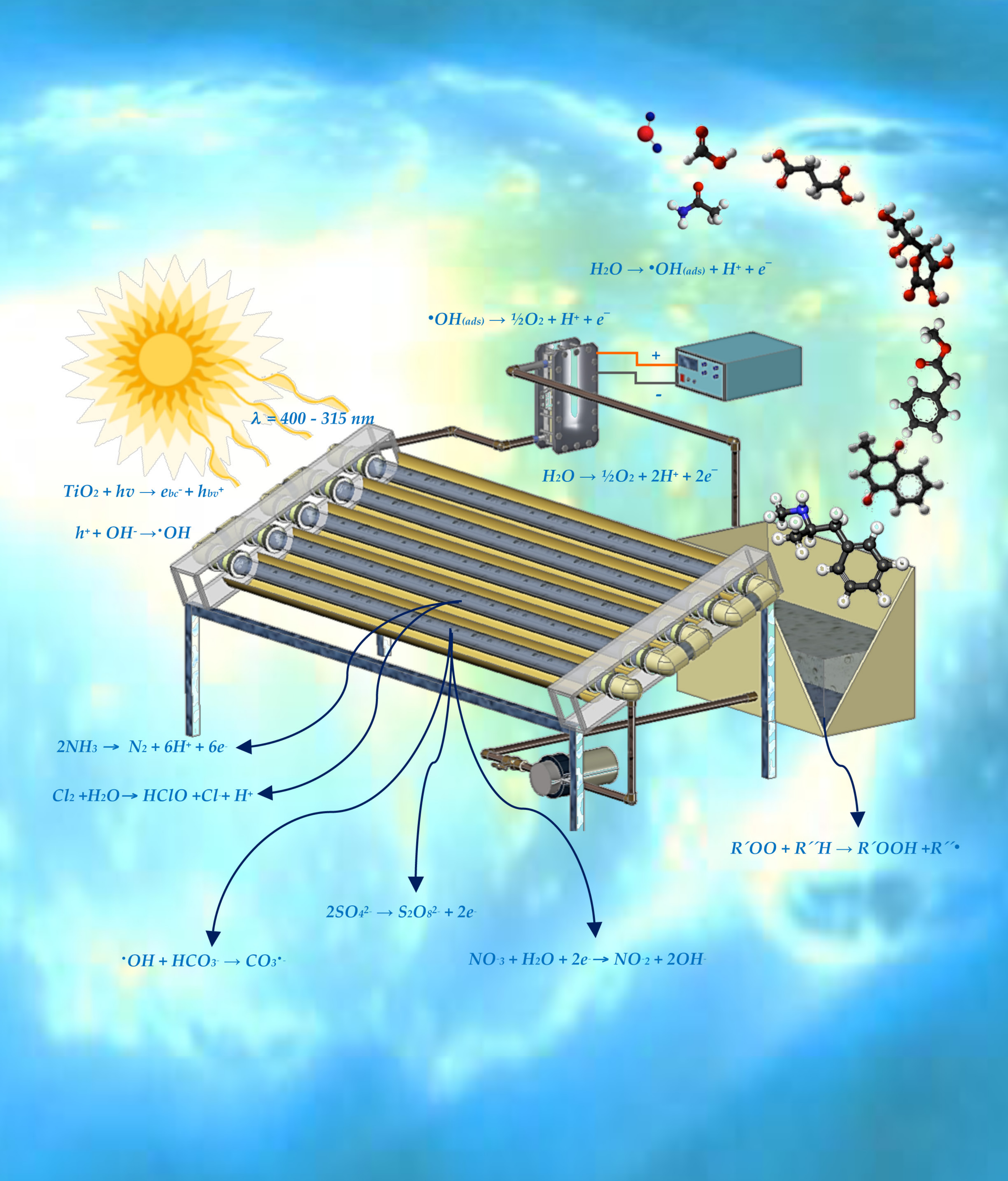
Unidad Regional Universitaria de Zonas Áridas (URUZA)
Universidad Autónoma Chapingo
Km. 35 Carretera Gómez Palacio-Ciudad Juárez
35230 Bermejillo, Durango, México
Teléfono: +52 (872) 7760 160
job77@chapingo.uruza.edu.mx

Dr. Ricardo Trejo-Calzada

Unidad Regional Universitaria de Zonas Áridas (URUZA)
Universidad Autónoma Chapingo
Km. 35 Carretera Gómez Palacio-Ciudad Juárez
35230 Bermejillo, Durango, México
Teléfono: +52 (872) 7760 160

Dr. Ignacio Sánchez-Cohen

Centro Nacional de Investigación y Desarrollo en Relaciones Agua-Suelo-Planta-Atmósfera
Km. 6.5, margen derecha Canal de Sacramento
35150 Gómez Palacio, Durango, México
Teléfono: +52 (871) 7191 076
sanchez.ignacio@inifap.gob.mx



Experimental system to treat domestic wastewater using anodic oxidation and heterogeneous photocatalysis.

Figure designed by: Isarain Chávez.

Response Surface Applied to the Treatment of Wastewater with the Coupling of DSA and Photocatalysis

• Eloy Isarain-Chávez* • Saray Ramírez-Martínez • María Maldonado-Vega •
Juliette Lambert • Juan M. Peralta-Hernández •
Centro de Innovación Aplicada en Tecnologías Competitivas, México
*Corresponding Author

• Ulises Morales-Ortiz •
Universidad Autónoma Metropolitana-Iztapalapa, México

Abstract

Isarain-Chávez, E., Ramírez-Martínez, S., Maldonado-Vega, M., Lambert, J., Peralta-Hernández, J. M., & Morales-Ortiz, U. (March-April, 2015). Response Surface Applied to the Treatment of Wastewater with the Coupling of DSA and Photocatalysis. *Water Technology and Sciences* (in Spanish), 6(2), 51-67.

This study describes a response surface analysis based on a central composite design to evaluate a filter-press electrolytic flow cell coupled with a compound parabolic solar concentrator. This was used to treat 20 l of domestic wastewater with a chemical oxygen demand of 742 to 756 mg l^{-1} and total organic carbon of 248 a 253 mg l^{-1}. The anodes used in the electrolytic cell were IrPbO, IrSnO and RuPbO. They were coated with metallic chlorides on Ti plates and were activated with thermal decomposition. The area of the compound parabolic solar concentrator was 1 m^2 and was exposed for 4 hours per day, receiving an average radiation of 889 watts m^{-2}. The addition of TiO_2 in concentrations of 100 to 150 mg l^{-1} contributed to the degradation of the pollutants, and the effects from changing the concentration of the electrolyte support from 0.02 to 0.06 M of Na_2SO_4 were not very significant. Tests of the degradation were followed by an analysis of total organic carbon, with degradation percentages between 5 and 30% at the end of treatment when applying currents of 10 to 30 A, with an energetic consumption from 6 to 74 kW m^{-3}.

Keywords: Dimensional stable anodes, domestic wastewater, compound parabolic concentrator, photocatalysis, anodic oxidation, titanium oxide.

Resumen

Isarain-Chávez, E., Ramírez-Martínez, S., Maldonado-Vega, M., Lambert, J., Peralta-Hernández, J. M., & Morales-Ortiz, U. (marzo-abril, 2015). Superficie de respuesta aplicada al tratamiento de aguas residuales acoplando DSA y fotocatálisis. Tecnología y Ciencias del Agua, *6(2), 51-67.*

Este estudio empleó el análisis de superficie de respuesta basado en un diseño compuesto central para evaluar una celda electrolítica de flujo tipo filtro prensa, acoplada a un concentrador parabólico compuesto solar, los cuales se usaron para llevar a cabo el tratamiento de 20 l de agua residual doméstica de 742 a 756 mg l^{-1} en demanda química de oxígeno, y de 248 a 253 mg l^{-1} en carbono orgánico total. Los ánodos usados en la celda electrolítica fueron de IrPbO, IrSnO y RuPbO, recubiertos mediante la técnica de los cloruros metálicos sobre placas de Ti y activados por descomposición térmica. El concentrador parabólico compuesto solar posee un área de 1 m^2, la cual fue expuesta por cuatro horas por día, recibiendo una radiación promedio de 889 Watts m^{-2}. La degradación de los contaminantes se vio favorecida con la adición de TiO_2 a concentraciones de 100 a 150 mg l^{-1}, con efectos poco significativos al cambiar la concentración de 0.02 a 0.06 M de Na_2SO_4 del electrolito soporte. Los ensayos de la degradación fueron seguidos por el análisis del carbono orgánico total, con porcentajes de degradación de 5 a 30% al final del tratamiento, al aplicar intensidades de corriente de 10 a 30 A, con consumos energéticos desde 6 hasta 74 kW m^{-3}.

Palabras clave: *ánodos dimensionalmente estables, aguas residuales domésticas, concentrador parabólico compuesto, fotocatálisis, oxidación anódica, óxido de titanio.*

Received: 06/02/13
Accepted: 11/09/14

Introduction

There are two reasons for treating wastewater — to reduce pollution in receptor water bodies and decrease water consumption by its reuse. The technologies existing today to treat wastewater largely depend on the type of effluent and the level of treatment required for its reuse. Conventional treatments are applied in most cases, which include different stages involving physical separation— such as screening, desanding, sedimentation and separation of greases and oils— followed by a process with or without aeration, and finally disinfection (chlorination, ozonation or UV). The application of alternatives developed over recent years has been projected to be highly feasible, such as chemical oxidation (O_3, O_3/H_2O_2, H_2O_2/Fe^{+2}), photocatalysis (TiO_2/UV, photo-Fenton) and photochemical degradation (O_3/UV, O_3/H_2O_2), or a combination thereof (electro-Fenton, photoelectro-Fenton, electrocoagulation/O_3 (Fernandes, Pacheco, Ciríaco, & López, 2012; Lambert, Maldonado-Vega, Isarain-Chávez, & Peralta- Hernández, 2013; Isarain-Chávez, De la Rosa, Martínez-Huitle, & Peralta-Hernández, 2013; García, Isarain-Chávez, García-Segura, Brillas & Peralta-Hernández, 2013)). Anodic oxidation (AO) or electro-oxidation are also promising, which can result in the partial or complete oxidation of pollutants (Isarain-Chávez, Peralta-Hernández, Guerra, & Morales-Ortiz, 2012; García, Isarain-Chávez, El-Ghenymy, Brillas, & Peralta-Hernández, 2014).

These processes have been useful in stages previous to the degradation of pollutants that are resistant to biodegradation, or as post-treatment before the effluent is discharged into receptor bodies. These technologies present several advantages, including the size of the equipment, which can be operated at room temperature and with low pressure. These technologies are versatile and generate little sludge, and their use is highly viable for degrading several types of compounds using metal-plated oxidized electrodes (OE) (Zhou, Särkkä, & Sillanpää, 2011a; Isarain *et al*., 2012; Patel, Bandre, Saraf, & Ruparelia, 2013).

A large variety of dimensionally stable anodes deposited on titanium currently exist, such as SnOx, RuOx, PbOx, IrOx, PtOx, PdOx, among others. These electrodes achieve high rates of degradation or transformation of organic compounds due to the high overpotential of the oxygen evolution reaction, in addition to high stability and conductivity (Szpyrkowicz, Kaul, Neti, & Satyanarayan, 2005; Makgae, Klink, & Crouch, 2008; Fierro *et al*., 2009; Profeti, Profeti, & Olivi, 2009; Papastefanakis, Mantzavinos, & Katsaounis, 2010; Zhou *et al*., 2011a; Isarain *et al*., 2012; Wu *et al*., 2012; Patel *et al*., 2013; Chu, Zhang, Liu, Qian, & Li, 2013).

Various authors have documented the use of dimensionally stable anodes for several applications related to the treatment of effluents and treatment processes, including the removal of colorants— with 50 to 90% efficiency using Ir-Sn, RhOx, MnO_2-RuO_2, Pt-Ir, PdO-Co_3O_4 electrodes (Szpyrkowicz, Juzzolino, & Kaul, 2001; León, Pomposo, Suárez, & Vega, 2009).

Zanbotto-Ramalho, Martínez-Huitle and Ribeiro-Da-Silva (2010) used Ti/$Ru_{0.23}Ti_{0.66}Sn_{0.11}O_2$ electrodes in the removal of oil byproducts such as phenol, benzene, toluene and xylene, with degradations between 47 and 100%. Meanwhile, Feng and Li (2003), as well as Makgae *et al*. (2008) used Ti/IrO-PtO, Ti/Sb-Sn-RuO_2, Ti/Sb-Sn-RuO_2-Gd and Ti-β-PbO_2 anodes as well as Ti/SnO_2-RuO_2-IrO_2 to remove phenol, with mineralizations ranging from 50 to 100%. These results agree with studies by Cong, Wu and Tan (2005), who reported reductions of 60% for 2-chlorophenol. Chatzisymeon, Dimou, Mantzavinos and Katsaounis (2009) have focused on using IrO_2 to treat wastewater from process related to olive oil production, while others have focused on the degradation of tetracycline using RuO_2-IrO_2 electrodes, with removals of 33% (Wu *et al*., 2012). Studies indicate that during the degradation process, intermediate species are formed which in some cases are more difficult to oxidize than the original molecule, as in the case of oxalic acid, which can be degraded using IrO_2-Ta_2O_5 electrodes, as reported by Scialdone, Randazzo, Galia and Filardo (2003). Several years later, Huang, Shih and Liu (2011) confirmed the oxidizing power of Ti/ RuO_2 and IrO_2 in the degradation of oxalic acid. It is worth mentioning that investigators such as Kim, Kim, Kim, Park and Lee (2005) described the mechanisms involved in the removal of nitrogen and its ammonium, nitrite and nitrate ions, as well as chlorine. These results were confirmed by Lacasa, Llanos, Cañizares and Rodrigo (2012a) using $IrO_2$and RuO_2 electrodes. These same authors also performed studies on the removal of arsenic III (Lacasa, Cañizares, Rodrigo, & Fernández, 2012b). Other applications of DSA include inverse osmosis processes using IrO_2, RuO_2 and Ta_2O_5 anodes, as reported by Zhou, Liu, Jiao, Wang and Tan (2011b) .

Anodic oxidation is expressed by the oxidation of water at a potential of E° = 1.23V/SHE at 25 °C, as shown in reaction (1). Monoelectronic reactions generate the intermediate adsorbed hydroxyl radical $^{\bullet}OH_{(ads)}$ (reactions (2) and (3)) (Marselli, García-Gómez, Michaud, Rodrigo, & Comninellis, 2003; Scialdone, 2009; Chatzisymeon *et al*., 2009; Martínez-Huitle & Brillas, 2009; Zanbotto-Ramalho *et al*., 2010).

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \quad (1)$$

$$H_2O \rightarrow {}^{\bullet}OH_{(ads)} + H^+ + e^- \quad (2)$$

$${}^{\bullet}OH_{(ads)} \rightarrow \tfrac{1}{2}O_2 + H^+ + e^- \quad (3)$$

This process begins with the discharge of H_2O in an acid medium on the metallic anode (M), generating the adsorbed hydroxyl radical M($^{\bullet}$OH) (reaction (4), resulting in a superoxide (MO) from reaction (5), generating an M $^{\bullet}$OH physically adsorbed species) and the chemisorbed MO. In the absence of organic matter, both species contribute to oxygen evolution (reactions(6) and (7)) (Scialdone, 2009; Martínez-Huitle & Brillas, 2009; León *et al*., 2009; Fierro *et al*., 2009; Panizza & Cerisola, 2009; Zanbotto-Ramalho *et al*., 2010):

$$M + H_2O \rightarrow M({}^{\bullet}OH) + H^+ + e^- \quad (4)$$

$$M({}^{\bullet}OH) \rightarrow MO + H^+ + e^- \quad (5)$$

$$M({}^{\bullet}OH) \rightarrow \tfrac{1}{2}O_2 + M + H^+ + e^- \quad (6)$$

$$MO \rightarrow \tfrac{1}{2}O_2 + M \quad (7)$$

In the presence of organic matter (R), the chemisorbed species generate partially oxidized RO species (reaction (8))(Scialdone, 2009; León *et al*., 2009; Fierro *et al*., 2009; Panizza & Cerisola, 2009; Martínez-Huitle & Brillas, 2009; Zanbotto-Ramalho *et al*., 2010):

$$R + MO \rightarrow RO + M \quad (8)$$

The presence of M($^{\bullet}$OH) in inactive anodes is low when reaction (5) is quicker than reaction (4). Whereas a combustion occurs with a high concentration of $^{\bullet}$OH radicals, when the speed of reaction (4) is negligible. The electrochemical combustion was performed using hydroxylation or dehydrogenation (R or R´H) with M($^{\bullet}$OH) species, according to reactions (9) and (10):

$$R + M(^{\bullet}OH) \rightarrow ROH^{\bullet} + M \quad (9)$$

$$R'H + M(^{\bullet}OH) \rightarrow R` + M + H_2O \quad (10)$$

The oxygen dissolved in the medium reacts with the organic radical $R'^{\bullet}$, thereby generating the peroxyl radical $R'OO^{\bullet}$ (reaction (11)), taking a hydrogen atom from another R''H pollutant (reaction (12)). Thus, the structure of the hydroperoxides splits into CO_2, inorganic ions and water (Scialdone, 2009; Martínez-Huitle & Brillas, 2009; Panizza & Cerisola, 2009; Zanbotto-Ramalho *et al*., 2010):

$$R' + O_2 \rightarrow R'OO^{\bullet} \quad (11)$$

$$R'OO + R''H \rightarrow R'OOH + R''^{\bullet} \quad (12)$$

The $^{\bullet}OH$ radical also can be generated by photocatalytic reactions through direct adsorption or radiant energy with a wide band photocatalyst in the interface between the excited solid and the solution, where reactions involving the degradation of organic compounds occur (Malato, Fernández-Ibáñez, Maldonado, Blanco, & Gernjak, 2009).

Radiant energy has an average value known as the solar constant, FET = 1 367 Wm^{-2}, whose total UV spectral irradiance (280-400 nm) on the land surface is less than 103.9 Wm^{-2} (100% of the transmission in the atmosphere). Only 5 to 7.6% of this radiant energy contains the total UV spectrum (Gueymard, 2004), which can be divided into four regions: UV-A (long or black light λ = 400 – 315 nm, with an energy per photon of 3.10 - 3.94 eV); UV-B ((λ = 315 - 280 nm, 3.94 - 4.43 eV); UV-C (short UV light λ = 280 - 100 nm, 4.43 - 12.40 eV); and UV-V (vacuum ultraviolet λ = 200 - 10 nm, 6.20 - 124 eV). The fraction is large enough for a 254 nm photon to equal 4.89 eV, with an energy which generates excited states, producing homolytic and heterolytic ruptures in molecules, producing $^{\bullet}OH$ radicals (Legrini, Oliveros, & Braun, 1993).

TiO_2 is one of the most widely used photocatalysts in heterogeneous photocatalysis since it possesses high activity and stability in an aqueous medium. It is classified as a type **n** semiconductor composed of anatase, rutile and brookite. The bandwidth of the anatase is 3.20 eV and the Gibbs formation energy is 883.3 $kJmol^{-1}$. Rutile has a bandwidth of 3.03 eV and a Gibbs energy of 889.4 $kJmol^{-1}$ (Rodríguez, Candal, Solís, Estrada, & Blesa, 2005). Anatase is thermodynamically less stable than rutile, though the latter has a larger surface area and a high density of active centers, increasing adsorption and catalysis (Malato *et al*., 2009; Hapeshi *et al*., 2010).

The photocatalysis process is determined by the formation of a hole-electron pair, by the adsorption of a photon with a wavelength less than hγ/Eg, where Eg is the energy of the bandgap, and the electron of the valence band (bv) is promoted to the conduction band (bc), generating a hole (reaction (13)). The photogenerated species participates in redox reactions (h_{bv}+ is strongly oxidizing and e_{bc}- is a moderate redox). The holes are captured by the water, creating $^{\bullet}OH$ radicals according to reactions (14) and (15), which oxidize the pollutants in the surface of the catalyst (González & Braun, 1995; Malato *et al*., 2009; Chong, Jin, Chow, Christopher, & Saint, 2010):

$$TiO_2 + h\upsilon \rightarrow e_{bc}^{-} + h_{bv}^{+} \quad (13)$$

$$h^{+} + H_2O \rightarrow {}^{\bullet}OH + H^{+} \quad (14)$$

$$h^{+} + OH^{-} \rightarrow {}^{\bullet}OH \quad (15)$$

As mentioned, TiO_2 presents certain advantages such as greater photocatalytic activity and a polar and hydrophilic surface, giving it high chemical stability in aqueous solutions , with a high resistance to photocorrosion. It dissolves only in sulfuric acid or hydrofluoric concentrates. One advantage of the photocatalysis is that it prevents the formation of halogenated compounds and limits microorganism and bacterial activity— a non-selective process in the treatment of complex pollutant mixtures in aqueous medium. In addition, TiO_2 is relatively easy to recover or immobilize, it is low-cost and non-toxic, and therefore does not require special handling and does not represent any risk to human health or the environment. This combines with solar radiation as its only source of energy (González & Braun, 1995; Malato *et al*., 2009; Hapeshi *et al*., 2010; Chong *et al*., 2010), making photocatalysis a clean process.

It is worth mentioning that, for both photocatalytic and electrochemical systems, the reactions described above are strongly affected by the transference of matter as well as the concentrations of the photocatalyst, the dissolved oxygen in the medium and the pollutant. They are also affected by the pH and the irradiation intensity, and temperature to a lesser extent, , the latter being strongly influenced by the intensity of the current and the electrode materials (González & Braun, 1995; Martínez- Huitle & Brillas, 2009; Chong *et al*., 2010).

Statistical designs are tools which address clearly identified and specific problems. A central composite design was selected, with factors coded according to equation (16), selecting Xi as the real value of the independent variable i; xi_0 is the value at the center of the interval; Δxi is the mean of the difference between its lowest and highest value (Ramírez, Costa, & Madeira, 2005; Domínguez, González, Palo, & Sánchez- Martín, 2010; Almeida, García-Segura, Bocchia & Brillas, 2011; Zhang, Yang, Rong, Fu, & Gu, 2012):

$$X_i = \frac{x_i - x_{i0}}{\Delta x_i} \qquad (16)$$

With this design, the average and primary effects of each factor can be calculated, as well as their interactions from 2 to 2, 3 to 3, up to k factors. The response associated with a design with three variables is represented by the linear polynomial model described by equation (17):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \qquad (17)$$

where Y is the experimental response; X_i the code (-1 or + 1); b_i is the estimation of the primary effect of factor i and response Y; and b_{ij} is the estimation of the interaction effect between factors i and j for response Y (Hammami, Oturan, Bellakhal, Dachraoui, & Oturan, 2007; Zhang *et al*., 2012).

This work presents a first approach to the viability of treating domestic wastewater using a combination of two simultaneous processes— advanced oxidation with anodic oxidation and dimensionally stable anodes, and heterogeneous photocatalysis with TiO_2. The analysis is performed using a central composite design to evaluate the efficiency of the process according to the decrease in total organic carbon, degradation efficiency and energy costs. It is worth mentioning that the literature does not report the use of both technologies to treat domestic wastewater.

Methodology

The system was fed with 20 l of domestic wastewater previously filtered using a 0.5 mm mesh to retain thick solids. TiO_2 was added (Cabrera, Alfano, & Cassano, 1996) (Anatasa, d_p = 30-90 nm; d_a = 700; S_g = 48 m^2g^{-1}) as a photocatalyst, using three different concentrations (100, 150 and 200 mg l^{-1}). Na_2SO_4 was used as an electrolytic support with concentrations of 0.03, 0.04 and 0.05 molar (all reagents were supplied by Karal House). Current intensities of 10, 20 and 30 amperes were applied. These variables were evaluated using a central composite design with the response surface method (RSM). Random tests were performed using *Design-Expert* 7.0 software to ensure statistical validity. The response variables were total organic carbon, energy consumption and degradation efficiency.

The pH of the water was monitored with an Extech 407227 pH meter and conductivity with HACH (μScm^{-1} or mScm^{-1}). Solar radiation was monitored with a Daystar Inc. DS-05A pyrometer. COD was analyzed based on NMX-AA-030-SCFI-2001 and the percentage of degradation was quantified using a total organic carbon analyzer (Shimadzu L-CSN), injecting 50 μl aliquots which were previously filtered with 0.45 μm Whatman PTFE. The TSS, TDS, SS, and other parameters were evaluated according to the standardized method APHA-AWWA-WEF (1998).

Electrolytic cell

The electrolytic cell is multi-compartmental, with stainless steel plates outside and rectangular high-density polyethylene inside (195 x 41 mm), with a total volume of 421.73 ml. Ti/RuPbOx, Ti/IrPbOx, Ti/IrSnOx were used as anodes, which were coated with noble metal chloride and activated by thermal decomposition (Morales-Ortiz, Ávila-García, & Hugo-Lara, 2006; Profeti *et al*., 2009; Papastefanakis *et al*., 2010). Ti were used as cathodes, with an area of 79.95 cm^2, and the anode/cathode ratio was 1:1. The tests were performed with galvanostatic conditions maintaining a constant current intensity using a BK Precision Mod-1900 DC, 1-16 VDC/60 A. The electrical configuration was monopolar and a flow-by regime was used. The electrolysis time was 240 minutes.

Parabolic Solar Concentrator (PSC)

The PSC photoreactor was a static system consisting of four aluminum supports made of five SCHOTT-Duran borosilicate glass tubes 1.8 mm thick (refraction index of 1.51 – 1.54 with λ = 380-750 nm). The total capacity was 15.2 l, tube length was 145 cm and external diameter 5 cm. The system had a series of concave reflectors with a solar radiation distribution around the bulb. These reflectors (0.4 mm thick) had a mirror finish with anodized aluminum (with reflectance of 86%, of which 15% was diffuse and the rest was direct in the UV spectrum). The PSC had a concentration ratio CR = 1 and was aligned with the east-west axis, with a slope of 21° towards the south. All the connections were Teflon or plastic and resistant to UV radiation. The system was fed by a 12-volt Shurflo model 2088 magnetic diaphragm pump (25 l min^{-1}). Figure 1 shows the mounting of the experimental electrochemical cell system coupled with the parabolic solar concentrator.

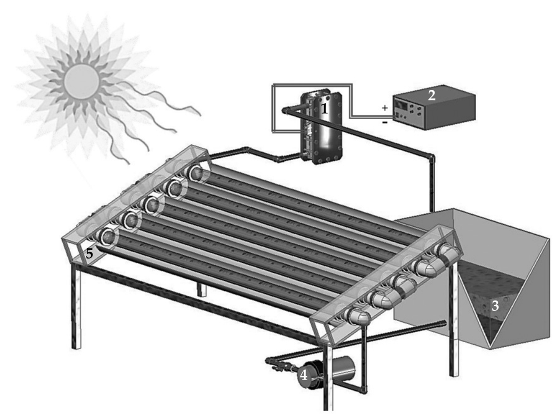


Figure 1. Experimental system to treat domesitc wastewater with anodic oxidation and heterogeneous photocatalysis. 1) filter-press electrolytic flow cell, 2) current rectifier, 3) 20 l reservoir, 4) diaphragm flow pump, 5) parabolic solar concentrator.

Results and Discussion

Characterization of Wastewater

Table 1 shows the characterization of the domestic wastewater, where the sedimentable solids, pH, temperature, phosphorus, grease and oils complied with the maximum allowable limits stipulated by Official Mexican Norm NOM-001-SEMARNAT-1996 (Semarnat, 1996) for discharge into receptor bodies. Nevertheless, there were high concentrations of BOD_5, TSS, nitrogen and chlorides, as well as COD, which are not included in the guidelines and would affect the aquatic medium if the effluent is not adequately treated.

Central Composite Design

The real values of the levels were coded as low (-1), middle (0) and high (1), considering six central points and six axial points. The distance α from the axial to the center was selected in order to obtain a stable response variance at the points of interest, with α = 1.68179, opting for a rotatable design, with a total of 20 tests. These data were generated using equation (16) with the *Design-Expert 7.0* program. The current intensities were 3.18, 10, 20, 30 and 36.82 amperes. The Na_2SO_4 concentrations were 0.02, 0.03, 0.04, 0.05 and 0.06 M, and TiO_2 concentrations were 65.9, 100, 150, 200 and 234.1 mg l^{-1}. The tests proposed are listed in Table 2, which shows some of the variables of interest that were monitored during the treatment of the domestic wastewater.

Energy Consumed by the Processes

The data obtained from the experimental design are shown in Table 2. For all cases, a slight increase in pH occurred. This effect can be attributed to the generation of OH^- on the surface of the cathode according to reaction (18) (Isarain-Chávez, De la Rosa, Godínez, Brillas, & Peralta-Hernández,

Table 1. Initial characterization of domestic wastewater.

Test	Method used	Results
Conductivity	NMX-AA-093-SCFI-2000	1 890-1 983 μS cm^{-1}
pH	NMX-AA-008-SCFI-2000	7.31-8.56
Temperature	NMX-AA-007-SCFI-2000	25.2 °C
Sedimentable solids	NMX-AA-004-SCFI-2000	0.3 ml l^{-1}
Total suspended solids	NMX-AA-034-SCFI-2001	132 mg l^{-1}
Total nitrogen	NMX-AA-026-SCFI-2001	44.6 mg l^{-1}
Grease and oil	NMX-AA-005-SCFI-2000	14.23 mg l^{-1}
Biochemical oxygen demand	NMX-AA-028-SCFI-2000	150 mg l^{-1}
Total phosphorus	NMX-AA-029-SCFI-2000	4.09 mg l^{-1}
Amoniacal nitrogen	NMX-AA-026-SCFI-2001	19.6 mg l^{-1}
Nitrates	NMX-AA-079-SCFI-2000	10.1 mg l^{-1}
Nitrites	NMX-AA-030-SCFI-2000	< 0.0123 mg l^{-1}
Chemical oxygen demand	NMX-AA-039-SCFI-2000	742.9-756.4 mg l^{-1}
Total organic carbon	---	248.4-252.9 mg l^{-1}
Methylene blue active substances	NMX-AA-073-SCFI-2000	12.16 mg l^{-1}
Chlorides	NMX-AA-093-SCFI-2000	49.5 mg l^{-1}
Total Iron	EPA6010C/2007/ICP	0.95 mg l^{-1}

Table 2. Energy consumption and variables monitored during the treatment of wastewater using anodic oxidation coupled with photocatalysis.

Test number	pH_i	pH_f	Initial conductivity (μScm^{-1})	Conductividad final ($mScm^{-1}$)	Initial radiation (Wm^{-2})	Final radiation (Wm^{-2})	Initial TOC (mg l^{-1})	Final TOC (mg l^{-1})	Cell tension (Volts)	C_{EP} ($kWhm^{-3}$)
1	8.51	8.65	1 934	8.92	1 060	780	249.8	227.4	6.75	27.0
2	8.47	8.54	1 921	7.34	1 090	760	251.7	210.6	10.9	65.4
3	8.43	8.52	1 898	6.40	910	780	251.6	201.4	11.9	47.6
4	8.36	8.47	1 890	8.44	952	790	250.5	193.1	10.1	40.2
5	8.57	8.68	1 917	7.50	962	874	249.3	208.2	11.5	69.0
6	8.46	8.53	1 918	8.25	920	790	250.2	212.7	10.2	40.8
7	8.22	8.32	1 935	8.75	1 027	845	251.1	209.8	9.9	39.6
8	7.89	8.42	1 925	8.65	995	856	252.8	194.2	10.1	74.0
9	7.93	8.24	1 963	9.33	1 003	838	251.1	195.9	8.9	53.7
10	8.28	8.52	1 949	8.56	1 050	856	249.6	227.3	10.1	40.2
11	8.08	8.27	1 953	8.28	926	738	252.5	235.6	9.6	6.1
12	7.39	8.52	1 918	8.59	964	880	252.4	215.6	9.9	39.8
13	7.88	8.45	1 895	8.99	925	870	252.3	215.6	9.2	54.9
14	7.94	8.35	1 931	8.22	990	803	252.2	204.2	10.1	40.4
15	7.83	8.31	1 936	7.03	893	834	252.9	215.2	11.5	23.0
16	7.91	8.42	1 892	9.19	842	780	252.9	219.6	7.8	15.7
17	8.20	8.56	1 910	8.13	885	823	250.9	230.9	9.7	38.8
18	7.95	8.51	1 983	8.60	888	873	249.5	202.4	9.7	38.6
19	7.81	8.43	1 943	7.86	815	931	248.7	202.2	11.7	23.3
20	7.94	8.35	1 927	9.09	867	905	252.6	197.3	9.1	18.2

2014). In the case of solar irradiation, this was an important factor which could not be controlled, with variations over the days from 1 090 to 738 Wm^{-2} at the beginning and end of the tests. These variations affected the photocatalytic reaction speeds, which were proportional to the radiant flow. Table 2 presents the initial and final values, quantified in terms of TOC, which show a low degradation percentage:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (18)$$

As expected, conductivity increased when adding Na_2SO_4 for the sole purpose of decreasing cell voltage and electric costs, which is related to the energy consumption used by the processes (C_{EP}), where an increase in the current's intensity increases the voltage of the cell. This C_{EP} is defined as the amount of energy consumed during the degradation process for time *t*. It is expressed in $kWhm^{-3}$ and is defined by equation (19) (Isarain- Chávez *et al.*, 2012) as:

$$C_{EP} = \frac{V * I * t}{Vs} \qquad (19)$$

where *I* is the intensity of the current (A); *t* is electrolysis time (hours); *V* is average voltage of the cell (*V*) and V_S is the volume of the treated water (l).

Table 3. Factors and responses for the experimental design.

Test number	X_1: current (ampere)	X_2: Na_2SO_4 (moles)	X_3: catalyst (mgl^{-1})	ΔTOC Response (mgl^{-1})	EC_{TOC} Response (kWh COT^{-1})	Response efficiency (%)
1	20.0	0.06	150	22.43	1.21	10
2	30.0	0.03	200	41.10	1.59	20
3	20.0	0.02	150	50.18	0.95	25
4	20.0	0.04	150	57.38	0.70	30
5	30.0	0.03	100	41.08	1.68	20
6	20.0	0.04	234	37.47	1.09	18
7	20.0	0.04	150	41.26	0.96	20
8	36.8	0.04	150	58.57	1.26	30
9	30.0	0.05	200	55.21	0.97	28
10	20.0	0.04	150	22.33	1.80	10
11	3.18	0.04	150	16.92	0.36	7
12	20.0	0.04	150	36.85	1.08	17
13	30.0	0.05	100	36.71	1.49	17
14	20.0	0.04	150	47.92	0.84	23
15	10.0	0.03	100	37.80	0.61	18
16	10.0	0.05	100	33.33	0.47	15
17	20.0	0.04	65.9	20.03	1.94	9
18	20.0	0.04	150	47.05	0.82	23
19	10.0	0.03	200	46.50	0.50	23
20	10.0	0.05	200	55.32	0.33	28

Responses Obtained with the Experimental Designs

Table 3 presents the factors and responses obtained with the rotatable central composite design using the RSM. The graphic profiles indicate differences in the concentration of total organic carbon (ΔTOC), degradation efficiency (h) and energy consumption per unit mass of TOC (EC_{TOC}). The first two parameters were evaluated by equations (20) and (21):

$$\Delta TOC = \left[TOC_0 - TOC_t \right] \tag{20}$$

$$n = \frac{\left[TOC_0 - TOC_t \right]}{TOC_0} * 100 \tag{21}$$

where TOC_0 is the initial concentration of total organic carbon (mg l^{-1}) and TOC_t is the concentration of total organic carbon at time t (min). The energy consumption per unit mass of TOC (EC_{COT}) is expressed in kWh $(gTOC)^{-1}$ for electrolysis time t, expressed by equation (22), where $\Delta(TOC)_{exp}$ is the decrease in experimental TOC (g m^{-3}) (Isarain-Chávez *et al.*, 2012):

$$EC_{TOC} = \frac{C_{EP}}{\Delta\left(TOC\right)_{exp}} \tag{22}$$

This table shows the ΔTOC values ranging from 16 to 57 mg l^{-1} and indicates that the highest efficiency was obtained when applying a current of 30 and 36.8 amperes, as well as the addition of 150 to 200 mg l^{-1} of TiO_2 with 0.04, 0.05 molar of Na_2SO_4.

Equations (23), (24) and (25) are predictive mathematical models obtained in linear terms with the interactions of the three independent variables, according to equation (17), for EC_{TOC} and ΔTOC and for η from anodic oxidation coupled with photocatalysis in the treatment of 20 l of domestic wastewater:

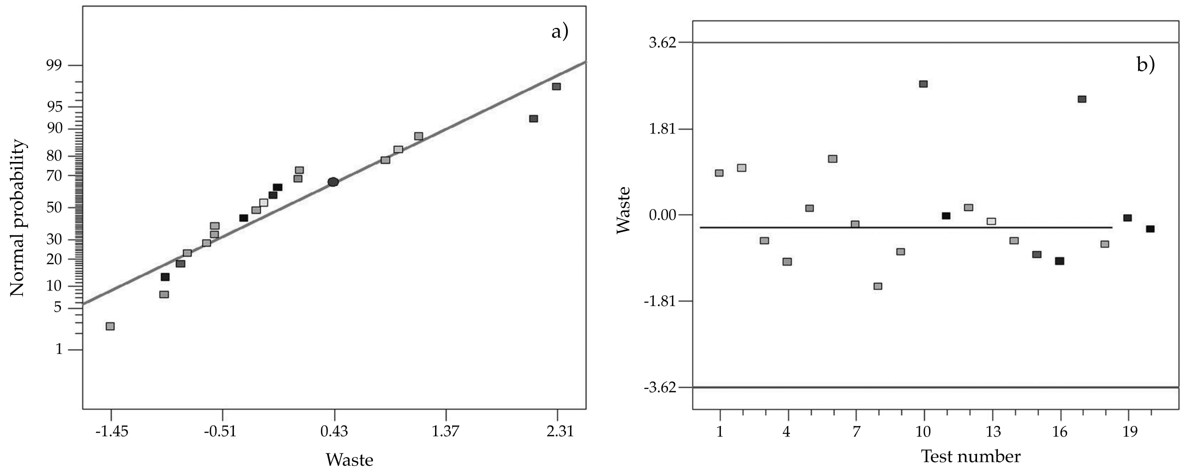


Figure 2. (a) Correlation between the normal probability predicted by the model versus the residuals and (b) the residuals versus number oftests, for analysis of EC_{TOC} at 240 minutes of degradation with electro-oxidation combined with photocatalysis to treat 20 l of domestic wastewater with COD of 742.9-756.4 mgl[-1].

$$CE_{COT} = 0.95287 + 0.039131 * X_1 -5.00314 * X_2 -3.34979E^{-003} * X_3 \quad (23)$$

$$\Delta COT = 22.13172 + 0.52146 * X_1 -238.59172 * X_2 + 0.11502 * X_3 \quad (24)$$

$$\eta = 8.88318 + 0.28792 * X_1 -122.14836 * X_2 + 0.064847 * X_3 \quad (25)$$

Figure 2a shows an acceptable correlation among the normal probability of the residuals for EC_{TOC}, where the points near the diagonal indicate the model's optimum condition. This results in the smallest deviation among these values (Ramírez *et al*., 2005; Almeida *et al*., 2011). In the case of Figure 2b, the wastewater was within allowable limits (Domínguez *et al*., 2010).

ANOVA Variance Analysis for the Linear Modeling

Table 4 shows the variance analysis, which indicates that the linear model is statistically significant (Model F = 7.19), with a low probability value (0.0028), with suggested models with $p < 0.05$, which were validated by independent tests.

Table 4. ANOVA analysis of the linear response surface model for EC_{Toc}.

Factors	Sum of squares	Degrees of freedom	Mean squared	*F* value	*P*-Probability value > *F*
Model	2.51	3	0.84	**7.19**	**0.0028**
X_1-*I*	2.09	1	2.09	17.98	0.0006
X_2-Na_2SO_4	0.034	1	0.034	0.29	0.5952
X_3-catalyst	0.38	1	0.38	3.29	0.0883
Residual	1.86	16	0.12		
Pure error	0.79	5	0.16		
Total (corr.)	4.37	19			

Response Surfaces

Effect of the Intensity of the Current

Figure 3 presents a three-dimensional graphic of the response surface for EC_{TOC}, ΔTOC and h, showing the effect of the concentrations of Na_2SO_4, TiO_2 and *I*. Table 3 presents the tests with five different current intensities: 10, 20 and 30 A, with a minimum of 3.18 and maximum of 36.82A. When applying 3.18 A, the degradation efficiency was low (7%) (test 11), the photocatalyst effect was insignificant and consumption was 0.36 kWh TOC^{-1}. Whereas degradation was 30% with 36.8 A and the same concentration of the photocatalyst and sodium sulfate, while consumption was 1.26 kWh TOC^{-1} (higher than that of test 4 which had the same TiO_2 and Na_2SO_4 conditions). This shows that electrochemically the $^{\cdot}OH$ radical was the primary oxidizing species. Competition reactions also occurred (equation (1)), which with high current intensities consume electrons, decreasing the efficiency of the overall process and increasing energy consumption (Figures 3a and 3b).

It is worth mentioning that the effluent had a high concentration of chlorides (49.5 mg l^{-1}), which theoretically can lead to the formation of species that contribute to oxidation processes with low energy consumption (tests 4, 14, and 18), as shown in reaction (26), where the species formed is hydrolyzed to chlorine ion and hypochlorous acid (reaction (27)). The latter has a lower oxidizing potential (E° = 1.49 V vs SHE) than the $^{\bullet}OH$ radical (E° = 2.80 V *vs.* SHE) (De Laat, Le, & Legube, 2004; Kim *et al.*, 2005; Isarain-Chávez *et al.*, 2014):

$$2Cl^{-} \rightarrow Cl_{(aq)} + 2e^{-} \qquad (26)$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^{-} + H^{+} \qquad (27)$$

These reactions can be affected by high current densities where excess $^{\bullet}OH$ radicals can transform the Cl^{-} ions into other less oxidizing species, according to reactions (28), (29) and (30) (De Laat *et al.*, 2004; Kim *et al.*, 2005; Isarain-Chávez *et al.*, 2014):

$$^{\bullet}OH + Cl^{-} \leftrightarrow ClOH^{\bullet} \qquad (28)$$

$$ClOH^{\bullet-} + Cl^{-} \rightarrow Cl_2^{\bullet-} + OH^{-} \qquad (29)$$

$$2Cl_2^{\bullet-} \rightarrow Cl_{2(aq)} + 2Cl^{-} \qquad (30)$$

Other species to consider is ammoniacal nitrogen (19.6 mg l^{-1}), nitrite and nitrate ions. The first species could theoretically be oxidized by six electrons, with inhibition by the oxygen evolution reaction, following reaction (31)(Kim *et al.*, 2005; Michels, Kapalka, Abd-El-Latif, Baltruschat & Comninellis, 2010) :

$$2NH_3 \rightarrow N_2 + 6H^{+} + 6e^{-} \qquad (31)$$

Meanwhile, in the cathode the nitrate ion (10.1 mg l^{-1}) could be reduced to nitrite by two electrons (reaction (32)), or the nitrate ion could convert into ammonium by eight electrons, according to reaction (33) (Kim *et al.*, 2005; Michels *et al.*, 2010). And the inverse of the reaction of the nitrite ion could occur in the photocatalytic medium, converting into nitrate ion, as shown in reaction (34):

$$NO^{-}_3 + H_2O + 2e^{-} \rightarrow NO^{-}_2 + 2OH^{-} \qquad (32)$$

$$NO^{-}_3 + 6H_2O + 8e^{-} \rightarrow NH_3 + 9OH^{-} \qquad (33)$$

$$NO^{-}_2 + ½\, O_2 \rightarrow NO^{-}_3 \qquad (34)$$

According to the results shown, efficiencies are 23 to 30% with current intensities of 20 A and consumption ranges from 0.7 to 0.84 kWh TOC^{-1}, reflecting an energy savings.

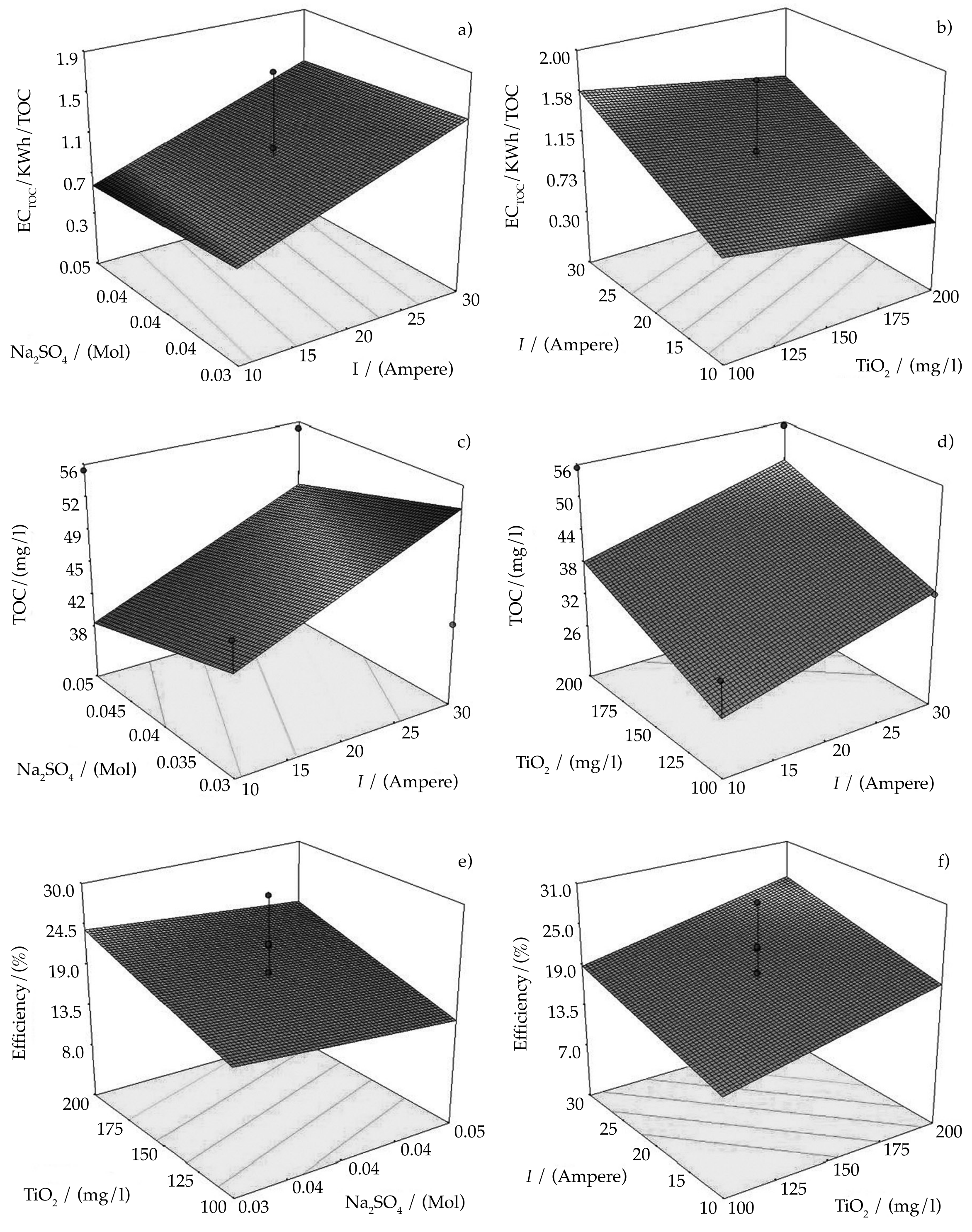


Figure 3. Graphics of the response surface generated with the central composite design for anodic oxidation combined with photocatalyst to treat 20 l of domestic wastewater (1) EC_{TOC} with Na_2SO_4 *vs.* I; (b) EC_{TOC} wit I *vs.* TiO_2; (c) TOC with Na_2SO_4 *vs.* I; (d) TOC with TiO_2 *vs. I*; (e) efficiency with TiO_2 *vs.* Na_2SO_4; (f) efficiency with I *vs.* TiO_2.

Effect of the Concentration of Na_2SO_4

In order to evaluate the influence of Na_2SO_4, experiments were conducted with five different concentrations, whose values are shown in Table 3 and in Figure 3. Degradation was significantly higher at 0.02 and 0.04 M (tests 2, 7 and 12) than at 0.06 M (test 1). All of these were subject to current intensities of 20A and 150 mg l^{-1} of TiO_2. Degradations were 18 and 15% with tests 15 and 16, respectively, with 0.03 and 0.05 M of Na_2SO_4, currents of 10A and 100 mg l^{-1} of TiO_2. These results are consistent with those reported by the literature, where an increase in the Na_2SO_4 concentration results in a smaller reduction in TOC (Figure 3c) since the SO_4^{2-} anion has a higher radical-scavenging reaction constant than other ions, even though it disappears more quickly in water, as has been reported ($SO_4^{2-} > NO^-_3 > Cl^-$). This effect also can be attributed to a high intensity current, which creates a high concentration of $^{\bullet}OH$ radicals, leading to the formation of weak oxidants such as $S_2O_8^{2-}$, according to reaction (25)(Domínguez *et al*., 2010; García *et al*., 2014).

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (35)$$

The decrease in cost per kWh TOC^{-1} for all the systems with high Na_2SO_4 contents does not compensate for the low degradation efficiency resulting at the end of the electrolysis.

Effect of TiO_2 Concentration

As in the previous cases, five different photocatalyst concentrations were tested with the lowest and highest TiO_2 values (65.9 and 234 mgl^{-1}) with efficiencies of 9 and 18% using 20 A and 0.04 M of Na_2SO_4 (tests 6 and 17). In the first case the photocatalyst is clearly deficient, with a minimal contribution, whereas the excess TiO_2 produces a screen effect or possibly dimerization (equation (36)), generating a hydroperoxyl radical (equation (37)), which is less reactive and contributes less to the oxidizing process (Figures 3e and 3f). It is worth mentioning that these systems consume a large amount of energy (1.09 and 1.94 kWh TOC^{-1}).

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (36)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \qquad (37)$$

An insignificant difference was found with concentrations of 100, 150 and 200 mg l^{-1} of TiO_2, (Figure 3d), which indicates that the larger contribution of the oxidizing process is due to the production of the $^{\bullet}OH$ radical electrochemically. Another aspect to consider is the concentration of dissolved oxygen in the medium, since the photocatalytic process stops if the oxygen is depleted (Figure 1), and therefore the oxygen becomes the primary acceptor of electrons, generating the superoxide $O_2^{\bullet}$radical ($K_{O2} = 2 \times 10^{10}$ $M^{-1}s^{-1}$), as shown by equation (38). Although this has less oxidizing power it can degrade substituted aromatic compounds with high absorption in the UV interval:

$$O_2 + e^- \rightarrow O_2^{\bullet} \qquad (38)$$

It is also worth noting that the domestic wastewater used for the tests contain a certain amount of HCO_3^-, which can decrease the efficiency of the process, as shown in reaction (39):

$$^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet -} + H_2O \qquad (39)$$

Optimization of the Process

Based on the above results, sodium sulfate was selected as the variable to be minimized, in order to maximize the degradation efficiency, maintaining energy consumption and the catalyst in the interval. The optimal conditions were thereby determined, whose limits are listed in Table 5.

Optimal Experiments and Characterization of the Wastewater

The solution obtained by the system predicts a ΔTOC of 54 mg l^{-1} and a maximum degradation efficiency of 26.8%, with a minimum consumption of 1.30 kWh TOC^{-1} and a desirability of 0.768, applying a current intensity of 29.78 A with Na_2SO_4 concentrations of 0.03 M and TiO_2 concentrations of 200 mg l^{-1}. Testing these conditions with the system resulted in a decrease in COD from 793.7 to 479.7 mg l^{-1} and in TOC from 265.7 to 212.9 mg l^{-1}, with an increase in pH from 8.1 to 8.42. Even though the optimal parameters were used, the percentage in TOC barely reached 19.8%, indicating that under these test conditions neither of the advanced oxidation processes was sufficiently robust to treat wastewater that is not previously treated.

Conclusions

The tests showed an increase in degradation when increasing the current intensity of the DSA electrodes, and a decrease in cell voltage when increasing the Na_2SO_4 concentration since wastewater has low conductivity. This increases treatment costs because of the addition of reagents, making this alternative not very feasible. Since the high energy consumption and low degradation percentage makes this technology undesirable, the use of anodic oxidation for these effluents is not recommended in spite of its high power to oxidize the materials. This was demonstrated when increasing from 30 to 36 A, with which low degradations were obtained. An increase in the TiO_2 concentration increases degradation while an excess of the photocatalyst can create a negative screen effect. Likewise, an increase in the Na_2SO_4 concentration contributes to the generation of the SO_4^{2-} anion, which has a very high $^{\bullet}OH$ radical scavenging reaction constant, decreasing the overall efficiency of the process. The combination of TiO_2 and DSA represents an alternative for polishing waters to eliminate trace pollutants but nor for effluents with a high concentration of suspended solids, colorants or COD.

Acknowledgements

The authors thank the Centro de Innovación Aplicada en Tecnologías Competitivas (Ciatec; Center for Applied Innovation in Competitive Technologies) for its support for this work through project 000HD0072.

References

APHA, AWWA, WEF (1998). *Standard Methods for the Examination of Water and Wastewater, Method 9222D*. 20th edition. American Public Health Association, American Water Works Association and Water Environment Federation.

Almeida, L. C., García-Segura, S., Bocchia, N., & Brillas, E. (March 14, 2011). Solar Photoelectro-Fenton Degradation of Paracetamol Using a Flow Plant with a Pt/air-Diffusion Cell Coupled with a Compound Parabolic Collector: Process Optimization by Response Surface Methodology. *Applied Catalysis B: Environmental*, *103*(1-2), 21-30.

Cabrera, M. I., Alfano, O. M., & Cassano, A. E. (December, 1996). Absorption and Scattering Coefficients of Titanium Dioxide Particle Suspensions in Water. *Journal Physical Chemistry*, *100*(51), 20043-20050.

Cong, Y., Wu, Z., & Tan, T. (May 22, 2005). Dechlorination by Combined Electrochemical Reduction and Oxidation. *Journal of Zhejiang University Science*, *6*(6), 563-568.

Chatzisymeon, E., Dimou, A., Mantzavinos, D., & Katsaounis, A. (August 15, 2009). Electrochemical Oxidation of Model Compounds and Olive Mill Wastewater over DSA Electrodes: The Case of Ti/IrO_2 Anode. *Journal of Hazardous Materials*, *167*(1-3), 268-274.

Chong, M. N., Jin, B., Christopher-Chow, W. K., & Saint, C. (May, 2010). Recent Developments in Photocatalytic

Table 5. Optimization of the experimental designs.

Factor/Response	Objective	Upper limit	Lower limit
I	In the interval	10	30
Na_2SO_4	Minimize	0.03	0.05
Catalyst	In the interval	100	200
ΔTOC	Maximize	16.91	58.57
EC_{TOC}	Minimize	0.328	1.937
η	Maximize	7.2	30.2

Water Treatment Technology: A Review. *Water Research*, *44*(10), 2997-3027.

Chu, Y., Zhang, D., Liu, L., Qian, Y., & Li, L. (May 15, 2013). Electrochemical Degradation of M-cresol Using Porous Carbon-Nanotube-Containing Cathode and Ti/SnO_2-Sb_2O_5-IrO_2 Anode: Kinetics, Byproducts and Biodegradability. *Journal of Hazardous Materials, 252-253*, 306-312.

De Laat, L., Le, G. T., Legube, B. (May, 2004). A Comparative Study of the Effects of Chloride, Sulfate and Nitrate Ions on the Rates of Decomposition of H_2O_2, and Organic Compounds by Fe(II)/H_2O_2 and Fe(III)/H_2O_2. *Chemosphere*, *55*(5), 715-723.

Domínguez, J. R., González, T., Palo, P., & Sánchez-Martín, J. (September 1, 2010). Anodic Oxidation of Ketoprofen on Boron-doped Diamond (BDD) Electrodes. Role of Operative Parameters. *Chemical Engineering Journal*, *162*(3), 1012-1018.

Feng, Y. J., & Li, X. Y. (May 2003). Electro-Catalytic Oxidation of Phenol on Several Metal-Oxide Electrodes in Aqueous Solution. *Water Research*, *37*(10), 2399-2407.

Fernandes, A., Pacheco, M. J., Ciríaco, L., & López, A. (January 15, 2012). Anodic Oxidation of a Biologically Treated Leachate on a Boron-doped Diamond Anode. *Journal of Hazardous Materials*, *199-200*, 82-87.

Fierro, S., Ouattara, L., Herrera, C. E., Passas-Lagos, E., Baltruschat, H., & Comninellis, C. (February 28, 2009). Investigation of Formic Acid Oxidation on Ti/IrO_2 Electrodes. *Electrochimica Acta*, *54*(7), 2053-2061.

García, O., Isarain-Chávez, E., El-Ghenymy, A., Brillas, E., & Peralta-Hernández, J. M. (August 15, 2014). Degradation of 2, 4-D Herbicide in a Recirculation Flow Plant with a Pt/Air-Diffusion and a BDD/BDD Cell by Electrochemical Oxidation and Electro-Fenton Process. *Journal of Electroanalytical Chemistry*, *728*, 1-9.

García, O., Isarain-Chávez, E., García-Segura, S., Brillas, E., & Peralta-Hernández, J. M. (December, 2013). Degradation of 2, 4-Dichlorophenoxyacetic Acid by Electro-Oxidation and Electro-Fenton/BDD Processes Using a Pre-pilot Plant. *Electrocatalysis*, *4*(4), 224-234.

González, M. C., & Braun, A. M. (August, 1995). Photolysis of Aqueous Solutions of Nitrate and Nitrite. *Res. Chem. Intermed*, *21*(8-9), 837-859.

Gueymard, C. A. (April, 2004). The Sun´s Total and Spectral Irradiance for Solar Energy Applications and Solar Radiation Models. *Solar Energy*, *76*(4), 423-453.

Hammami, S., Oturan, N., Bellakhal, N., Dachraoui, M., & Oturan, M. A. (November 15, 2007). Oxidative Degradation of Direct Orange 61 by Electro-Fenton Process Using a Carbon Felt Electrode: Application of the Experimental Design Methodology. *Journal of Electroanalytical Chemistry*, *610*(1), 75-84.

Hapeshi, E., Achilleos, A., Vasquez, M. I., Michael, C., Xekoukoulotakis, N. P., Mantzavinos, D., & Kassinos, D. (March, 2010). Drugs Degrading Photocatalytically: Kinetics and Mechanisms of Ofloxacin and Atenolol Removal on Titania Suspensions. *Water Research*, *44*(6), 1737-1746.

Huang, Y. H., Shih, Y. J., & Liu, C. H. (April 15, 2011). Oxalic Acid Mineralization by Electrochemical Oxidation Processes. *Journal of Hazardous Materials*, *188*(1-3), 188-192.

Isarain-Chávez, E., De la Rosa, C., Godínez, L. A., Brillas, E., & Peralta-Hernández, J. M. (January 15, 2014). Comparative Study of Electrochemical Water Treatment Processes for a Tannery Wastewater Effluent. *Journal of Electroanalytical Chemistry*, *713*, 62-69.

Isarain-Chávez, E., De la Rosa, C., Martínez-Huitle, C. A., & Peralta-Hernández, J. M. (March, 2013). On-Site Hydrogen Peroxide Production at Pilot Flow Plant: Application to Electro-Fenton Process. *International Journal Electrochemical Science*, *8*, 3084-3094.

Isarain-Chávez, E., Peralta-Hernández J. M., Guerra, R., & Morales-Ortiz, U. (August, 2012). Caracterización de ánodos de PtPdOx y RuO_2 usados en una celda electroquímica para la eliminación del cloruro de metiltionina en una solución sintética. *Revista Académica de la FI-UADY*, *16*(2), 131-140.

Kim, K. W., Kim, Y. J., Kim, I. T., Park, G. I., & Lee, E. H. (August 10, 2005). The Electrolytic Decomposition Mechanism of Ammonia to Nitrogen at an IrO_2 Anode. *Electrochimica Acta*, *50*(22), 4356-4364.

Lacasa, E., Cañizares, P., Rodrigo, M. A., & Fernández, F. J. (February 15, 2012b). Electro-Oxidation of As(III) with Dimensionally-Stable and Conductive-Diamond Anodes. *Journal of Hazardous Materials*, *203-204*, 22-28.

Lacasa, E., Llanos, J., Cañizares, P., & Rodrigo, M. A. (March, 2012a). Electrochemical Denitrificacion with Chlorides Using DSA and BDD Anodes. *Chemical Engineering Journal*, *184*(1), 66-71.

Lambert, J., Maldonado-Vega M., Isarain-Chávez, E., & Peralta-Hernández, J. M. (July, 2013). Ozone and Electrocoagulation Processes for Treatment of Dye in Leather Industry Wastewater: A Comparative Study. *International Journal of Emerging Technology and Advanced Engineering*, *3*(7), 1-9.

Legrini, O., Oliveros, E., & Braun, A. M. (January, 1993). Photochemical Processes for Water Treatment. *Chem. Rev.*, *93*(2), 671-698.

León, M. T., Pomposo, G. G., Suárez, G. J., & Vega, S. S. (2009). Treatment of Acid Orange 24 Solutions with Dimensionally Stable Anodes. *Portugaliae Electrochimica Acta*, *27*(3), 227-236.

Makgae, M. E., Klink, M. J., & Crouch A. M. (December, 2008). Performance of Sol-Gel Titanium Mixed Metal Oxide Electrodes for Electro-catalytic Oxidation of Phenol. *Applied Catalysis B: Environmental*, *84*(3-4), 659-666.

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (September 15, 2009). Decontamination and Disinfection of Water by Solar Photocatalysis: Recent Overview and Trends. *Catalysis Today*, *147*(1), 1-59.

Marselli, B., García-Gómez, J., Michaud, P. A., Rodrigo, M. A., & Comninellis, C. (February, 2003). Electrogeneration of Hydroxyl Radicals on Boron-doped Diamond Electrodes. *Journal of the Electrochemical Society*, *150*(3), D79-D83.

Martínez-Huitle, C. A., & Brillas, E. (April 7, 2009). Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods: A General Review. *Applied Catalysis B: Environmental*, *87*(3-4), 105-145.

Michels, N. L., Kapałka, A., Abd-El-Latif, A. A., Baltruschat, H., & Comninellis, C. (September, 2010). Enhanced Ammonia Oxidation on BDD Induced by Inhibition of Oxygen Evolution Reaction. *Electrochemistry Communications*, *12*(9), 1199-1202.

Morales-Ortiz, U., Ávila-García, A., & Hugo-Lara, C. (April 14, 2006). Ruthenium Oxide Films for Selective Coatings. *Solar Energy Materials & Solar Cell*, *90*(6), 832-840.

Panizza, M., & Cerisola, G. (April, 2009). Direct and Mediated Anodic Oxidation of Organic Pollutants. *Chem. Rev.*, *109*, 6541-6569.

Papastefanakis, N., Mantzavinos, D., & Katsaounis, A. (April, 2010). DSA Electrochemical Treatment of Olive Mill Wastewater on Ti/RuO_2 Anode. *Journal of Applied Electrochemistry*, *40*(4), 729-737.

Patel, P. S., Bandre, N., Saraf, A., & Ruparelia, J. P. (2013). Electro-Catalytic Materials (Electrode Materials). Electrochemical Wastewater Treatment. *Procedia Engineering*, *51*, 430-435.

Profeti, L. P., Profeti, D., & Olivi, P. (March, 2009). Pt-RuO_2 Electrodes Prepared by Thermal Decomposition of Polymeric Precursors as Catalysts for Direct Methanol Fuel Cell Applications. *International Journal of Hydrogen Energy*, *34*(6), 2747-2757.

Ramírez, J. H., Costa, C. A., & Madeira, L. M. (October, 2005). Experimental Design to Optimize the Degradation of the Synthetic Dye Orange II Using Fenton's Reagent. *Catalysis Today*, *107-108*(30), 68-76.

Rodríguez, J., Candal, R. J., Solís, J., Estrada, W., & Blesa, M. A. (2005). El fotocatalizador: síntesis, propiedades y limitaciones (pp. 129-145). En R. J. Candal (Ed.). *Tecnologías solares para la desinfección y descontaminación del agua*. San Martín, Argentina: UNSAM Edita, Universidad Nacional de San Martín.

Scialdone O. (November 1, 2009). Electrochemical Oxidation of Organic Pollutants in Water at Metal Oxide Electrodes: A simple Theoretical Model Including Direct and Indirect Oxidation Processes at the Anodic Surface. *Electrochimica Acta*, *54*(26), 6140-6147.

Scialdone, O., Randazzo, S., Galia, A., & Filardo, G. (January, 2003). Electrochemical Oxidation of Organics at Metal Oxide Electrodes: The Incineration of Oxalic Acid at IrO_2-Ta_2O_5 (DSA-O_2) Anode. *Electrochimica Acta*, *54*(4), 1210-1217.

Semarnat (1996). Norma Oficial Mexicana NOM-001-SEMARNAT-1996. Que establece los límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales. *Diario Oficial de la Federación*, 6 de enero de 1997.

Szpyrkowicz, L., Juzzolino C., & Kaul, S. N. (June, 2001). A Comparative Study on Oxidation of Disperse Dyes by Electrochemical Process, Ozone, Hypochlorite and Fenton Reagent. *Water Research*, *35*(9), 2129-2136.

Szpyrkowicz, L., Kaul, S. N., Neti, R. N., & Satyanarayan, S. (April, 2005). Influence of Anode Material on Electrochemical Oxidation for the Treatment of Tannery Wastewater. *Water Research*, *39*(8), 1601-1613.

Wu, J., Zhang, H., Oturan N., Wang, Y., Chen, L., & Oturan, M. A. (May 2012). Application of Response Surface Methodology to the Removal of the Antibiotic Tetracycline by Electrochemical Process Using Carbon-felt Cathode and DSA (Ti/RuO_2-IrO_2) Anode. *Chemosphere*, *87*(6), 614-620.

Zanbotto-Ramalho, A. M., Martínez-Huitle, C. A., & Ribeiro Da Silva, D. (February, 2010). Application of Electrochemical Technology for Removing Petroleum Hydrocarbons from Produced Water Using a DSA-type Anode at Different Flow Rates. *Fuel*, *89*(2), 531-534.

Zhang, C., Yang, L., Rong, F., Fu D., & Gu, Z. (March, 2012). Boron-Doped Diamond Anodic Oxidation of Ethidium Bromide: Process Optimization by Response Surface Methodology. *Electrochimica Acta*, *64*(1), 100-109.

Zhou, M., Liu, L., Jiao, Y., Wang, Q., & Tan, Q. (August 15, 2011b). Treatment of High-Salinity Reverse Osmosis Concentrate by Electrochemical Oxidation on BDD and DSA Electrodes. *Desalination*, *277*(1-3), 201-206.

Zhou, M., Särkkä, H., & Sillanpää, M. A. (April 29, 2011a). Comparative Experimental Study on Methyl Orange Degradation by Electrochemical Oxidation on BDD and MMO Electrodes. *Separation and Purification Technology*, *78*(3), 290-297.

Institutional Address of the Authors

Dr. Eloy Isarain Chávez
Ing. Saray Ramírez Martínez
Dra. María Maldonado Vega
Dra. Juliette Lambert
Dr. Juan M. Peralta Hernández

Centro de Innovación Aplicada en Tecnologías Competitivas (CIATEC)
Departamento de Investigación Ambiental
Omega-201, Fraccionamiento Industrial Delta
37545 León, Guanajuato, México
Teléfono: +52 (477) 7100 011, extensión 1508
isarain_chavez@yahoo.com.mx
vega.maldonado.m@gmail.com
jlambert@ciatec.mx
jperalta@ciatec.mx

M.C. Ulises Morales-Ortiz

Universidad Autónoma Metropolitana-Iztapalapa
Departamento de Química
Av. San Rafael Atlixco núm. 186
09340 México, D.F., México
Teléfono: +52 (55) 5804 4671, extensión 15
ulis@xanum.uam.mx

Verde River, San Luis Potosi, Mexico.

Photo: David Vinicio Carrera Villacrés.

Qualitative and Quantitative Salinity of the Santa María-Verde River Hydrographic System, Mexico

• David Vinicio Carrera-Villacrés* •
Universidad de las Fuerzas Armadas, Ecuador y Colegio de Postgraduados, México
*Corresponding Author

• Tania Crisanto-Perrazo •
Escuela Politécnica Nacional, Ecuador

• Héctor Ortega-Escobar • Jazmín Ramírez-García • David Espinosa-Victoria •
• Carlos Ramírez-Ayala • Víctor Ruiz-Vera •
Colegio de Postgraduados, México

• Martha Velázquez-Machuca •
Instituto Politécnico Nacional, México

• Edgar Sánchez-Bernal •
Universidad del Mar, México

Abstract

Carrera-Villacrés, D. V., Crisanto-Perrazo, T., Ortega-Escobar, H., Ramírez-García, J., Espinosa-Victoria, D., Ramírez-Ayala, C., Ruiz-Vera, V., Velázquez-Machuca, M., & Sánchez-Bernal, E. (March-April, 2015). Qualitative and Quantitative Salinity of the Santa María-Verde River Hydrographic System, Mexico. *Water Technology and Sciences* (in Spanish), 6(2), 69-83.

This investigation took place in the Santa Maria-Verde River hydrographic system in order to identify the evolution of the salinity of irrigation water. It included both a quantitative (electrical conductivity) and qualitative (calculated using the sodium and magnesium adsorption ratio) analysis in order to predict effects on soil and crops. The investigation used a non-experimental, descriptive cross-sectional design in which 69 stations were sampled from winter 2009 to spring and autumn of 2010. Ten measurements were taken for each water sample, cations, anions, pH and electrical conductivity (CE). An alkalinity model was used to determine the evolution of the waters, which was experimentally verified by re-concentration of salts through evaporation. The saturation index (SI) and changes in the sodium adsorption ratio (SAR and SAR_{adj}) were calculated. The salinity of most of the rivers in the Santa Maria-Verde River hydrographic system was classified as high or very high, according to the quantitative analysis. The most critical qualitative salinity was that of magnesium, as compared to sodium, even with the precipitation of calcite. The waters evolved from calcium sulfate to magnesium and sodium sulfate. There was a trend of increasing concentrations and changes in the type of salinity of the waters in the Santa Maria-Verde River hydrographic system, which affects the soils and crops.

Kewords: sodium, magnesium, evolution of water, geostatistical.

Resumen

Carrera-Villacrés, D. V., Crisanto-Perrazo, T., Ortega-Escobar, H., Ramírez-García, J., Espinosa-Victoria, D., Ramírez-Ayala, C., Ruiz-Vera, V., Velázquez-Machuca, M., & Sánchez-Bernal, E. (marzo-abril, 2015). Salinidad cuantitativa y cualitativa del sistema hidrográfico Santa María-Río Verde, México. Tecnología y Ciencias del Agua, *6(2), 69-83.*

La investigación se desarrolló en el sistema hidrográfico Santa María-Río Verde, con el objetivo de conocer la evolución y salinidad de las aguas de riego tanto cuantitativa, expresada como conductividad eléctrica, como cualitativa, calculada mediante la relación de adsorción de sodio y magnesio, para posteriormente predecir sus efectos sobre los suelos y cultivos. La investigación fue no experimental transversal descriptiva, con el muestreo a juicio en 69 estaciones, muestreadas desde el invierno de 2009, y primavera y otoño de 2010. Se determinaron 10 mediciones en cada muestra de agua: cationes, aniones, pH y conductividad eléctrica (CE). Se siguió el modelo basado en la alcalinidad para determinar la vía evolutiva que toman las aguas, y se comprobó con un experimento de reconcentración de sales por evaporación. Se calculó el índice de saturación (IS) y las modificaciones de la relación de adsorción de sodio (RAS); éstas fueron, RAS y RAS_{aj} El sistema hidrográfico Santa María-Río Verde, de acuerdo con la salinidad cuantitativa, se clasificó en su mayoría de ríos como alta y muy altamente salinas; la salinidad cualitativa más crítica fue la magnésica, en comparación con la sódica, a pesar de que la calcita precipitará. La evolución de las aguas fueron de sulfatadas cálcicas a sulfatadas magnésicas y sódicas. Existe la tendencia a que aumente la concentración y cambie la tipología de la salinidad de las aguas del sistema hidrográfico Santa María-Río Verde, afectando los suelos y cultivos.

Palabras clave: *sódica, magnésica, evolución de las aguas, geoestadística.*

Received: 17/05/2011
Accepted: 15/10/2014

Introduction

The salinity of soils creates serious problems for agriculture, and therefore this study will contribute to the development of arid and semi-arid regions that are most severely affected by this phenomenon. Agronomic resources in arid and semi-arid regions represent 60% of the Mexican territory, and even though they are considered to have high agricultural potential they are little used. The Santa María-Verde River Hydrographic System is a region which is highly affected by the salinity of the soil. This salinity can be determined by measuring the ions in irrigation water, since water saturates the soil when irrigating crops, at which point a chemical balance exists between these two matrices.

This study measures quantitative salinity based on the electrical conductivity (EC) of the water and qualitative salinity according to Na^+ and Mg^{2+} adsorption ratios.

Quantitative salinity includes primary and secondary salinity. In this study area, secondary salinity is caused by human activity related to poor irrigation practices. Meanwhile, primary salinity is related to its geological past, which produces geochemical processes among waters, soil and crops. This can create serious problems for agriculture, making crops physically and chemically poor and decreasing their fertility. Damages to leaves and fruits occur from the accumulation of toxic ions in cells, decreasing their size, color and therefore their commercial value (Shani & Dudley, 2001).

To determine the evolution of saline, an experiment involving the re-concentration of salts was performed to simulate what occurs in the area of the Verde River irrigation zone as a result of evaporation-precipitation processes. This experiment determined that the dissolved salts in the water changed from calcium sulfates (with a solubility around 10 g l^{-1}) to magnesium and sodium sulfates (with a solubility of approximately 350 g l^{-1}). These results corroborate those reported by Szabolcs (1994), and therefore this water is considered to have high energy, impeding the adsorption of nutrients in the crops.

The objective of the present work was to quantitatively and qualitatively determine the evolution and concentration of the salinity of irrigation water. The quantitative analysis was based on electrical conductivity and the qualitative analysis on the sodium and magnesium adsorption ratio. The effects on the soils and crops in the Santa María-Verde River Hydrographic System were then predicted.

Materials and Methods

This work was a cross-sectional, non-experimental prospective study, based on the researcher's judgment. It is cross-sectional in the sense that variables such as physical and chemical characteristics were measured only once at a given moment. The study did not intend to evaluate their evolution over time. It was descriptive in terms of the universe of waters included, with the intention to describe them according to a group of variables, and about which there is no central hypothesis.

The criteria of the investigator were based on observations of the region and preliminary soil and water studies conducted since 1967 by the Montecillo campus Post-graduate School Hydrosciences Program (Grande, Hernández, Aguilera, & Boulaine, 1967).

Water samples were taken from runoff in the Eastern Sierra Madre at the headwaters of the Extorax, Autla, Jalpan Santa María and Verde rivers and along their courses to the valleys where the water is used for irrigation, with a total of 69 stations. The samples were taken from springs and rivers before and after they passed through urban zones in order to identify the increase in quantitative and qualitative salinity.

The physiochemical variables used and measured by this work to study the evolution and qualitative salinity of irrigation water included concentrations of anion and cations (Ca^{2+} + Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-} y SO_4^{2}), pH and electrical conductivity.

To determine the evolution of salinity, an experiment was performed based on the evaporation of the Media Luna spring, which is the main source of irrigation water for the Verde River valley. This experiment tested the models proposed by Hardie and Eugster (1970) and by Risacher and Fritz (2009).

The method proposed by APHA (1995) was used for the analytical determination of ion concentrations. Specifically, 0.5 l water samples were taken in duplicate at each sampling station in the Santa María-Verde River Hydrographic System. The containers used to collect the water samples were rinsed several times with the water to be sampled. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-} and SO_4^{2-} ions were determined analytically according to methods 4500-H+B, 2510 B, 3500 Ca D, 3500 Na K D, 2320 B, 4500 Ci B, 4500-SO_4 B, 2540 D and 2540 E, respectively. The electrical conductivity and pH values were measured based on Official Mexican Norms NOM-AA-93-1984 and NMX-AA-008-SCFI-2000, respectively.

The Richards (1962) method was used to interpret quantitative and qualitative salinity, which evaluates salinity based on electrical conductivity and the Na^{+} adsorption ratio, respectively, in order to classify salinity and predict salinity levels and its effect on soil and crops.

To generate the spatial distribution maps, the geostatistical Kriging method was used with the *Arc Gis*, version 9.3. Webster and Oliver (2007) reported that this method presents excellent results since the concentrations are variable, random and spatially continuous.

Results and Discussion

Ionic Composition of the Water in the Santa María-Verde River Hydrographic System

Table 1 presents the cation and anion concentrations of the samples taken in the years 2009 and 2010 in the Santa María-Verde River Hydrographic System. The data shown were validated according to APHA (1995) in terms of acceptable errors. The primary statistical parameters are shown at the bottom of Table 1. A variation in pH between 6.9 and 8.2 is also observed, with mean conditions around neutral for all the water. These conditions are due, in part, to the weak base of the HCO_3^{-} ion and the strong base of the CO_3^{2-} ion. Therefore, the HCO_3^{-}/CO_3^{2-} is a buffer (Figueruelo & Dávila, 2004).

The salinity of the continental water was determined according to four main cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and the anions CO_3^{2-}, HCO_3^{-}, Cl^{-} and SO_4^{2-}, whose mean concentration worldwide is 120 mg l^{-1} (Wetzel, 1981). This varies considerably from one continent to another and according to the lithology of the land masses. Based on the concentration averages of the data from the water samples, where $Na^{+}/Na^{+} + Ca^{2+} = 0.24$ and TDS = 1 090.88 mg l^{-1}, and after placing the data on the Gibbs graph (1970) (Figure 1), the water in the Santa María-Río Hydrographic System was determined to be located in a zone where there is more evaporation than precipitation. If this trend is maintained, the concentration would increase and the typology of the salinity of the water would change, thereby changing the salinity of the soil.

Figure 2 shows the predominance of Ca^{2+}, Mg^{2+}, Na^{+} andK^{+}, O_3^{2-}, HCO_3^{-}, Cl^{-} and

Table 1. Ionic composition, pH, EC, TDS, Saturation Index (SI), SAR_{orig} and SAR_{aj} for the Santa Maria-Verde River hydrographic system.

No.	pH	EC	mmol$_c$ l^{-1}											mg l^{-1}	SI	SAR_{orig}	SAR_{aj}
		µS cm^{-1}	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Sum	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	Sum	% error	TDS			
1	7.7	426.00	2.32	1.42	0.28	0.19	4.21	0.00	3.27	0.68	0.17	4.12	1.04	309.57	0.79	0.20	0.37
2	8.1	1 700.00	8.20	3.70	4.63	0.27	16.80	0.00	6.73	2.90	6.74	16.37	1.30	1 163.43	1.70	1.90	5.12
3	7.2	1 272.73	4.21	3.00	4.90	0.43	12.54	0.00	4.22	3.20	4.78	12.20	1.37	850.81	1.02	2.58	5.22
4	8.2	336.25	2.40	0.40	0.50	0.06	3.36	0.00	2.33	0.80	0.14	3.27	1.41	243.89	0.65	0.42	0.70
5	7.5	305.45	1.47	0.85	0.65	0.09	3.06	0.00	1.71	1.20	0.07	2.98	1.32	208.50	0.30	0.60	0.79
6	8.2	337.85	2.36	0.42	0.52	0.08	3.38	0.00	2.36	0.76	0.16	3.28	1.50	246.11	0.90	0.44	0.84
7	7.7	330.91	1.57	0.96	0.64	0.09	3.26	0.00	1.83	1.26	0.10	3.19	1.09	222.50	0.36	0.57	0.78
8	7.5	372.00	2.03	1.25	0.21	0.18	3.67	0.00	2.79	0.72	0.08	3.59	1.07	267.46	0.66	0.16	0.27
9	7.9	308.25	1.66	0.72	0.60	0.08	3.06	0.00	2.03	0.78	0.17	2.98	1.32	218.62	0.61	0.55	0.88
10	7.7	254.55	1.23	0.72	0.48	0.04	2.47	0.00	1.40	0.95	0.06	2.41	1.23	167.98	0.09	0.49	0.53
11	7.9	480.50	2.60	1.10	0.92	0.12	4.74	0.00	3.13	1.20	0.27	4.60	1.50	337.81	0.82	0.68	1.23
12	7.5	509.09	1.76	1.20	1.96	0.12	5.04	0.00	2.81	1.28	0.82	4.91	1.31	355.83	0.59	1.61	2.56
13	7.4	432.73	1.48	1.02	1.65	0.10	4.25	0.00	2.37	1.08	0.69	4.14	1.31	299.94	0.42	1.48	2.09
14	7.4	381.82	1.31	0.90	1.45	0.09	3.75	0.00	2.09	0.95	0.61	3.65	1.35	264.55	0.31	1.38	1.81
15	7.5	352.90	1.87	1.22	0.22	0.18	3.49	0.00	2.69	0.65	0.06	3.40	1.31	254.46	0.61	0.18	0.29
16	7.8	467.00	2.08	1.65	0.75	0.16	4.64	0.00	2.50	0.84	1.17	4.51	1.42	323.75	0.97	0.55	1.08
17	7.5	356.36	1.81	0.84	0.82	0.09	3.56	0.00	1.92	0.94	0.60	3.46	1.42	248.15	0.42	0.71	1.01
18	7.7	324.50	1.30	0.80	0.65	0.25	3.00	0.00	2.37	0.60	0.14	3.11	1.80	233.10	0.39	0.63	0.88
19	7.9	151.30	0.40	0.64	0.30	0.16	1.50	0.00	1.13	0.22	0.11	1.46	1.25	111.12	-0.35	0.42	0.27
20	7.7	232.20	0.52	1.07	0.38	0.32	2.29	0.00	1.72	0.42	0.08	2.22	1.55	168.36	-0.14	0.43	0.37
21	7.6	723.00	2.53	4.20	0.15	0.26	7.14	0.00	5.39	0.60	0.96	6.95	1.38	511.42	1.00	0.08	0.16
22	8.0	675.50	3.11	2.30	1.10	0.20	6.71	0.00	3.56	1.12	1.86	6.54	1.30	469.57	1.08	0.67	1.39
23	7.6	585.45	2.03	1.40	2.26	0.14	5.83	0.00	3.26	1.48	0.95	5.69	1.22	412.14	0.73	1.73	2.99
24	7.9	645.50	2.89	2.30	1.05	0.18	6.42	0.00	3.46	1.16	1.62	6.24	1.44	447.00	1.20	0.65	1.43
25	7.6	534.55	1.81	1.26	2.03	0.13	5.23	0.00	2.90	1.33	0.86	5.09	1.36	368.75	0.62	1.64	2.66
26	7.5	1 088.50	6.48	4.00	0.20	0.08	10.76	0.00	4.92	0.80	4.75	10.47	1.37	742.88	1.46	0.09	0.22
27	7.2	890.91	4.97	2.17	1.40	0.25	8.79	0.00	3.68	1.80	3.07	8.55	1.38	603.74	1.07	0.74	1.53
28	7.1	1061.50	6.09	4.06	0.22	0.10	10.47	0.00	5.10	0.82	4.27	10.19	1.36	725.70	1.50	0.10	0.24
29	7.2	890.91	4.67	2.26	1.55	0.30	8.78	0.00	3.60	1.86	3.10	8.56	1.27	602.91	1.03	0.83	1.69
30	7.5	1 770.00	12.09	4.71	0.42	0.26	17.48	0.00	5.77	1.27	9.96	17.00	1.39	1 194.82	1.62	0.14	0.38
31	7.0	2 258.00	13.39	8.21	0.38	0.32	22.30	0.00	7.03	2.12	12.58	21.73	1.30	1 497.58	1.69	0.12	0.31
32	7.0	2 265.00	13.26	8.43	0.36	0.32	22.37	0.00	7.15	2.08	12.58	21.81	1.27	1 503.09	1.69	0.11	0.29
33	7.1	2077.00	12.02	8.10	0.30	0.12	20.54	0.00	6.04	1.02	12.94	20.00	1.33	1 377.11	1.62	0.09	0.25
34	7.3	1909.09	10.11	8.23	0.35	0.17	18.86	0.00	5.76	1.13	11.48	18.37	1.32	1 260.21	1.51	0.12	0.29
35	7.3	2 009.00	11.59	8.00	0.18	0.08	19.85	0.00	4.80	1.54	12.98	19.32	1.35	1 307.65	1.52	0.06	0.14
36	7.2	1 909.09	10.15	8.24	0.33	0.18	18.90	0.00	5.80	1.14	11.46	18.40	1.34	1 262.90	1.51	0.11	0.27
37	7.2	1 909.09	10.17	8.22	0.32	0.17	18.88	0.00	5.83	1.12	11.44	18.39	1.31	1 262.60	1.52	0.11	0.27
38	7.5	1 771.00	12.60	4.28	0.36	0.25	17.49	0.00	5.83	1.26	9.92	17.01	1.39	1 199.37	1.64	0.12	0.33

Table 1 (continuation). Ionic composition, pH, EC, TDS, Saturation Index (SI), SAR_{orig} and SAR_{aj} for the Santa Maria-Verde River hydrographic system.

No.	pH	EC µS cm^{-1}	mmol$_c$ l^{-1}											mg l^{-1}	IS	SAR_{orig}	SAR_{aj}
			Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Sum	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	Sum	% error	TDS			
39	7.3	1 901.00	13.55	4.56	0.38	0.28	18.77	0.00	6.23	1.42	10.61	18.26	1.38	1 286.72	1.68	0.13	0.34
40	7.6	2 221.00	12.27	8.67	0.82	0.16	21.92	0.00	7.82	1.40	12.13	21.35	1.33	1 485.54	1.69	0.25	0.68
41	7.9	2 290.91	7.36	12.00	2.88	0.38	22.62	0.00	11.81	2.62	7.59	22.02	1.34	1 552.44	1.64	0.93	2.44
42	7.0	2 047.00	8.00	11.99	0.18	0.08	20.25	0.00	4.40	1.22	14.09	19.71	1.35	1 301.74	1.24	0.06	0.13
43	7.0	1 400.00	7.10	4.69	1.76	0.28	13.83	0.00	5.30	1.60	6.56	13.46	1.36	945.88	1.39	0.72	1.73
44	7.7	2 145.50	11.80	8.50	0.78	0.16	21.24	0.00	7.70	1.20	11.82	20.72	1.24	1 444.04	1.65	0.24	0.65
45	7.5	1 272.73	6.60	4.09	1.60	0.25	12.54	0.00	4.73	1.45	6.02	12.20	1.37	857.68	1.30	0.69	1.59
46	8.2	2 374.50	15.65	7.00	0.60	0.16	23.41	0.00	6.48	1.60	14.71	22.79	1.35	1 577.21	1.90	0.18	0.52
47	7.6	1 463.64	7.52	4.75	1.85	0.30	14.42	0.00	4.78	1.60	7.68	14.06	1.26	979.94	1.35	0.75	1.76
48	7.8	2 163.64	5.90	12.53	2.58	0.32	21.33	0.00	8.40	2.42	9.86	20.68	1.55	1 414.23	1.41	0.85	2.05
49	7.6	674.50	2.87	2.26	1.24	0.25	6.62	0.00	4.02	1.60	0.80	6.42	1.57	463.49	1.01	0.77	1.56
50	7.4	644.50	3.00	1.96	1.15	0.21	6.32	0.00	4.12	1.70	0.32	6.14	1.41	445.81	1.01	0.73	1.46
51	7.2	2 306.50	14.98	6.39	1.30	0.14	22.81	0.00	3.70	2.27	16.28	22.25	1.25	1 501.24	1.46	0.40	0.98
52	7.4	2 418.18	7.36	13.12	2.90	0.52	23.90	0.00	8.29	3.12	11.78	23.19	1.51	1 576.16	1.48	0.91	2.25
53	7.7	2 729.00	16.76	8.90	1.20	0.10	26.96	0.00	4.50	2.60	19.16	26.26	1.32	1 762.52	1.56	0.34	0.86
54	7.9	2 418.18	7.70	12.89	2.86	0.45	23.90	0.00	8.89	3.10	11.28	23.27	1.34	1 588.41	1.53	0.89	2.25
55	7.7	2 485.50	14.27	9.12	1.12	0.08	24.59	0.00	6.74	2.60	14.61	23.95	1.32	1 630.88	1.65	0.33	0.87
56	7.8	2 290.91	7.23	12.30	2.68	0.40	22.61	0.00	10.53	2.92	8.59	22.04	1.28	1 530.22	1.58	0.86	2.21
57	7.2	4 730.00	27.79	9.56	9.00	0.36	46.71	0.00	4.40	7.60	33.48	45.48	1.33	3 040.00	1.71	2.08	5.65
58	7.6	3 175.50	19.05	8.82	3.31	0.22	31.40	0.00	5.18	3.18	22.23	30.59	1.31	2 070.15	1.69	0.89	2.39
59	7.0	3 563.64	9.42	18.90	6.30	0.45	35.07	0.00	9.33	6.02	18.91	34.26	1.17	2 271.73	1.61	1.67	4.38
60	7.8	2 100.00	6.54	11.12	2.76	0.32	20.74	0.00	6.50	3.14	10.46	20.10	1.57	1 352.47	1.35	0.93	2.18
61	6.9	4 200.00	11.11	22.30	7.43	0.64	41.48	0.00	8.61	8.20	23.50	40.31	1.43	2 634.32	1.62	1.82	4.76
62	7.5	1 781.82	5.45	9.43	2.30	0.40	17.58	0.00	5.78	2.62	8.72	17.12	1.33	1 156.71	1.28	0.84	1.92
63	7.2	3 818.18	6.86	20.29	9.80	0.78	37.73	0.00	11.33	7.46	17.86	36.65	1.45	2 453.43	1.60	2.66	6.90
64	7.5	3 844.50	15.80	15.94	5.84	0.34	37.92	0.00	3.80	5.80	27.18	36.78	1.53	2 400.80	1.46	1.47	3.60
65	7.4	3 975.00	16.60	16.80	5.54	0.37	39.31	0.00	3.60	6.40	28.27	38.27	1.34	2 482.98	1.45	1.36	3.32
66	7.2	3 945.45	7.48	20.69	10.12	0.72	39.01	0.00	11.53	7.98	18.40	37.91	1.43	2 532.30	1.59	2.70	6.99
67	7.0	2 418.18	4.66	12.62	6.17	0.45	23.90	0.00	5.38	4.55	13.22	23.15	1.59	1 530.70	1.10	2.10	4.42
68	7.0	5 727.27	6.66	16.00	33.10	0.83	56.59	0.00	10.41	33.50	11.12	55.03	1.40	3 478.18	1.45	9.83	24.08
69	7.3	2 036.36	7.32	11.95	0.70	0.18	20.15	0.00	5.00	3.24	11.30	19.54	1.54	1 277.71	1.27	0.23	0.51
Desv. est.	0.33	1 252.43	5.48	5.73	4.43	0.17	12.37	0.00	2.62	4.22	7.92	12.03	0.12	784.37	0.51	1.28	3.16
CV	0.04	0.75	0.76	0.87	1.84	0.68	0.75		0.51	1.61	0.95	0.75	0.09	0.72	0.44	1.43	1.59
Media	7.5	1 664.76	7.21	6.59	2.40	0.25	16.44	0.00	5.08	2.63	8.29	16.00	1.36	1 090.88	1.17	0.90	1.99
Mediana	7.5	1 770.00	6.60	4.69	1.10	0.20	17.48	0.00	4.78	1.45	7.68	17.00	1.35	1 163.43	1.35	0.65	1.08
Mínimo	6.9	151.30	0.40	0.40	0.15	0.04	1.50	0.00	1.13	0.22	0.06	1.46	1.04	111.12	-0.35	0.06	0.13
Máximo	8.2	5 727.27	27.79	22.30	33.10	0.83	56.59	0.00	11.81	33.50	33.48	55.03	1.80	3 478.18	1.90	9.83	24.08
Moda	7.2	1 909.09	2.03	0.72	0.38	0.08	12.54	0.00	2.37	1.60	0.06	12.20	1.37		1.69		

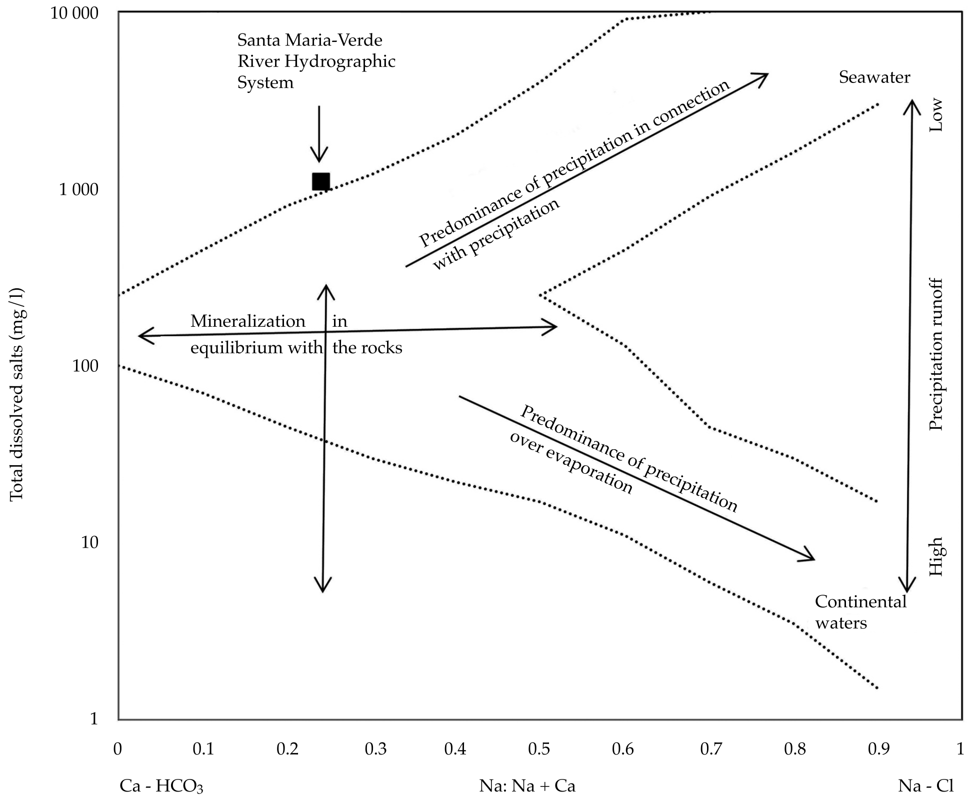


Figure 1. Gibbs diagram of the water sampling from the Santa Maria-Verde River hydrograph system.

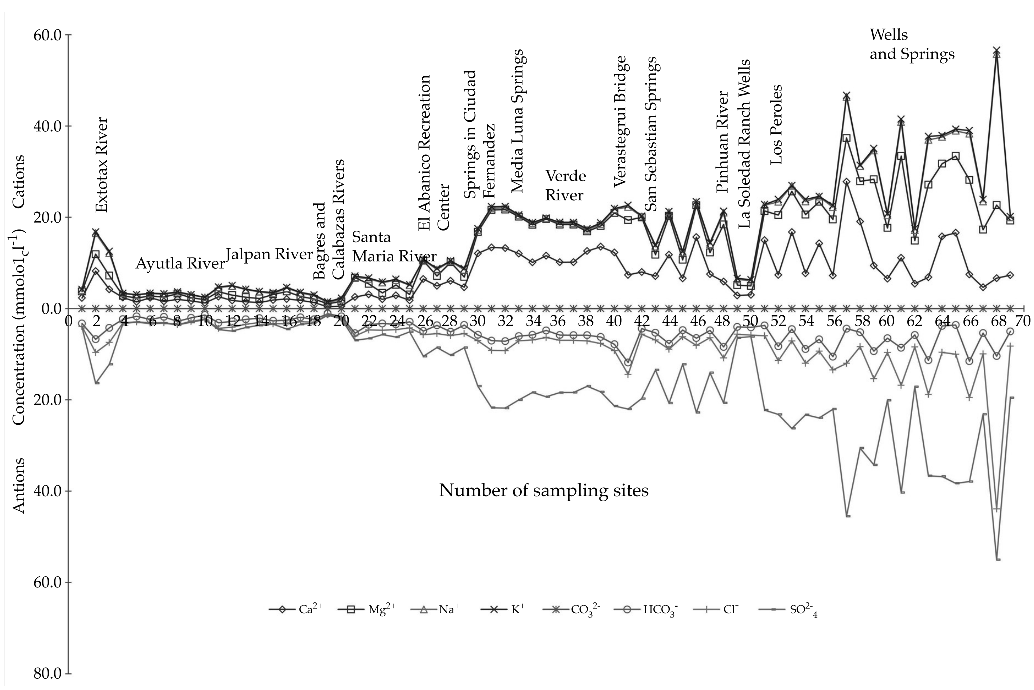


Figure 2. Ionic composition of the waters in the Santa Maria-Verde River Hydrographic System, states of Queretaro and San Luis Potosi.

SO_4^{2-} and their increased concentrations at the sampling stations in the Santa María-Verde River Hydrographic System. For example, the concentration of Ca^{2+} began to increase from the action of geological formations through which the water runs. Stations 21-25 are in the Santa María River which contains large sections of limestone, and where increases in concentrations of Ca^{2+} and SO_4^{2-} are observed. As of station 52, after the springs, in Ciudad Fernandez, the salinity increases substantially due to formations rich in sea salts and because of its location on the Valles-San Luis Platform.

Quantitative Salinity in the Santa María-Verde River Hydrographic System

Table 2 presents a summary of the quantitative salinity values determined based on electrical conductivity, the classifications based on Richards (1962) and the percentages represented in the hydrographic system. This information was used to generate a map of the spatial distribution of the quantitative salinity of the basin using the Kriging geostatistical method (as seen in Figure 3), which agrees with the individual description of the components of the hydrographic system studied, thereby validating the method.

Qualitative Salinity of the Santa María-Verde River Hydrographic System

Qualitative Salinity: Sodium Adsorption Ratio (SAR)

Sodification is an increase in the proportion of Na^+ retained in the soil exchange complex and is the result of using poor quality water (wastewater, saline and sodic water) (Heidarpour, Mostafazadeh, Abedi, & Malekian, 2007). The concentration of Ca^{2+} varies considerably as a result of precipitation or dissolution processes.

Sodium chloride salinity is determined by the sodium adsorption ratio (SAR), as indicated by relation (1):

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (1)$$

Table 2. Summary of quantitative salinity values for the Santa Maria-Verde River Hydrographic System.

Hydrographic System	Electrical Conductivity EC (μS/cm)	Classification	% of the Santa Maria-Verde River Hydrographic Region
Bagres and Santa Maria Rivers (headwaters of the system)	< 250	S1. Low salinity	2.9
Ayutla, Jalpan, Santa Maria Rivers (middle course)	250-750	S2. Moderate salinity	33.3
Extorax Rivers, Springs in the Valles San Luis Platform, Media Luna and Verde River before entering the city (agricultural valleys before reaching urban zones)	750-2 250	S3. High salnity	34.8
Springs in Ciudad Fernandez, Verde River after urban discharges, Baqueros River, Peroles springs (agricultural valleys after entering urban zones)	> 2 250	S4. Very high salinity	29

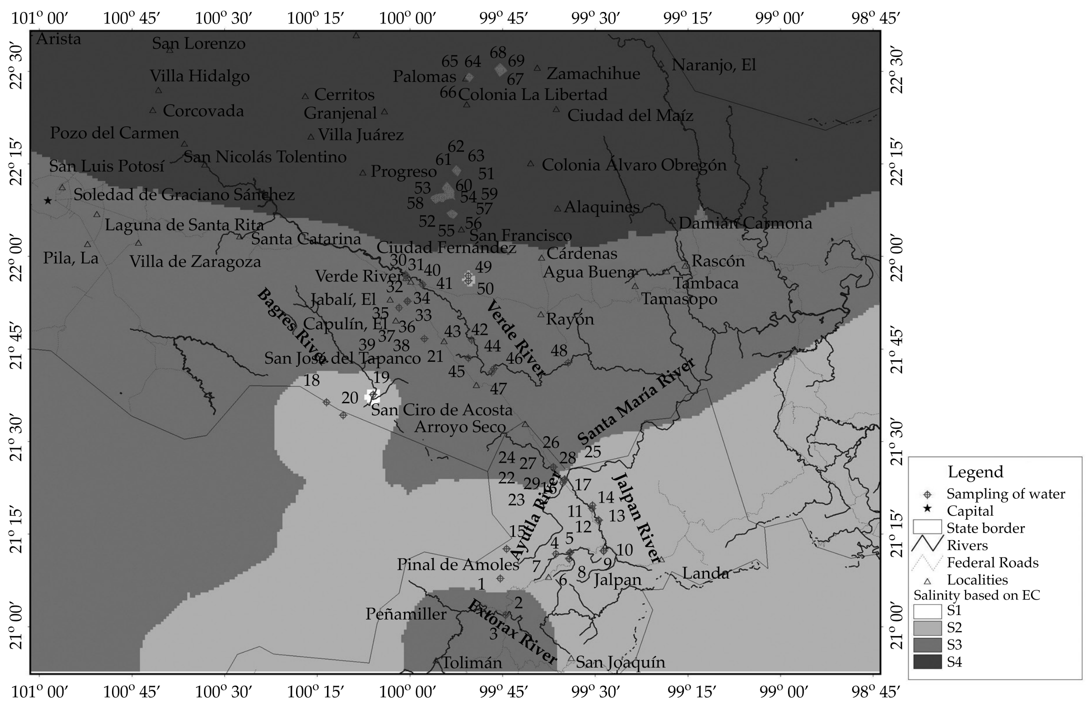


Figure 3. Spatial distribution of the quantitative salinity based on electrical conductivity at the sampling stations in the hydrographic system.

The SAR expresses the possibility of Na^+ being adsorbed in the soil exchange complex and the presence of other cations reduces this possibility, especially Ca^{2+} (Ortega & Orellana, 2007).

The SAR formulas that are most often used to manage saline water and soils are SAR and adjusted SAR (SAR_{adj}) (Carrera-Villacrés *et al*., 2011). SAR_{adj} presented the most critical values in the Santa María-Verde River Hydrographic System. It is calculated with relation (2) (Ayers & Westcot, 1987):

$$SAR_{adj} = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}\left(pH_{water} - pH_{calculated}\right) \quad (2)$$

which relates the Langelier Saturation Index (SI) with the calculated pH, taking into account the precipitation of $CaCO_3$.

Given what has been described previously, $CaCO_3$ is projected to precipitate in the Extorax, Ayutla, Jalpan Santa María and Verde rivers, since the SI is positive and remains in solution only in the Bagres River. In other words, the concentration of Ca^{2+} will decrease in 98% of the water samples just from the effect of the precipitation of calcite.

The Media Luna spring is the main Verde River tributary. Before the river passes through population and agricultural zones, the Na^+ concentration is 0.30 $mmol_c\ l^{-1}$, increasing to 2.88 $mmol_c\ l^{-1}$ after industrial urban water from the cities is discharged into the river. That is a 10-fold increase and, therefore, the water in this part of the system presents a sodium chloride salinity.

The same behavior is observed with Mg^{2+}, though to a smaller degree. At the beginning of the Verde River, the concentration of this ion was 8.23 $mmol_c\ l^{-1}$ and increased to 12 $mmol_c\ l^{-1}$ after passing through the urban centers.

Figure 4 shows the spatial distribution of salinity based on the SAR_{adj}, considering the limits proposed in the classification diagram for the irrigation water (Richards, 1962). The Ayutla, Jalpan, Santa María, Verde and Bagres rivers do not have problems with sodicity since they are exorheic basins; as explained by Dregne (1976), Na^+ are the first of the salts to be leached. The Extorax River is classified as S2 because of the discharge from urban and industrial water. The northern portion of the Santa María-Verde River Hydrographic System is classified as S3 and S4. This is due to these basins being endorheic, where the hydrographic systems are not permanent, evaporation exceeds precipitation and salts accumulate; in addition to their marine history. All these factors contribute to the damage of soils and crops.

When water with a high SAR is used for irrigation, the soil should not be allowed to dry out since calcium and magnesium bicarbonates precipitate, followed by gypsum. The soil solution will thereby lose the alkaline earth cations, the SAR will increase and some of the Na^+ will have more opportunity to enter and become part of the exchange complex. To avoid this, irrigating should be done frequently and/or gypsum added (Halliwell, Barlow, & Nash, 2001; Surapanemi & Olsson, 2002).

Qualitative Magnesium Salinity in the Santa María-Verde River Hydrographic System

At some of the sampling stations in the hydrographic system studied, the predominant cation is Mg^{2+} because of evapo-

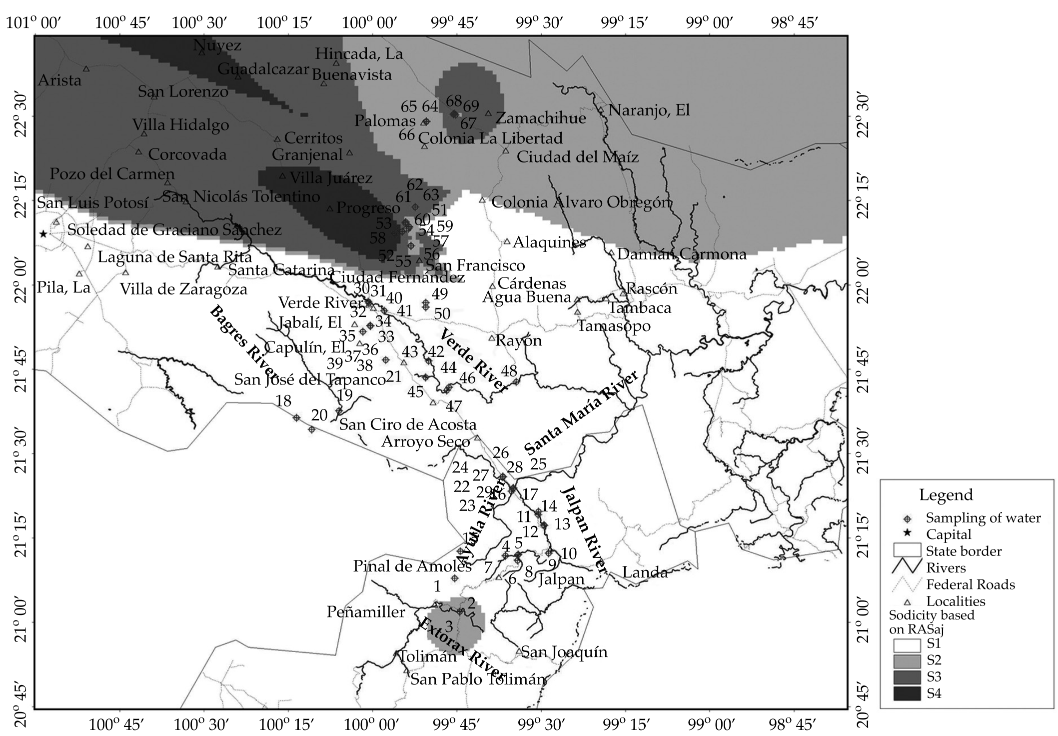


Figure 4. Spatial distribution of the qualitative salinity based on SARadj at the sampling stations in the hydrographic system.

rites from the sea containing dolomites and limestone. López (1993) explains that dolomite is a mineral whose carbonate position is twice that of magnesium and calcium [$CaMg(CO_3)_2$]. Its rock form is called dolostone, 25% of which is Mg^{2+}. Most of these rocks are created through the replacement of Ca^{2+} with Mg^{2+}, a complete replacement reduces the volume up to 12.3%, resulting in the formation of porous spaces. The predominant anion in the Santa María-Verde River Hydrographic System is So_4^{2-}, and $MgSO_4$ is a common salt, especially where coral reefs exist. Szabolcs (1994) reports that $MgSO_4$ is highly soluble, the main product in weathering and is a common component of seawater. It never accumulates in soil in a pure form and is found with other easily soluble salts, such as Na_2SO_4, NaCl and $MgCl_2$. The solubility of $MgSO_4$ depends little on temperature. The saturation concentration of this salt decreases as the concentration of Na_2SO_4 increases. A solution with a high Mg^{2+} concentration is harmful to plants. The increase in Mg^{2+} in the soil solution during the accumulation period increases the saturation of Mg^{2+} and the amount of Mg^{2+} absorbed by the minerals in the soil. Szabolcs and Darab (1973) consider the concentration of Mg^{2+} to be one of the most important qualitative criteria for irrigation water. It is calculated according to relation (3):

$$\frac{\left[Mg^{2+}\right]}{\left[Ca^{2+}\right]\left[Mg^{2+}\right]}100 \qquad (3)$$

A high adsorption of Mg^{2+} unfavorably affects the soil, which is damaged when the relation above exceeds 50. Figure 5 indicates the spatial distribution of the harmful effects from Mg^{2+} at the water sampling stations, where 30% of the points exceeded 50% of this relation. The Bagres, Caracol and Santa María rivers in the Eastern Sierra Madre, near San Luis de la Paz, present intense Cenozoic volcanic activity.

Evolution and Geochemical Weathering from Evaporation of Water from the Media Luna Spring Due to Farming

The Media Luna spring is the economic engine of the Río Verde municipality and all the agricultural fields in its southern portion. This region has fluvial and lacustrine sediments that fill the valley and compose a granular aquifer. Mountains and hills on the border of the Verde River valley are made of limestone, shale, and volcanic rocks. Ballin, Cardona and Cisneros (2004) describe the Media Luna spring as having a flow of 5 $m^3\ s^{-1}$, and it is used to irrigate approximately 5 000 ha. The primary crops are beans, oranges, corn, tomato, sugar cane, peanuts, alfalfa, zucchini and peppers.

Salinity tolerance is expressed as the ratio of the yield of a crop with a particular electrical conductivity to the yield with normal conditions (without salts). Using this approach, Mass and Hoffman (1977) generated a series of graphs to estimate the decrease in yield caused by salts. They found that the growth of vegetation decreases linearly with an increase in salinity over the salinity threshold (Ayers & Westcot, 1987). This threshold is defined as the salinity at which the potential yield is still 100%, expressed according to the conductivity of the saturation extract. According to this classification, crops can be divided into four groups: tolerant, moderately tolerant, moderately sensitive and sensitive to salinity. The crops in the study area which are sensitive to salinity include beans and oranges, while corn, tomato, cane sugar, peanuts, alfalfa, zucchini and peppers are moderately sensitive.

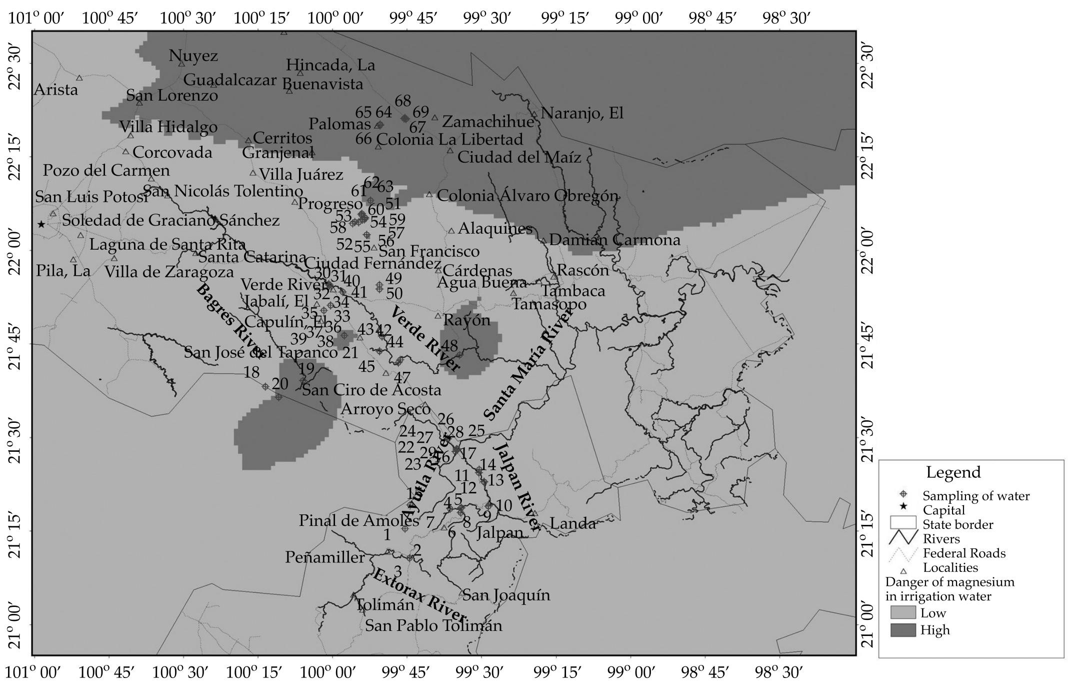


Figure 5. Spatial distribution of the salinity based on harm caused by Mg^{2+} at the sampling stations in the hydrographic system.

In the Verde River farming valleys, most of the irrigation is applied to the surface. Water does not drain easily and accumulates in agricultural fields in the form of wells and puddles because of its low topography and type of soil. This generates the precipitation and evaporation processes involved in the evolution of the salinity. What occurred in the field was studied in the laboratory with the irrigation water from the Media Luna springs to determine the geochemical evolution based on evaporation. The models by Hardie and Eugster (1970) and by Risacher and Fritz (2009) were used to meet this objective, which are based on the concept of alkalinity (Stumm & Morgan, 1970; Al-Droubi, Fristz, Gac, & Tardi, 1980). When water evaporates, the dissolved components become concentrated and a sequence of minerals is precipitated in order of increasing solubility. Because of its low solubility, the first to be deposited is calcite ($CaCo_3$). During its precipitation, the product of the ionic activity remains constant and equal to the product of the solubility of $CaCO_3$. Concentrations and activities vary when salinity is low. The product of the concentrations of Ca^{2+} and CO_3^{2-} remains roughly constant. Figure 6a presents the relationship among alkalinity, Ca^{2+} and the equilibrium of $CaCo_3$ in the Santa María-Verde River Hydrographic System. The saturation index shows that $CaCO_3$ will precipitate in the Verde River agriculture region; that is, Ca^{2+} will decrease. Following the precipitation of $CaCO_3$, silicates or $MgCO_3$ will precipitate— salts which are also not very soluble. In terms of alkalinity, the increase in the pH often causes silicates to form. The concentration of the CO_3^{2-} solution can become less than that of Ca^{2+}, changing the solution from an alkaline to a sulfate pathway. In the case of the pre-

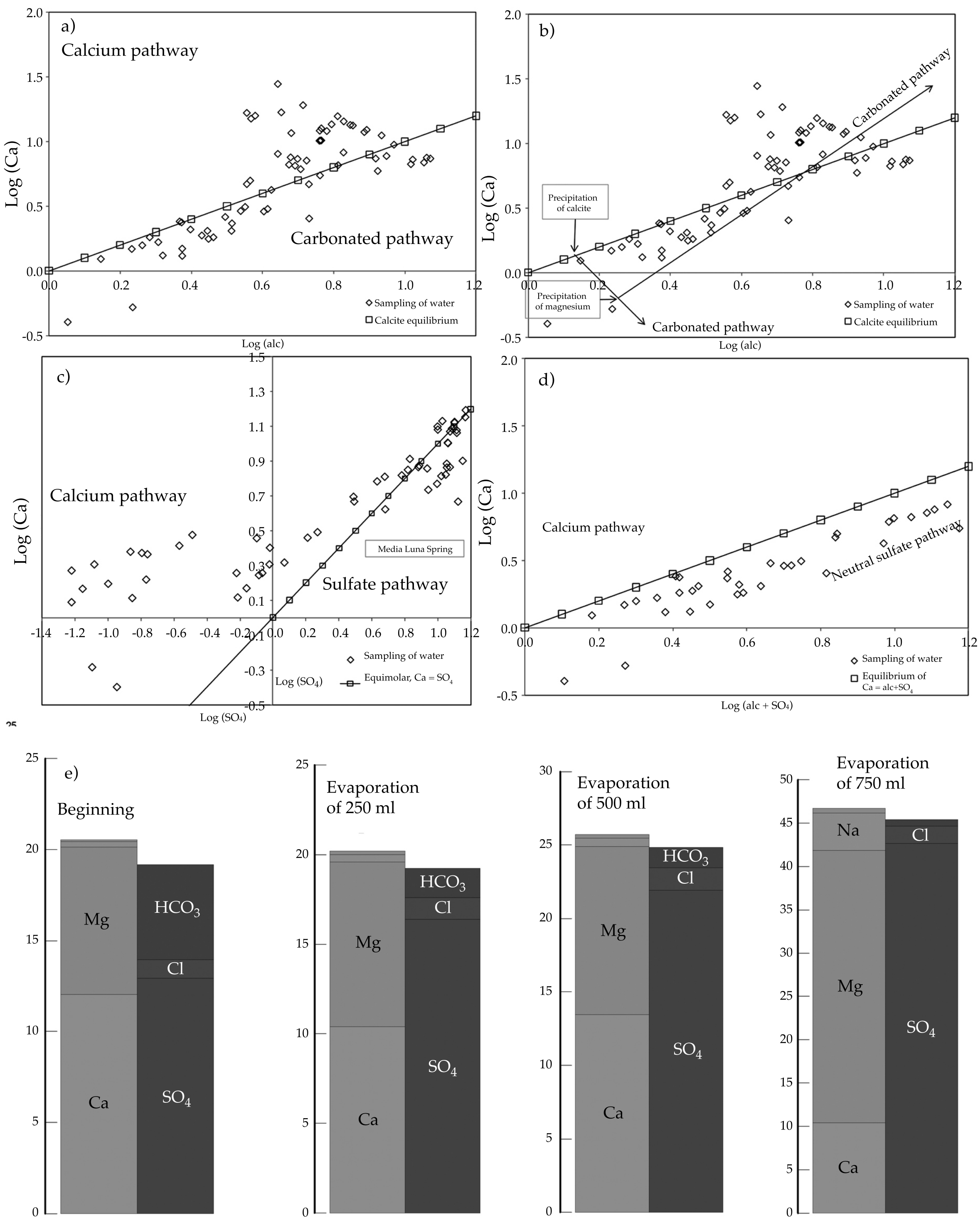


Figure 6. a) Relation between alkalinity and Ca^{2+}; b) evolutional change from carbonated to sulfate pathway; c) relation between Ca^{2+} and SO_4^{2-}; d) relation between Ca^{2+} and alc $+SO_4^{2-}$; e) balance of ions in the experiment with the Media Luna Spring.

cipitation of $MgCO_3$ (magnesite), the consumption of CO_3 by this mineral can also lead to the concentration of CO_3 becoming less than that of Ca^{2+}, thereby resulting in the solution following a sulfate pathway.

Figure 6b shows the change in evolution from a carbonate to a sulfate pathway from the effect of the precipitation of $CaCO_3$ in the Santa María-Verde River Hydrographic System. In addition, it can be observed that $MgCO_3$ is not going to precipitate. If the silicates and $MgCO_3$ precipitate, the evolutional pathway does not change. With a neutral pathway, as in the case of the Santa María-Verde River Hydrographic System, the next mineral to precipitate is gypsum ($CaSO_4.2H_2O$). The same mechanisms as those for calcite are also involved here. The product of activities remains constant and equal to the product of the solubility of gypsum. In low saline solutions, the activities vary, since the concentrations and the activity of the water is slightly lower than 1. In the first case, the product of the concentrations of Ca^{2+} and SO_4^{2-} remains constant. If there is more SO_4^{2-} when precipitation begins, then the solution will concentrate into SO_4^{2-} and become poor in Ca^{2+}.The result is sulfate brine of the general Na/SO_4-Cl type. Meanwhile, if there is more Ca^{2+} than SO_4^{2-} when gypsum begins to precipitate, the Ca^{2+} will concentrate until producing calcium brine of the Na-Ca/Cl type. This mechanism is shown in Figure 6c.

The Extorax, Ayutla, Jalpan, Santa María, Bagres, Calabazas hydrographic systems and wells 1 and 2 in La Soledad ranch have more Ca^{2+} than SO_4^{2-} and therefore follow the calcium pathway. When gypsum begins to precipitate, the solution contains more SO_4^{2-} than Ca^{2+} and follows the sulfate pathway. This occurs in the other stations, especially in the agricultural regions of Ciudad Fernández, Verde River and Ciudad del Maíz. The Valles-San Luis Platform has a direct influence in these regions. Figure 6d shows whether the water follows the calcium or sulfate pathway. Figure 6e shows the diagrams of the ion balance from the experiment with the Media Luna spring. According to the theory of the weathering and evolution of water from evaporation, the Santa María-Verde River Hydrographic System follows the neutral sulfate pathway. The experiment with the Media Luna spring confirmed that the magnesite will not precipitate in the Río Verde's agricultural fields, and the concentrations of Mg^{2+}, Na^+ and SO_4^{2-} will significantly increase due to evaporation.

The results of many experiments based on isosmotic solutions show that NaCl is less harmful than Na_2SO_4 to the growth of cereals (Steppuhn, Genuchten, & Grieve, 2005). Richards (1962) indicated that this is because SO_4^{2-} changes the optimal cationic balance in the plant, since it favors the absorption of Na^+ and decreases Ca^{2+}. Joshi and Naik (1980) found that the foliage area of sugar cane decreases with NaCl Na_2SO_4, $MgCl_2$ and $MgSO_4$ salts. Nevertheless, the largest reduction was due to Na_2SO_4, while $MgCl_2$ resulted in the lowest reduction. Therefore, Na^+ and SO_4^{2-} ions were the most toxic, while SO_4^{2-} caused the most harm.

Conclusions

According to the quantitative salinity, the water at the headwaters of the Bagres and Santa María rivers is classified as low salinity (C1). In the middle portion of the Ayutla, Jalpan and Santa María rivers, it is classified as moderately saline (C2). Before reaching the urban populations, the Extorax, Valles-San Luis Platform, Media Luna and Verde rivers are classified as high salinity (C3). After passing through the urban centers, these hydrographic systems are classified as very high salinity (C4).

According to the sodium adsorption ratio, the qualitative salinity indicated that the application of irrigation water did not pose any problems for the sodicity of the soils, except in the localities of Progreso, Palomas and Ciudad del Maíz, even though the Langelier Index projected that calcite will precipitate in all the rivers except the Bagres. According to the magnesium ratio, the qualitative salinity was most critical in the Santa María-Verde River Hydrographic System, affecting the soils and crops in the Verde River agricultural valleys after passing through the cities of Palomas and Ciudad del Maiz. The experiment in which the salts were re-concentrated corroborated the model based on alkalinity, determining that the waters were initially calcium sulfate (generating optimal conditions for crops) and became magnesium and sodium sulfate (causing unfavorable crop conditions). The waters in the Santa María-Verde River Hydrographic System were located in the region where there is more evaporation than precipitation. This would cause the concentration to increase and change the salinity of the waters and soils.

References

Al-Droubi, A., Fristz, B., Gac, J. Y., & Tardi, Y. (1980). Generalized Residual Alkalinity Concept. Application to Prediction of the Chemical Evolution of Natural Waters by Evaporation. *Am. J. Sci.*, *280*, 560-572.

APHA (1995). *Standard M. D. Methods for the Examination of Water and Waste Water*. 19th ed. Baltimore: American Public Health Association, Port City Press.

Ayers, R., & Westcot, D. (1987). *La calidad del agua y su uso en la agricultura* (176 pp.). Estudio FAO *Riego y Drenaje 29 Rev. 1*. Traducido al español por J. F. Alfaro de Water Quality and Use in Agriculture. Roma: FAO.

Ballín, J. R., Cardona, A., & Cisneros, R. (2004). *Evaluación del impacto agrícola sobre el agua subterránea de la zona de Río Verde, S.L.P.* (28 pp.). Folleto técnico. San Luis Potosí, México: Instituto de Investigaciones de Zonas Desérticas de la UASLP.

Carrera-Villacrés, D., Ortega-Escobar, H., Ramírez-García, J., Ramírez-Ayala, C., Trejo-López, C., & Becerril-Román, A. (abril-junio, 2011). Boro, fosfatos e índices de salinidad del sistema hidrográfico Zahuapan-Atoyac, México. *Tecnología y Ciencias del Agua*, *2*(2), 5-21.

Dregne, H. (1976). *Soils of Arid Regions* (238 pp.). Amsterdam: Elsevier Scientific Publishing Company.

Figueruelo, J., & Dávila, M. (2004). *Química física del ambiente y de los procesos medioambientales* (592 pp.). Barcelona: Reverté.

Gibbs, R. J. (1970). Mechanisms Controlling Word Water Chemistry. *Science*, *170*, 1088-1090.

Grande, R., Hernández, E., Aguilera, N., & Boulaine, J. (1967). Morfología y génesis de los suelos yesiferos de Matehuala, S.L.P. *Agrociencia*, 1(2), 130-146.

Halliwell, D., Barlow, K., & Nash, D. (2001). A Review of the Effects of Wastewater Sodium on Soil Physical Properties and their Implications for Irrigation Systems. *Aust. J. Soil Res.*, *39*, 1259-1267.

Hardie, L., & Eugster, H. (1970). The Evolution of Closed-basin Brines. Mineral. *Soc. Amer. Spec. Paper*, *3*, 273-290.

Heidarpour, M., Mostafazadeh, B., Abedi, J., & Malekian, R. (2007). The Effects of Treated Wastewater on Soil Chemical Properties Using Subsurface and Surface Irrigation Methods. *Agricultural Water Management*, *90*, 87-94.

Joshi, G. V., & Naik, G. R. (1980). Response of Sugarcane to Different Types of Salt Stress. *Plant and Soil*, *56*, 255-263.

López, E. (1993). *Geología general y de México* (288 pp.). México, DF: Editorial Trillas.

Maas, E. V., & Hoffman, G. J. (1977). Crop Salt Tolerance: Revaluation of Existing Data. *Journal of the Irrigation and Drainage Division of the American Society Engineer*, *103*, 115-134.

Ortega, S. F., & Orellana, G. R. (2007). El riego con aguas de mala calidad en la agricultura urbana. Aspectos a considerar. I. Aguas salinas o alcalinas. *Revista Ciencias Técnicas Agropecuarias*, *16*(1), 41-44.

Richards, L. (Ed.) (1962). *Diagnóstico y rehabilitación de suelos salinos y sódicos* (172 pp.). México, DF: Editorial Cultura.

Risacher, F., & Fritz, B. (2009). Origin of Salts and Brine Evolution of Bolivian and Chilean Salars. *Aquat Geochem*, *15*, 123-157.

Shani, U., & Dudley, L. (2001). Field Studies of Crop Response to Water and Salt Stress. *Soil Science Society American Journal*, *65*, 1522-1528.

Steppuhn, H., Genuchten, M., & Grieve, C. (2005). Root-Zone Salinity: I. Selecting a Product-Yield Index and Response Function for Crop Tolerance. *Crop Science*, *45*(1), 209-220.

Stumm, W., & Morgan, J. J. (1970). *Aquatic Chemistry an Introduction Emphasizing Chemical Equilibria in Natural Waters* (583 pp.). New York: Wiley-Interscience.

Surapanemi, A., & Olsson, K. A. (2002). Sodification under Conjunctive Water Use in the Shepparton Irrigation Region of Northern Victoria: A Review. *Australia Journal Experimental Agricultural*, *42*, 24-263.

Szabolcs, I. (1994). *Salt-Affected Soils* (274 pp.). Boca Raton, USA: CRC Press, Inc.

Szabolcs, I., & Darab, K. (1973). An International Source Book , Chapter 7. In *Irrigation/Drainage and Salinity*. Rome: FAO/UNESCO.

Webster, R., & Oliver, M. (2007). *Geostatistic for Environmental Scientist* (334 pp.) (2nd edition). Barcelona: Ediciones John Wiley and Sons.

Wetzel, R. (1981). *Limnología* (666 pp.). Barcelona: Ediciones Omega.

Institutional Address of the Authors

Dr. David Vinicio Carrera-Villacrés

Universidad de las Fuerzas Armadas-ESPE
Av. Gral. Rumiñahui s/n
Departamento de Ciencias de la Tierra y la Construcción
Sangolquí, Ecuador
Teléfono: +59 (3) 3989 400 extensión 1701
dvcarrera@espe.edu.ec
david_carrera@yahoo.com

Programa de Hidrociencias
Colegio de Postgraduados
km 36.5 carretera México-Texcoco
56230 Texcoco, Estado de México, México
villacres@colpos.mx

M.C. Tania Crisanto-Perrazo

Universidad de las Fuerzas Armadas-ESPE
Av. Gral. Rumiñahui s/n
Departamento de Ciencias de la Tierra y la Construcción
Sangolquí, Ecuador
Teléfono: +59 (3) 3989 400 extensión 1701
ttcrisanto@espe.edu.ec

Dr. Héctor Ortega-Escobar
M.C. Jazmín Ramírez-García
Dr. Carlos Ramírez-Ayala

Programa de Hidrociencias
Colegio de Postgraduados
km 36.5 carretera México-Texcoco
56230 Texcoco, Estado de México, México
Teléfono: +52 (15) 8046 800
manueloe@colpos.mx
escosia90@hotmail.com
cara@colpos.mx
Dr. David Espinosa-Victoria

Programa de Edafología
Colegio de Postgraduados
km 36.5 carretera México-Texcoco
56230 Texcoco, Estado de México, México
Teléfono: +52 (15) 8046 800
despinosstar@gmail.com

Dr. Víctor Ruiz-Vera

Colegio de Postgraduados
Campus San Luis Potosí
Agustín de Iturbide Nº 73
78600 Salinas de Hidalgo, Salinas, S.L.P., México
Teléfono: +52 (496) 9630 240
vmanuel@colpos.mx

Dra. Martha Velázquez-Machuca

Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional del Instituto Politécnico Nacional, Unidad Michoacán (CIIDIR-IPN-UMICHP)
Justo Sierra No. 28
9510 Jiquilpan, Michoacán, México
Télefono: +52 (353) 5330 083 extensión 82955
mvelazquezm@ipn.mx

Dr. Edgar Sánchez-Bernal

Universidad del Mar, Ciudad Universitaria
Puerto Ángel, Distrito de San Pedro Pochutla
70902 Oaxaca, México
Teléfono: +52 (15) 8046 800
edgarivansb@zicatela.umar.mx


Pátzcuaro, Michoacán, México.

Photo: Roberto Menéndez.

Design Optimization for Stabilization Ponds Using Non-Linear Programming

• Facundo Cortés-Martínez* • Alejandro Treviño-Cansino •
Universidad Juárez del Estado de Durango, México
*Corresponding Author

• María Aracelia Alcorta-García•
Universidad Autónoma de Nuevo León, México

• Agustín Sáenz-López •
Universidad Juárez del Estado de Durango, México

• José Luis González-Barrios •
Instituto Nacional de Investigaciones Forestales Agrícolas y Pecuarias

Abstract

Cortés-Martínez, F., Treviño-Cansino, A., Alcorta-García, M. A., Sáenz-López, A., & González-Barrios, J. L. (March-April, 2015). Design Optimization for Stabilization Ponds Using Non-Linear Programming. *Water Technology and Sciences* (in Spanish), 6(2), 85-100.

The article herein presents a mathematical optimization model to design lagoon systems containing two ponds: facultative and maturation. The objective function of the model was the cost. Four decision variables were considered: hydraulic retention time and number of screens in the facultative pond; in the maturation pond, also number of screens and retention time. Fecal coliform and organic matter were considered as restrictions. The resulting model was non-linear since the relations among the variables were not proportional. A pond system was designed using the traditional methodology adopted by the National Water Commission for Mexico. The mathematical model was then applied. A comparison of the results indicated a reduction in retention time of 14.16% and a decrease in cost of 12.04%. This finding is important given that the primary disadvantage of these systems is the need for land. In addition, a sensitivity analysis of the objective function and the restrictions is included. This analysis is sensitive to changes in the parameters. Both studies fully meet the quality standards stipulated by norms for treated water discharged into receptor bodies. Additional optimization studies that include different configurations are recommended.

Keywords: Pond systems, fecal coliform, retention time, organic matter, construction cost, mathematical model optimization.

Resumen

Cortés-Martínez, F., Treviño-Cansino, A., Alcorta-García, M. A., Sáenz-López, A., & González-Barrios, J. L. (marzo-abril, 2015). Optimización en el diseño de lagunas de estabilización con programación no lineal. Tecnología y Ciencias del Agua, *6(2), 85-100.*

El estudio presenta un modelo matemático de optimización para el diseño de sistemas lagunares integrado por dos lagunas: facultativa y de maduración. El modelo tiene como función objetivo el costo y considera cuatro variables de decisión: tiempo de retención hidráulico y número de mamparas en la laguna facultativa; en la laguna de maduración, también número de mamparas y tiempo de retención. Se consideran como restricciones los coliformes fecales y la materia orgánica. Dicho modelo resultó ser no lineal, ya que las relaciones entre las variables no son proporcionales. Se diseñó un sistema lagunar utilizando la metodología tradicional adoptada por la Comisión Nacional del Agua para México, luego se aplicó el modelo matemático. Se lleva a cabo una comparación de los resultados, los cuales indican una reducción del tiempo de retención de 14.16% y una disminución del costo de 12.04%. El resultado anterior es importante, ya que la principal desventaja de estos sistemas es el requerimiento de terreno. Se incluye, además, el análisis de sensibilidad de la función objetivo y las restricciones consideradas. El citado análisis es sensible a la variación de los parámetros. Ambos estudios cumplen perfectamente con las condiciones de calidad del agua tratada que indica la normatividad para el vertido a los cuerpos receptores. Se recomienda llevar a cabo otros estudios de optimización, considerando diferentes configuraciones.

***Palabras clave**: sistemas lagunares, coliformes fecales, tiempo de retención, materia orgánica, costo de construcción, modelo matemático de optimización.*

Received: 25/01/2013
Accepted: 07/05/2014

Introduction

Stabilization ponds have three primary purposes— the removal of a) fecal coliform, b) organic matter, also called biochemical oxygen demand (BOD) and c) nutrients (nitrogen and phosphorus) (CNA and IMTA, 2007a). According to Senzia, Mayo, Mbwette, Katima and Jorgensen (2002), Agunwamba, Ochonogar and Ukpong (2003), Mara (2004), Abbas, Nasr and Seif (2006), Hamzeh and Ponce (2007), and Naddafi *et al*. (2009), stabilization ponds are recommended in countries with tropical climates, since the environmental conditions increase the efficiency of removing pollutants.

Pond systems can be classified as anaerobic, facultative and maturation, according to the presence of oxygen (Metcalf & Eddy, Inc., 1991).

- *Anaerobic*. The bacteria present do not require dissolved oxygen to decompose organic matter. The process described is also known as anaerobic digestion (Rolim, 2000).
- *Facultative*. The mechanism occurs in the upper stratum, that is, a commensalism between anaerobic bacteria and algae. The organic matter is decomposed by heterotrophic bacteria, generating inorganic compounds. The oxygen needed for symbiosis is supplied primarily by photosynthesis.
- *Maturation*. Receives the effluent from facultative ponds, which is used to remove pathogens from the effluent through polishing, depending on the quality required. Only one zone exists, which is aerobic (CNA and IMTA, 2007b).

Baffles

Shilton and Mara (2005), Abbas *et al*. (2006), Cortés, Treviño, Luévanos, Luévanos and Uranga (2014a), and Cortés *et al*. (2014b) recommend the use of baffles in pond systems since they significantly improve hydraulic conditions and contribute to reducing dead areas.

Laboratory studies that consider the use of baffles have been performed to increase hydraulic efficiency and remove pollutants. Killani and Ogunrombi (1984); Pedahzur, Nasser, Dor, Fattal and Shuval (1993); Muttamara and Puetpaiboon (1997); Zanotelli, Medri, Belli-Filho, Perdomo and Costa (2002); Shilton and Harrison (2003a); Sperling, Chernicharo, Soares and Zerbini (2003); Shilton and Mara (2005), and Abbas *et al*. (2006) reported that hydraulic efficiency and treatment of wastewater are improved with baffles along 70% of the length. Later, Banda (2007), and Winfrey, Stronsnider, Nairn and S trevett (2010) concluded that better results are obtained using a larger number of baffles.

Mathematical Models

Killani and Ogunrombi (1984) recommended studies of operations of stabilization ponds in order to optimize financial resources, that is, to determine the optimal cost of the system. Nelder and Mean (1965); Fonseca and Fleming (1993, 1995); Oke and Otun (2001); Bracho, Lloyd and Aldana (2006); Winfrey *et al.* (2010), and Olukanni and Ducoste (2011) applied linear programming to the design of pond systems, concluding that optimization could improve the design by increasing the efficiency of treatment and lowering costs. Lastly, Sah, Rousseau and Hooijmans (2012) performed comparative studies of existing models and concluded the need for an integral optimization model that considers all the variables involved in treating water with stabilization ponds.

According to the literature review, in Mexico there are few mathematical optimization models for stabilization ponds. Therefore, the following objectives were proposed: a) perform a mathematical analysis to obtain an optimization model for two ponds; b) design a pond system using the traditional methodology, including costs; c) apply the mathematical optimization model using the *Solver* Excel system; and d) compare the results between the two analyses and define the financial advantages of both studies.

Non-linear Programming

The Generalized Reduced Gradient (GRG) is an algorithm used by the *Solver* system in Excel. It begins with a known solution, that is, one that has been calculated previously. The objective is to find a new improved proposal. The algorithm reviews the feasible region of the known solution and determines a new solution until the result cannot be further optimized. The tool acts on a group of cells called decision variables, which are included in the formula of the objective function and the restrictions. The GRG method can be used with programming problems having characteristics such as: linear or non-linear objective functions, equality or inequality restrictions and a feasible or unfeasible starting point for applying the GRG (Muramatsu, 2011).

Sensitivity Analysis

According to Anderson, Sweeney and Williams (2004), a tornado diagram is recommended to determine the sensitivity of the project. This analysis consists of modifying the ranges of values considered by the study, a condition that provides information about how the improved solution is affected. The tornado diagram presents the information using bars, where the widest bar indicates the parameter that is most sensitive to change.

The present study is a continuation of the mathematical optimization model published by Olukanni and Ducoste (2011). The present article contributes to this method by determining a mathematical model for two ponds— facultative and maturation. Chemical oxygen demand and the number of fecal coliform in the effluent are considered restrictions.

The mathematical model published by Olukanni and Ducoste (2011) includes two considerations: 1) the use of a multi-objective model, that is, maximization of pollutant removal and minimization of cost; and 2) the concentration of fecal coliform in the effluent , the number of baffles and the area as restrictions. Meanwhile, the present study includes as restrictions both fecal coliforms and organic matter, as well as the number of baffles and retention time. Another important difference is that the present study uses a single model for two ponds, while Olukanni studied only one pond.

As has been mentioned, the use of one mathematical model for two ponds, with four decision variables, is the contribution made by the present work to the studies that have already been published by the authors cited (Cortés, Treviño, Luévanos & Luévanos, 2013; Cortés *et al*., 2014a; Cortés *et al*., 2014b). Previous publications have defined the model for only one pond with two control variables. It is important to note that the present mathematical model is unique, that is, according to the literature review it has not been previously published.

The document is organized as follows: first the nomenclature for the design of a facultative and maturation pond is described, as well as the traditional design methodology. The second part presents the analysis performed to define the preliminary objective function, mathematical relations, decision variables, and the restrictions considered. In the third section, a design example is developed with the traditional methodology and the proposed mathematical model is then applied. This section also includes a comparative table containing the results and a sensitivity analysis of the model. The fourth part presents the conclusions.

Materials and Methods

The design of the pond system was based on the methodology established for Mexico by the National Water Commission (CNA, Spanish acronym) and the Mexican Institute of Water Technology (IMTA, Spanish acronym). The manual consulted was the *National Water Commission's Technological Packages to treat excrement and wastewater in rural communities* (CNA and IMTA, 2007a).

Nomenclature for the Design of Stabilization Ponds

OL = organic load.

Q_i = flow in the pond influent (m^3/day).

BOD_i = biochemical oxygen demand in the pond influent, mg/l.

1 000 = conversion factor.

λv = surface organic load (kg/ha-day).

T = minimum mean monthly air temperature (°C).

L_i = $cBOD_5$ concentration in the pond influent (mg/l).

Af = area of the facultative pond (m^2).

Qmed = influent flow (m^3/day).

Z = depth (m).

V = volume (m^3).

O_F = mean hydraulic retention time, facultative pond (days).

O_M = mean hydraulic retention time, maturation pond (days).

X = ratio of length to with.

W_{avg} = average width (m).

L_{avg} = average length (m).

W_{up} = upper width (m).

L_{up} = upper length (m).

A_{up} = upper area (m^2).

Qe = flow in the pond effluent (m^3/day).

e = evaporation (mm/day).

d = dimensionless dispersion factor.

K_b = bacterial reduction coefficient (d^{-1}).

a = dimensionless constant.

Ne = fecal coliform corrected for evaporation in the pond effluent (NMP/100 ml).

Ni = fecal coliform in the pond influent (NMP/100 ml).

Nf/No = number of fecal coliform in the effluent ((NMP/100 ml)..

Kf = BOD_5 decay constant (day^{-1}).

BODef = BOD_5 concentration in the pond effluent (mg/l).

BODe = BOD_5 concentration in the pond effluent corrected for evaporation (mg/l).

N_{bafF} = number of baffles in the facultative pond.

N_{bafM} = number of baffles in the maturation pond.

A_M = area of the maturation pond (m^2).

Design of the Facultative Pond (Disperse flow. Yanez Method)

a) Organic load:

$$OL = Q_i(COD_i)/1\,000 \qquad (1)$$

b) Design surface load:

$$\lambda s = 250(1.085)^{T-20} \qquad (2)$$

c) Area of the facultative pond:

$$Af = 10 L_i Qmed/\lambda s \qquad (3)$$

d) Volume of the pond:

$$V = (Af)(Z) \quad (4)$$

e) Mean hydraulic retention time:

$$O_F = V / Q_i \quad (5)$$

f) Dimensioning. Length:width ratio $X = 3$:

$$V_{avg} = \sqrt{\frac{Af}{X}} \quad (6)$$

$$L_{avg} = \frac{Af}{B_{avg}} \quad (7)$$

g) For length and width:

$$W_{up} = W_{avg} + (Z)(\text{Slope}) \quad (8)$$

$$L_{up} = L_{avg} + (Z)(\text{Slope}) \quad (9)$$

h) Calculation of surface area:

$$A_{up} = (W_{up})(L_{up}) \quad (10)$$

i) Flow of the effluent:

$$Qe = Q_i - 0.001 A_{up} e \quad (11)$$

j) Removal of fecal coliform: considering baffles with lengths 0.70 of the length of the pond, then:

$$X = (L_{avg})\ (0.70)\ (\text{no. of baffles} + 1) / (W_{avg}) / (\text{no. of baffles} + 1) \quad (12)$$

$$d = \frac{X}{-0.26118 + 0.25392(X) + 1.0136(X)^2} \quad (13)$$

k) Bacterial reduction coefficient:

$$K_b = 0.841(1.075)^{T-20} \quad (14)$$

l) Constant "a". Determined with the following formula:

$$a = \sqrt{1 + 4(K_b O_F d)} \quad (15)$$

m) Fecal coliform in the effluent of the facultative pond:

$$\frac{Nf}{No} = \frac{4a \exp^{(1-a)/2d}}{(1+a)^2} Ni \quad (16)$$

n) Fecal coliform corrected for evaporation:

$$Ne = (Ne)(Q_i) / Qe \quad (17)$$

o) BOD concentration in the effluent of the pond:

$$Kf = \frac{Kf_{35}}{(1.085)^{35-T}} \quad (18)$$

p) Concentration of the biochemical oxygen demand in the effluent of the pond:

$$\text{BODef} = \frac{\text{BODi}}{Kf O_F + 1} \quad (19)$$

q) BOD removal efficiency:

$$\% = \frac{(\text{BOD}_i - \text{BODe})}{\text{BOD}_i} x 100 \quad (20)$$

r) BOD corrected for evaporation:

$$\text{BODe} = (\text{BODi})(Q_i) / Qe \quad (21)$$

Maturation pond (disperse flow method)

1. Hydraulic retention time (O). This is analyzed in batches, that is, a hydraulic retention time is proposed and the concentration of fecal coliform in the effluent is evaluated. These should be equal to or less than 1 000 NMP/100 ml.
2. Volume of the pond:

$$V = (Q_i)(O_M) \tag{22}$$

3. Area of the pond:

$$A_M = \frac{V}{Z} \tag{23}$$

For the rest of the design, the equations from f) to r) are applied, as indicated by the methodology used for the facultative pond.

Preliminary Objective Function

The following costs were included to determine the objective function: land ($750.00/meter squared); index cost of the embankment, $1 200.00/ linear meter; baffles, $500.00/ linear meter.

According to Cortés *et al*. (2014a; 2014b), the length of the baffle is considered to be 70% of the length of the pond: $(0.7)N_{baf}L_{up}$. The area of the facultative pond is defined by the upper width plus the length of each of the sides, as shown in Figure 1. The length is (W_{up} + 12) (L_{up} 12). The perimeter is: 2 (W_{up} 3) + 2 (L_{up} 3). The same criteria is followed to determine the maturation length, based on the information indicated in Figure 2. With the above data, expression (24) was determined:

$$\text{Total cost } = 750\Big[\big(W_{upF}+12\big)\big(L_{upF}+12\big) + \big(L_{upM}+10\big)\big(L_{upM}+3\big)\Big] + 1\,200\Big[2\big(W_{upF}+3\big)+2\big(L_{upF}+3\big)+\big(B_{upM}+3\big) + 2\big(L_{upM}+3\big)\Big] + 500(0.7)\big[N_{baf\,F}L_{upF}+N_{baf\,M}L_{upM}\big] \tag{24}$$

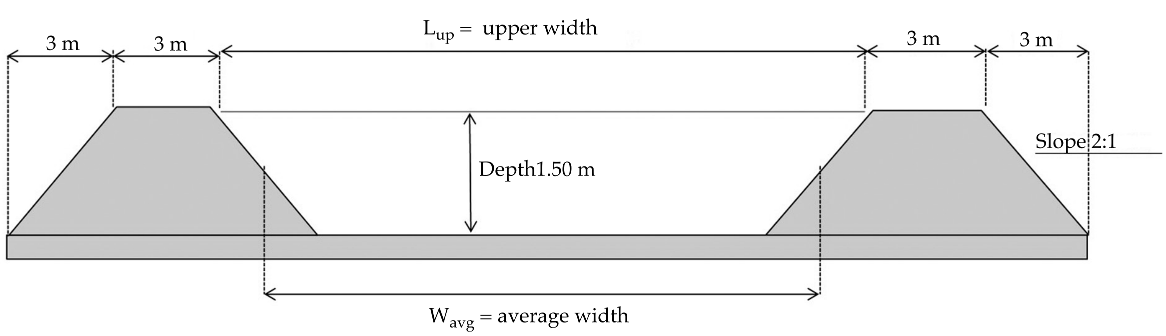


Figure 1: Cross-section of a facultative lagoon.

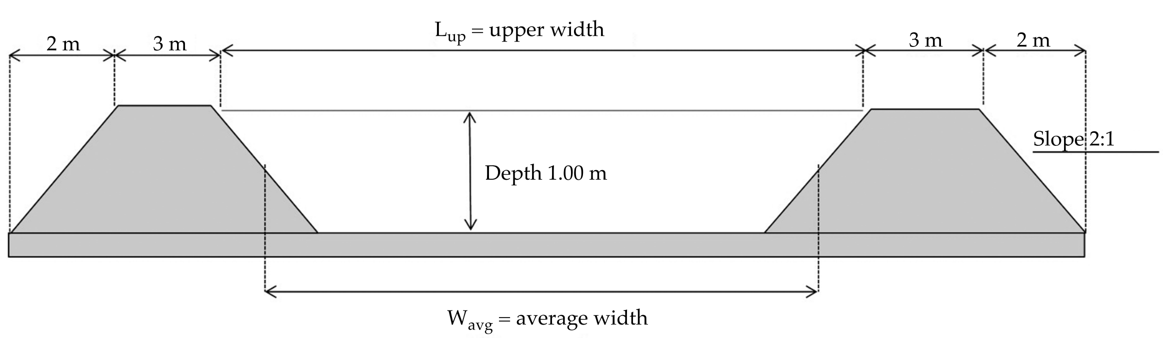


Figure 2. Cross-section of a maturation lagoon.

Where $W_{upF} = W_{avgF} + 3$. According to CNA and IMTA (2007a; 2007b), this expression refers to the upper width of the facultative pond plus three meters (according to the ratio 2:1) considered on the embankments (Figure 1). The following equation determines the length:width ratio:

$$L_{upF} = 3W_{avg\,F} + 3$$

The operations performed to calculate the average width of the facultative pond are: solve for the volume in equation (5) with the traditional methodology; b) then substitute the volume in expression (4); and c) lastly the expression for the width of the pond is determined by substituting in equation (6):

$$W_{Avg\,F} = \sqrt{\frac{O_F * Q_F}{4.5}}$$

The slope ratio of the embankment is used to calculate the upper width of the pond, thus defining expression (25):

$$W_{upF} = \sqrt{\frac{O_F * Q_F}{4.5}} + 3 \qquad (25)$$

Similarly, for the upper length of the facultative pond, expression (26) is determined (Cortés *et al*., 2014a, 2014b):

$$L_{upF} = 3\sqrt{\frac{O_F * Q_F}{4.5}} + 3 = \sqrt{2O_F * Q_F} + 3 \qquad (26)$$

For the maturation pond, with a depth of 1.0 meter, the following is determined:

$$W_{upM} = W_{upF} - 1$$

Substituting expression (25) in $W_{upM} = W_{upF}$ -1, we have:

$$W_{upM} = \sqrt{\frac{O_F * Q_F}{4.5}} + 2 \qquad (27)$$

The length of the maturation pond is calculated with equation (7) in the methodology, then following the same criteria for the surface width of the maturation pond, we have:

$$L_{upM} = \frac{\text{Area}_{avg}}{W_{avg\,M}} + 2$$

For the area, equation (22) is substituted in expression (23). As mentioned a depth of 1.0 meters is considered for the maturation pond. The average width is obtained by subtracting the depth from ratio of the embankment slope to the surface width. Finally, the expression to calculate the upper length is obtained:

$$L_{upM} = \frac{O_M * Q_M}{\sqrt{\frac{O_F * Q_F}{4.5}}} + 2 \qquad (28)$$

The objective function (29) is determined by substituting equations (25), (26), (27) and (28) in equation(24):

$$\begin{aligned} \text{Total cost} = {} & 750\Bigg[\left(\sqrt{\frac{O_F*Q_F}{4.5}} + 15\right)\left(\sqrt{2O_F * Q_F} + 15\right) \\ & + \left(\sqrt{\frac{O_F*Q_F}{4.5}} + 12\right)\left(\frac{O_M * Q_M}{\sqrt{\frac{O_F*Q_F}{4.5}}} + 5\right)\Bigg] \\ & + 1\,200\Bigg[2\left(\sqrt{\frac{O_F*Q_F}{4.5}} + 6\right) + 2\left(\sqrt{2O_F * Q_F} + 6\right) \\ & + \left(\sqrt{\frac{O_F*Q_F}{4.5}} + 5\right) + 2\left(\frac{O_M * Q_M}{\sqrt{\frac{O_F*Q_F}{4.5}}} + 5\right)\Bigg] \\ & + 500(0.7)\Bigg[N_{baf\,F}\left(\sqrt{2O_F * Q_F} + 3\right) \\ & + N_{baf\,M}\left(\frac{O_M * Q_M}{\sqrt{\frac{O_F*Q_F}{4.5}}} + 2\right)\Bigg] \end{aligned} \qquad (29)$$

As seen in expression (29), given the mathematical relations used to determine the objective function the resulting mathematical model is non-linear.

The decision variables considered are O_F, O_M, N_{bafF}, N_{bafM}.

The hydraulic retention time in both ponds directly influences their dimensions. The number of baffles improves the efficiency of the treatment of wastewater (Winfrey *et al.*, 2010).

Restrictions:

$$1 \le O_F \le 30$$

$$d \ge 0$$

$$1 \le O_M \le 10$$

$$0 \le \text{BODe} \le 75$$

$$\text{Ne} = 1\,000$$

$$0 \le N_{\text{baf}F} \le 4$$

$$0 \le N_{\text{baf}M} \le 4$$

$$N_{\text{baf}F}, N_{\text{baf}M} = \text{whole numbers}$$

$$N_{\text{baf}F}, O_F \ge 0$$

A stabilization pond treatment plant was designed for a town located on common lands. The community in question is located in the municipality of Gómez Palacio, Durango, Mexico. Data: Number of inhabitants during the project period = 1 500; supply = 154 l/inhab/day (CNA and IMTA, 2007a); design flow = 231 m^3/day; average temperature during the coldest month = 11.8°C (CNA and IMTA, 2007b); concentration of organic matter (BOD) in the influent = 220 mg/l; fecal coliforms 1.0 x 10^7 NMP/100 ml. These values are considered for domestic wastewater (Metcalf & Eddy, Inc., 1991).

Evaporation is 5 mm/day. The length:width ratio considered for the facultative pond is 3. The width of the maturation pond is considered to be the same as that of the facultative pond. The quality of the treated wastewater was determined according to Official Mexican Norm NOM-001-ECOL-96 (DOF, 1996).

Results and Discussion

Table 1 shows the results from the design of the pond system using the traditional method. Figure 3 shows the dimensions determined. With 2 and 4 baffles, the qual-

Table 1. Results form the design of the lagoon system, traditional method.

Data				Facultative lagoon		Maturation lagoon	
Qi	Ni	BODi	*T*	O_F	N_{bafF}	O_M	N_{bafM}
231	10 000 000	220	11.8	25.77	2	1.88	4

Results with the facultative lagoon									
X	*d*	*kb*	*a*	W_{up}	L_{up}	Qe	Ne	BODe	Area
18.9	0.0516	0.4648	1.8628	39.37	112.11	208.93	2 335	43	4 414.03

Results with the facultative lagoon									
X	*d*	*kb*	*a*	W_{up}	L_{up}	Qe	Ne	BODe	Area
58.94	0.0167	0.4648	1.0287	38.37	12.80	206.47	998.09	32	491.13

Total area	Cost, facultative lagoon	Cost, maturation lagoon	Total cost
4 905.16	$5 238 328.77	$678 661.09	$5 916 989.86

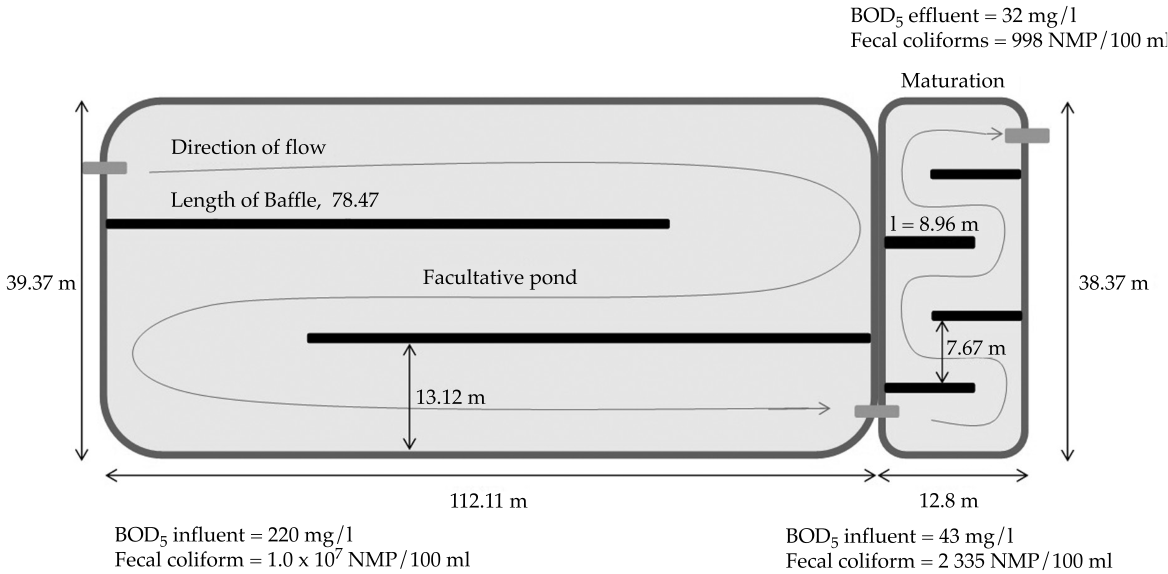


Figure 3. Dimensions of the lagoon system with the traditional method. Layout of the facultative lagoon with two baffles and the maturation lagoon with four.

ity complies with that indicated by the norm.

Application of the Mathematical Optimization Model

Table 2 indicates that the system found a solution in which all the restrictions and optimization conditions were satisfied. The first section of Table 2 shows the comparative costs. The result was 12.04% lower. The section presenting the decision variables shows that the system reduced the hydraulic retention time from 25.77 to 22.12 days, with a difference of 3.65 days, representing a reduction of 14.16%. According to CNA and IMTA (2007a; 2007b), the hydraulic retention time directly affects the size of the pond and thus the need for land. The results of the present study coincide with those reported by CNA and IMTA (2007a; 2007b). Another important change was the determination of four baffles for the facultative pond instead of the two originally proposed.

According to Killani and Ogunrombi (1984); Muttamara and Puetpaiboon (1996, 1997); Rolim (2000), Sperling, Chernicharo, Soares and Zerbini (2002); Shilton and Harrison (2003a); Shilton and Mara (2005); Oakley (2005); Abbas *et al.* (2006), and Cortés *et al*. (2013), this condition favors piston flow in the pond and therefore increases the efficiency of the removal of pollutants. The results of the present study agree with those found by the authors cited.

Tables 1 and 3 present the areas defined for the facultative pond for each one of the methods. The dimensions with the mathematical model are smaller. A difference of 594 meters squared exists (13.45%). Even though the area is smaller than that of the traditional design, the efficiency removal for fecal coliform was higher with the optimization model. As mentioned previously, this result is due to the use of four baffles instead of the two originally proposed. Olukanni and Ducoste (2011) conclude that the optimization of the design of pond systems can reduce the cost, conditioned

Cuadro 2. Informe de resultados de optimización y comparativo del diseño del sistema lagunar.

Microsoft Excel 12.0 Answer Report
Worksheet: [Artículo 1 solver.xls] DISEÑO facultativa Maduración
Report Created: 22/01/2013 16:29:42
Result: Solver found a solution. All constraints and optimality conditions are satisfied
Engine: Standard LSGRG Nonlinear
Solution Time: 05 seconds
Iterations: 6
Subproblems: 17
Incumbent Solutions: 3

Objective Cell (Min)

Cell	Name	Original Value	Final Value
J20	Costo total	5 916 989.864	5 204 275.071

Decision Variable Cells

Cell	Name	Original Value	Final Value	Type
G6	O_F	25.77	22.12	Normal
H6	N_{bafF}	2.00	4.00	Normal
I6	O_M	1.88	1.00	Normal
J6	N_{bafM}	4.00	2.00	Normal

Constraints

Cell	Name	Cell Value	Formula	Status	Slack
H20	Costa of facultative lagoon	$4 738 058.85	H20 >= 0	Not Binding	4 738 058.846
I20	Costa of maturation lagoon	$466 216.23	I20 >= 0	Not Binding	466 216.2251
J16	BODe	41	J16 <= 75	Not Binding	34.08882517
J16	BODe	41	J16 >= 0	Not Binding	40.91117483
I16	NF/No	1 000.00	I16 = 1 000	Binding	0
C16	*d*	0.0290	C16 >= 0	Not Binding	0.029014794
H6	N_{bafF}	4.00	H6 >= 1	Not Binding	3
I6	O_M	1.00	I6 <= 10	Not Binding	9
J6	N_{bafM}	2.00	J6 >= 1	Binding	0
J6	N_{bafM}	2.00	J6 <= 4	Not Binding	2
I6	O_M	1.00	I6 >= 1	Binding	0
G6	O_F	22.12	G6 >= 1	Not Binding	21.12037699
H6	N_{bafF}	4.00	H6 <= 4	Binding	0
G6	O_F	22.12	G6 <= 30	Not Binding	7.879623014

on including the adequate restrictions and considering quality norms related to treated effluents from these systems. As observed, the present study is consistent with reports by these authors.

With regard to the BOD_5, the two cases studied comply with Mexican norm NOM-001- ECOL-96 (DOF, 1996) in terms of the concentration of pollutants in the effluent of the facultative pond— 43 with

Table 3. Results from the optimization of the design of hte lagoon system with the Risk Solver Platform.

Data				Facultative lagoon		Maturation lagoon	
Qi	Ni	BODi	*T*	O_F	N_{bafF}	O_M	N_{bafM}
231	10 000 000	220	11.8	22.12	4	1.00	2

Results with the facultative lagoon									
X	*d*	*kb*	*a*	W_{up}	L_{up}	Qe	Ne	BODe	Area
52.5	0.0187	0.4648	1.3301	36.70	104.09	211.90	1 571	48	3 819.91

Results with the maturation lagoon									
X	*d*	*kb*	*a*	W_{up}	L_{up}	Qe	Ne	BOSe	area
33.76	0.0290	0.4648	1.0266	35.70	8.29	210.42	1 000.00	41	295.87

Total area	Cost, facultative lagoon	Cost, maturation lagoon	Total cost
4 115.78	$4 738 058.85	$466 216.23	$5 204 275.07

the traditional method and 48 mg/l for with the mathematical model. According to the results in Tables 1 and 3, a lower cost was obtained with the mathematical model— $500 269.92, representing a 9.55% reduction. Considering the availability of economic resources this amount is significant.

Maturation Pond or Polishing

Table 3 shows the results from the design of the maturation ponds. With the application of the proposed mathematical model, retention time was reduced and the area was thereby decreased 39.375%. The number of baffles calculated using the traditional method was four, versus two with the other design. Regardless of the above, the two cases analyzed fully complied with the quality requirements stipulated by the Official Mexican Norm for treated wastewater, in addition to reducing costs by 31.30% ($212 444.86). As can be seen, these are significant savings. The main disadvantage of these treatment systems is that they occupy a large area of land (CNA and IMTA, 2007a; 2007b).

The Pond System as a Whole

Retention time was reduced 4.53 days and the area decreased 16.09%. The difference in costs was $712 714.79 (12.04%).

It is worth mentioning that indiscriminately increasing the number of baffles is not recommended. According to Oke and Otun (2001), Shilton and Harrison (2003b), Bracho *et al*. (2006) and Winfrey *et al.* (2010), costs should be taken into account, which is why the authors cited recommend performing an economic cost-benefit analysis. According to Chávez, Hernández and Flores (1989), the optimal results that provide elements for decision-making are obtained.

Table 2 shows the comparison of the results and the decision variables included in the study. The section on restrictions shows that fecal coliform in the effluent fully complied with equality restriction. It also shows that the system takes the maximum number permitted by the restriction of the number of baffles in the facultative pond, unlike retention time in the maturation pond, in which the lower boundary of the restriction is selected. This is interpreted as

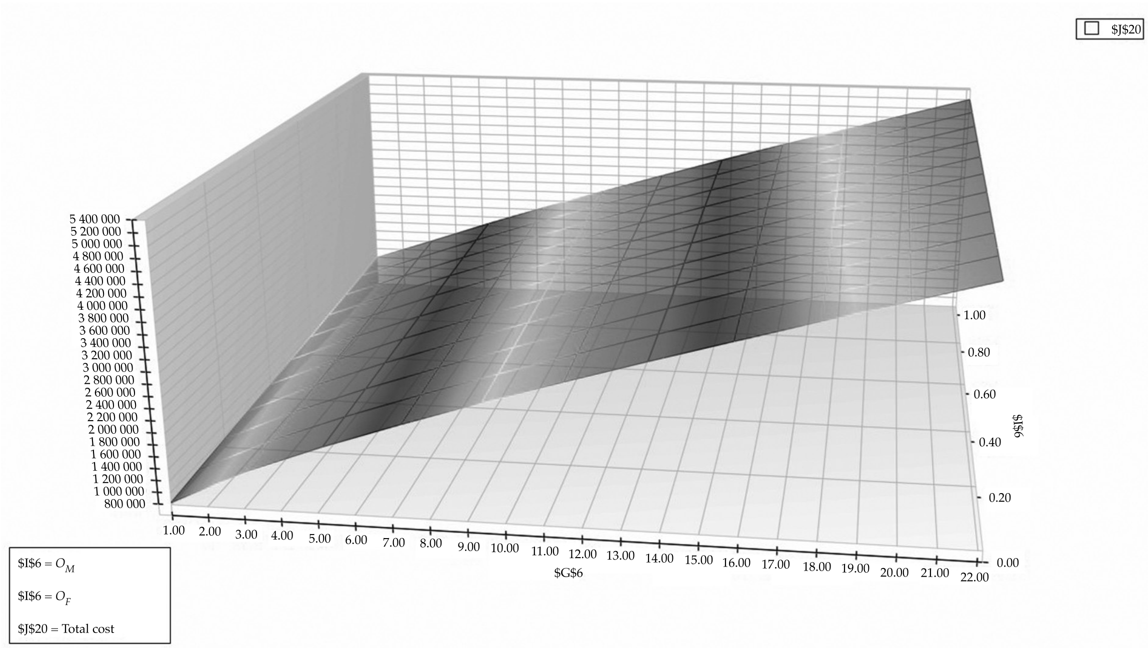


Figure 4. Sensitivity report of costs with independent variations, considering retention time only.

the retention time in the maturation pond tending towards zero when the number of baffles in the facultative pond increases. Table 3 shows the changes resulting from the *Solver* analysis system in the 20 dependent cells.

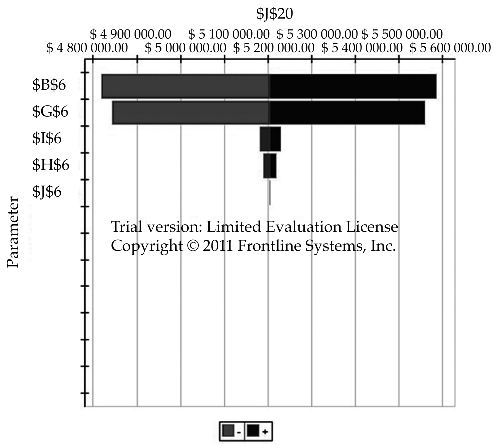
Sensitivity Report

For this analysis (Figure 4), the objective function was graphed and the number of baffles determined by the mathematical optimization model was considered to be constant (4 and 2) in both ponds. Setting the number of baffles to a constant number leaves only three variables (O_P, O_M and total cost), thereby making the graphic representation possible. The non-linearity of the function is confirmed, since the relation between the variables is not proportional. It can also be inferred that the model is sensitive to changes in the variables, since the higher the change in the variables the longer the retention in both ponds and the higher the construction costs. This is consistent with reality since more area is needed to contain the wastewater when these parameters are larger and, therefore, costs increase.

Sensitivity Analysis of the Pond System

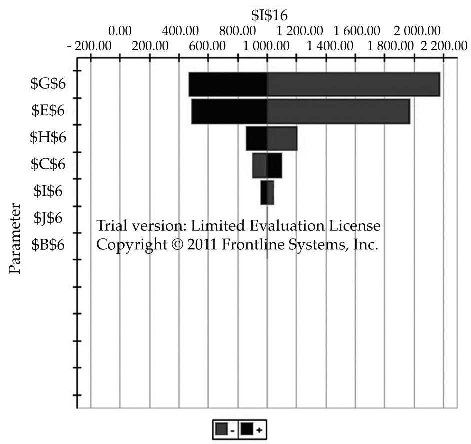
To verify sensitivity, a variation in the main parameters of plus or minus 10% was considered (Muramatsu, 2011) and a tornado graph was constructed to observe the parameters most sensitive to change. Figure 5 shows the analysis of the total cost of the project.

As can be seen, the widest bar is the volume of the water in the treatment system's influent. This is the parameter most sensitive to change; that is, the larger the volume the more land is needed and,



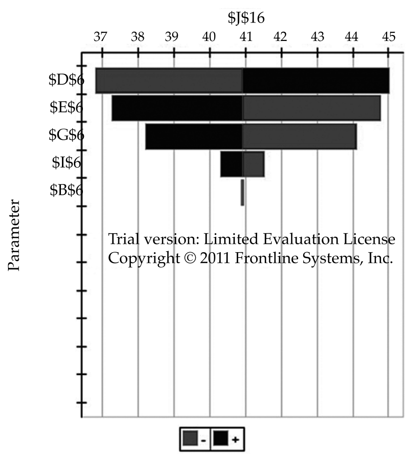
Sensitivity Analysis, Tornado Graph			
Parameters		Variation	
		-10%	+10%
J20	Total Cost	-	-
B6	*Qi*	207.9	254.1
G6	O_F	19.908	24.332
I6	O_M	0.9	1.1
H6	N_{BafF}	3.6	4.4
J6	N_{BafM}	1.8	2.2

Figure 5. Sensitivity analysis of total cost.



Sensitivity Analysis, Tornado Graph			
Parameters		Variation	
		-10%	+10%
I16	*NF/No*	-	-
G6	O_F	19.9	24.332
E6	*T*	10.62	12.98
H6	N_{BafF}	3.6	4.4
C6	NF/No_i	9 000 000	11 000 000
I6	O_M	0.9	1.1
J6	N_{BafM}	1.8	2.2
B6	*Qi*	207.9	254.1

Figura 6. Sensitivity analysis of number of fecal coliform.



Sensitivity Analysis, Tornado Graph			
Parameters		Variation	
		-10%	+10%
J16	BODe	-	-
D6	BOD_i	198	242
E6	*T*	10.62	12.98
G6	O_F	19.9	24.332
I6	O_M	0.9	1.1
B6	*Qi*	207.9	254.1

Figura 6. Sensitivity analysis of BODe.

therefore, the higher the cost. Next in order of significance is hydraulic retention time which affects the dimension of the pond system.

Figure 6 indicates that retention time is the most sensitive parameter affecting the removal of the indicator organism, that is, the less the hydraulic retention time the higher the concentration of fecal coliforms. Another significant parameter is temperature— the lower the temperature the higher the concentration of the indicator organism.

Regarding the biochemical oxygen demand in the effluent of the pond system, Figure 7 shows BOD_5 in the influent as the most sensitive bar, followed by temperature, indicating that the lower the temperature the higher the concentration of organic matter. The removal efficiency of the organic matter has upper and lower temperature limits of 37 and 4 degrees, that is, the activity of algae which produces oxygen decreases significantly outside of this range (Rolim, 2000; Oakley, 2005). In order of significance, hydraulic retention time follows, where the bar indicates that the less the retention time the higher the concentration of organic matter.

As can be seen, the sensitivity analysis responds adequately to the variation in the parameters involved in each factor.

Figure 8 shows the optimized dimensions of the pond system as determined by the mathematical model.

Conclusions

According to the proposed objectives, better results were obtained by applying the non-linear mathematical programming model— reduced costs, hydraulic retention time and area.

It is important to mention that the present mathematical analysis can be applied to different design conditions, that is, to any region. But changes are needed related to the cost of the land, embankments, baffles, evaporation and temperature, among others.

For developing countries, the application of non-linear programming is recommended as a helpful tool to optimize the design of stabilization ponds. Significant savings are obtained and it results in full

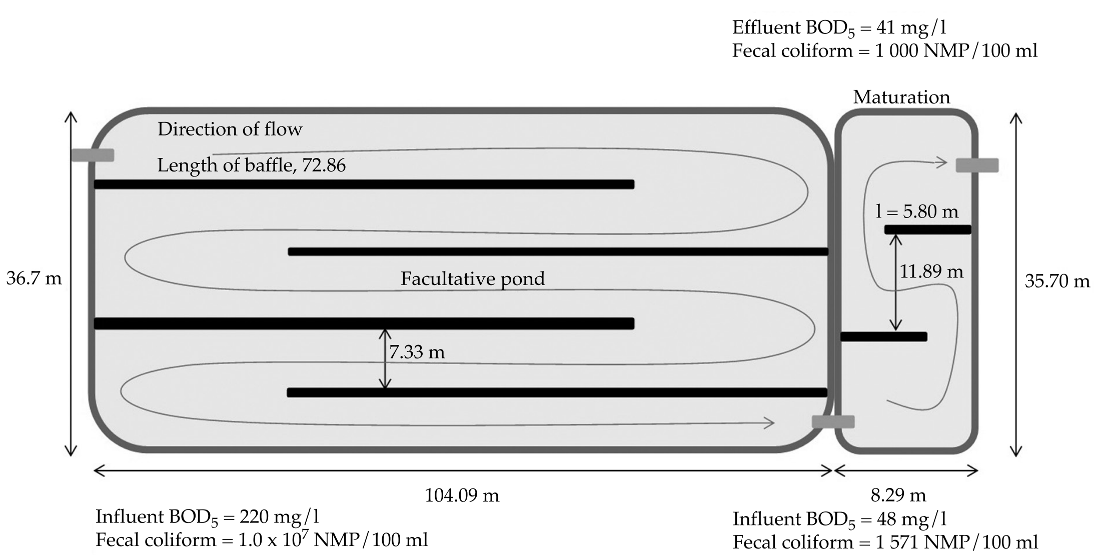


Figure 8. Dimensions of the lagoon system with the proposed mathematical model.

compliance with the norms related to discharge of wastewater into receptor bodies.

It would be useful to perform additional studies that include an anaerobic pond to compare the results, in order to more accurately determine the least area and cost for carrying out the project.

Referencss

Abbas, H., Nasr, R., & Seif, H. (2006). Study of Waste Stabilization Pond Geometry for Wastewater Treatment Efficiency. *Ecol. Eng.*, *28*(1), 25-34.

Anderson, D. R., Sweeney, D. J., & Williams, T. A. (2004). *Métodos cuantitativos para los negocios* (116 pp.). México, DF: Thomson Corporation.

Agunwamba, J. C., Ochonogar, A., & Ukpong, E. C. (2003). Experimental and Principal Component Analysis of Waste Stabilization Ponds. *Journal of Applied Science, Engineering and Technology*, *3*(1), 25-30.

Bracho, N., Lloyd, B., & Aldana, G. (2006). Optimization of Hydraulic Performance to Maximize Fecal Coliform Removal in Maturation Ponds. *Water Res.*, *40*, 1677-1685.

Banda, C. G. (2007). *Computational Fluid Dynamics Modeling of Baffled Waste Stabilization Ponds.* Ph.D. thesis. Leeds, UK: School of Civil Engineering, University of Leeds.

Chávez, A., Hernández N., M., & Flores, S. (1989). Modelación digital y optimación de acuíferos. *Ingeniería Hidráulica en México*, 2(3), 31-39.

CNA e IMTA (2007a). *Manual de diseño de agua potable, alcantarillado y saneamiento*. *Paquetes tecnológicos para el tratamiento de excretas y aguas residuales en comunidades rurales* (pp. 56-83). Jiutepec, México: Instituto Mexicano de Tecnología del Agua.

CNA e IMTA (2007b). *Manual de diseño de agua potable, alcantarillado y saneamiento*. *Manual de diseño de lagunas de estabilización* (234 pp.). Jiutepec, México: Instituto Mexicano de Tecnología del Agua.

Cortés, M. F., Treviño, C. A., Luévanos, R. A., Luévanos, R. R. & Uranga, S. A. C. (2014a). Función objetivo en el diseño de laguna facultativa (caso de estudio). *Revista Mexicana de Ciencias Agrícolas*, *5*(3), 433-447.

Cortés, M. F., Treviño, C. A., Alcorta, G. M. A., Luévanos, R. R., Kalashnikov, Vyacheslav, & Luévanos, R. R. (2014b). Mathematical Analysis for the Optimization of a Design in a Facultative Pond: Indicator Organism and Organic Matter. *Mathematical Problems in Engineering*, Article ID 652509.

Cortés, M. F., Treviño, C. A., Luévanos, R. A., & Luévanos, R. R. (2013). Mathematical Model for the Optimization of the Design of a Facultative Pond (case study). *Far East Journal of Mathematical Sciences (FJMS)*, *81*(1), 127-145.

DOF (1996). Norma Oficial Mexicana NOM-001-ECOL-1996. Que establece los límites máximos permisibles de contaminantes en las descargas de aguas residuales a los sistemas en aguas y bienes nacionales (30 pp.). *Diario Oficial de la Federación*. México, DF: Semarnat-Secretaría de Gobernación.

Fonseca, C. M., & Fleming, P. J. (1993). *Genetic Algorithms for Multi-Objective Optimization: Formulation, Discussion and Generalization*. Citado el 12 de enero de 2012. Recuperado de http://pdf.aminer.org/000/310/607/genetic_algorithms_for_multiobjective_optimization_formulationdiscussion_and_generalization.pdf.

Fonseca, C. M., & Fleming, P. J. (1995). An Overview of Evolutionary Algorithms in Multiobjective Optimization. *Evol. Comput.*, *3*(1), 1-16.

Hamzeh, R., & Ponce, V. M. (2007). *Design and Performance of Waste Stabilization Ponds*. Citado el 13 de enero de 2012. Recuperado de http://ponce.sdsu.edu/ramadan/stabilizationponds.html.

Killani, J. S., & Ogunrombi, J. A. (1984). Effects of Baffles on the Performance of Model Waste Stabilization Ponds. *Water Research*, *18*(8), 941-944.

Mara, D. D. (2004). *Domestic Wastewater Treatment in Developing Countries*. London: Earthscan Publications.

Metcalf & Eddy, Inc. (1991). *Wastewater Engineering: Treatment, Disposal, Reuse*. New York: McGraw-Hill.

Muramatsu, M. (2011). *Risk Solver Platform*. Versión 11.5. Programa computacional [descarga en línea]. Incline Village, USA: Frontline Systems Inc.

Muttamara, S., & Puetpaiboon, U. (1996). Nitrogen Removal in Baffled Waste Stabilization Ponds. *Water Sci. Technol.*, *33*(7), 173-181.

Muttamara, S., & Puetpaiboon, U. (1997). *Roles of Baffles in Waste Stabilization Ponds*. Water Sci. Technol., *35*(8), 275-284.

Naddafi, K., Hassanvand, A. S., Dehghanifard, E., Faezi-Razi, D., Mostofi, S., Kasaee, N., Nabizadeh, R., & Heidari, M. (2009), Performance Evaluation of Wastewater Stabilization Ponds in Arak-Iran, Iran. *J. Environ. Health. Sci. Eng.*, *6*(1), 41-46.

Nelder, J. A., & Mead, R. (1965). A Simplex Method for Function Minimization. *Comput. J.*, *7*(4), 308-313.

Oakley S. (2005). *Lagunas de estabilización en Honduras. Manual de diseño, construcción, operación y mantenimiento, monitoreo y sostenibilidad* (201 pp.). Long Beach, EU: Universidad Estatal de California.

Oke, I. A., & Otun, J. A. (2001). Mathematical Analysis of Economic Sizing of Stabilization Ponds. *Nigerian J. Eng.*, *9*(1), 13-21.

Olukanni, O. D., & Ducoste, J. J. (2011). Optimization of Waste Stabilization Pond Design for Developing Nations Using Computational Fluid Dynamics. *Ecol. Eng.*, *37*(11), 1878-1888.

Pedahzur, R., Nasser, A. M., Dor, I., Fattal, B., & Shuval, H. I. (1993). The Effect of Baffle Installation on the Performance of a Single-Cell Stabilization Pond. *Water Science and Technology*, *27*(7), 45-52.

Rolim, M. S. (2000). *Sistemas de lagunas de estabilización. Cómo utilizar aguas residuales tratadas en sistemas de regadío* (pp. 199-323). Bogotá: OPS y OMS, McGraw-Hill.

Sah, L., Rousseau, D. P. L., & Hooijmans, C. M. (2012). Numerical Modelling of Waste Stabilization Ponds: Where do we stand? *Water, Air & Soil Pollution*, *223*(6), 3155-3171.

Senzia, M. A., Mayo, A. W., Mbwette, T. S. A., Katima, J. H. Y., & Jorgensen, S. E. (2002). Modelling Nitrogen Transformation and Removal in Primary Facultative Ponds. *Ecological Modelling*, *154*(3), 207-215.

Shilton, A. N., & Harrison, J. (2003a). *Guidelines for the Hydraulic Design of Waste Stabilization Ponds*. Institute of Technology and Engineering, Massey University, New Zealand. Citado el 12 de enero de 2012. Recuperado de http://www.bvsde.paho.org/bvsacd/agua2003/hidra.pdf.

Shilton, A. N., & Harrison, J. (2003b). Integration of Coliform Decay within a CFD (Computational Fluid Dynamic) Model of a Waste Stabilization Pond. *Water Sci. Technol.*, *48*(2), 205-210.

Shilton, A. N., & Mara, D. D. (2005). CFD (Computational Fluid Dynamics) Modeling of Baffles for Optimizing Tropical Waste Stabilization Ponds System. *Water Sci. Technol.*, *51*(12), 103-106.

Sperling, M. V., Chernicharo, C. A., Soares, A. M., & Zerbini, A. M. (2002). Coliform and Helminth Eggs Removal in a Combined UASB Reactor-Baffled Pond System in Brazil: Performance Evaluation and Mathematical Modelling. *Water Science and Technology*, *45*(10), 237-242.

Sperling, M. V., Chernicharo, C. A., Soares, A. M., & Zerbini, A. M. (2003). Evaluation and Modelling of Helminth Eggs Removal in Baffled and Unbaffled Ponds Treating Anaerobic Effluent. *Water Science and Technology*, *48*(2), 113-120.

Winfrey, B. K., Stronsnider, W. H., Nairn, R. W., & Strevett, K. A. (2010). Highly Effective Reduction of Fecal Indicator Bacteria Counts in an Ecologically Engineered Municipal Wastewater and Acid Mine Drainage Passive Co-Treatment System. *Ecol. Eng.*, *36*(12), 1620-1626.

Zanotelli, C. T., Medri, W., Belli-Filho, P., Perdomo, C. C., & Costa, R. H. R. (2002). Performance of a Baffled Facultative Pond Treating Piggery Wastes. *Water Science and Technology*, *45*(1), 49-53.

Institutional Address of the Authors

Dr. Facundo Cortés-Martínez

Profesor investigador
Facultad de Ingeniería, Ciencias y Arquitectura
Universidad Juárez del Estado de Durango, campus Gómez Palacio Durango
Av. Universidad s/n, Fraccionamiento Filadelfia
35120 Gómez Palacio, Durango, México
Teléfono: +52 (871) 7152 017
facundo_cm@yahoo.com.mx

M.I. Alejandro Treviño-Cansino

Profesor investigador
Facultad de Ingeniería, Ciencias y Arquitectura
Universidad Juárez del Estado de Durango, campus Gómez Palacio Durango
Av. Universidad s/n, Fraccionamiento Filadelfia
35120 Gómez Palacio, Durango, México
Teléfono: +52 (871) 7152 017
atrevinoc@live.com.mx

Dra. María Aracelia Alcorta-García

Profesora investigadora
Facultad de Ciencias Físico Matemáticas
Centro de Investigaciones en Ciencias Físico Matemáticas
Universidad Autónoma de Nuevo León
Av. Universidad s/n
66451 San Nicolás de los Garza, Nuevo León, México
maaracelia@gmail.com

Dr. Agustín Sáenz López

Profesor investigador
Facultad de Ingeniería, Ciencias y Arquitectura
Universidad Juárez del Estado de Durango, campus Gómez Palacio Durango
Av. Universidad s/n, Fraccionamiento Filadelfia
35120 Gómez Palacio, Durango, México
Teléfono: +52 (871) 7152 017
agusgpl@hotmail.com

Dr. José Luis González-Barrios

Investigador titular
Centro Nacional de Investigación Disciplinaria Relación Agua-Suelo-Planta- Atmósfera
Instituto Nacional de Investigaciones Forestales Agrícolas y Pecuarias
Margen Derecha Canal Sacramento
35140 Gómez Palacio, Durango, México
Teléfono: +52 (871) 1590 105
gonzalez.barrios@inifap.gob.mx

Return to Dublin: Do Traditional Communities Manage Water as an Economic Resource?

• José Antonio Batista-Medina* •
Universidad de La Laguna, España
*Corresponding Author

Abstract

Batista-Medina, J. A. (March-April, 2015). Return to Dublin: Do Traditional Communities Manage Water as an Economic Resource? *Water Technology and Sciences* (in Spanish), 6(2), 101-111.

While the idea of water as an economic good is not new, it has expanded since the Dublin Conference was held (1992). What is the meaning of water as an economic resource? We can identify two approaches or interpretations. The first considers water to be an *input* (a productive *input*), as any other in an economic system. In this context, water must have a price or be transferred through market institutions. These economic tools will create an efficient use of the water, that is, more benefits. Water thereby becomes a commodity. The second interpretation is defined in broader economic terms. Water as an economic resource means that it is a scarce resource and must be carefully managed to attain the goals established by a particular society. Treating water as an economic good does not imply the use of one specific set of economic tools. While prices, markets, private property, etcetera are tools that can all be found in a particular toolbox, other toolboxes exist. There are other ways to sustainably manage water from a social, economic and ecological point of view. We will apply this second interpretation to the analysis of water management in traditional communities. We will attempt to answer the question of whether traditional communities manage water as an economic resource. Social science research about the management of small scale irrigation systems shows that those systems generally manage water as an economic resource; that is, as a scarce resource. Although traditional irrigation systems had generally operated well in social, economic and ecological terms, modern water science and policies have ignored them, transforming or destroying them by applying universal concepts, criteria and tools. We conclude that traditional and indigenous institutions and organizations have many lessons to teach in regard to the treatment and management of water, and they should be supported and protected.

Keywords: Water, water as an economic good, traditional and indigenous irrigation systems, sustainable management, Integrated Water Resources Management, water culture.

Resumen

Batista-Medina, J. A. (marzo-abril, 2015). Regreso a Dublín: ¿gestionan las comunidades tradicionales el agua como recurso económico? Tecnología y Ciencias del Agua, *6(2), 101-111.*

La idea del agua como bien económico no es nueva, pero se ha extendido desde la Conferencia de Dublín (1992). ¿Cuál es el significado del agua como recurso económico? Podemos identificar dos acercamientos o interpretaciones. La primera considera que el agua es un input *(un* input *productivo), como otros, en un sistema económico. En este sentido, el agua debe tener precio o debe ser transferida mediante las instituciones de mercado. Esas herramientas económicas llevarán a un uso eficiente o, en otras palabras, al uso más beneficioso. Así pues, el agua se convierte en una mercancía. La segunda interpretación es menos estrecha en su sentido económico. El agua como recurso económico significa que es escasa y debe ser gestionada cuidadosamente para alcanzar los objetivos establecidos en una sociedad concreta. Tratar el agua como un recurso económico no implica el uso de un conjunto específico de herramientas económicas. Los precios, los mercados, la propiedad privada, etcétera, son herramientas en una caja de herramientas; pero hay otras, otros medios para gestionar el agua de una manera social, económica y ecológicamente sostenible. Aplicaremos esta segunda interpretación al análisis de la gestión del agua en las comunidades tradicionales. En este sentido, intentaremos responder a la siguiente cuestión: ¿gestionan estas comunidades el agua como recurso económico? La investigación en ciencias sociales sobre la gestión de sistemas de riego de pequeño tamaño muestra que tratan el agua en general como un recurso económico, esto es, como un recurso escaso. Esos sistemas de riego tradicionales han funcionado generalmente bien en términos sociales, económicos y ecológicos; pero la política y la ciencia modernas del agua han ignorado esos sistemas, transformándolos o destruyéndolos por la aplicación de conceptos, criterios y herramientas universales. Concluimos que estas organizaciones e instituciones tradicionales e indígenas tienen muchas lecciones que enseñar en el tratamiento y gestión del agua, y deben ser apoyadas y protegidas.*

Palabras clave*: agua, agua como bien económico, sistemas de riego tradicionales e indígenas, gestión sostenible, gestión integrada de los recursos hídricos, cultura del agua.*

Received: 12/11/2013
Accepted: 03/12/2014

Introduction

The nature of water has been highly debated in recent times (here we focus on its agricultural use), and it is not a trivial issue or a mere academic or intellectual exercise. We need to consider that the ways in which this recourse is perceived or conceptualized are expressed in practical ways in different contexts— such as the design of policies; considering institutions and organizations as better managers of water; those who are responsible for it; priority uses; etcetera. As we will see in the first section, in the West the dominant concept of water is as a resource, as an *input*, and particularly an *economic resource* (which is reinforced by the 1992 Dublin Conference). According to some interpretations, this implies that as a *commodity* water is subject to market principles. What is significant is the rapid expansion of this focus from the West to many other places, in a manner which we could understand, in general terms, as "assimilationist water policies."

Nevertheless, not everyone holds and accepts the same vision (section 2). That is, not everyone considers the economic perspective to be that which appears in conventional formulations (prices, markets, goods, private sector…). There are alternative positions that suggest a definition or concept that is less rigid or strict, less *economistic,* while not rejecting water as an economic resource. This other interpretation proposes an economic perspective related to the concept of scarcity, based on which water as an *economic good* means understanding that we find ourselves relating to a *scarce resource*, without specific tools to manage it. In addition, it should be noted that water is not only an *economic resource* but is also social, cultural, biological, political…. We find ourselves faced with a multidimensional element, not only an *input*.

Therefore, the present study is aimed at responding to the question: Do traditional and indigenous communities manage water as an *economic resource*? Our proposal is that if we accept that alternative definition of water as an *economic resource (scarcity*), then we will find (as seen in the third section) that numerous communities— present and past societies, indigenous and farmers from different parts of the world (transcultural perspective)— have recognized the scarcity of water and its importance, and have built and implemented management systems that are economically, socially and environmentally quite efficient, systems which are similar to what is called Integrated Water Resources Management (IWRM). According to the definition by Global Water Partnership: "Integrated Water Resources Management (IWRM) is a process which promotes the coordinated development and management of water, land and related resources in order to maximise economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems" (GWP, 2000; see also Rahaman & Varis, 2005). "IWRM is based on the understanding that water resources are an integral component of the ecosystem, a natural resource, and a social and economic good" (GWP, 2010).

This means that many of the elements currently considered to be fundamental to water management (for example, integrating economic, social and ecological aspects and using participatory methods, etc.) and the objectives considered priorities (efficiency, sustainability, equity) already exist. They are functioning in many areas and in many cases have been working for centuries. Nevertheless, these systems have been ignored, undervalued by Western techno-science and strongly ethnocentric development policies. And even worse, more than a few have been replaced by "modern" systems or have undergone significant changes ("modernizing")from the imposition of water policies that do not understand or value diversity, policies that do not conceive of the management of this resource in other than techno-economic principles, criteria and tools.

Our final reflection takes two directions. First, we consider that traditional water management systems should be supported, recognized and strengthened (and improved when appropriate) as socially, economically and environmentally viable methods to manage this scarce resource. Second, we understand that we can learn from them, without overvaluing them or romanticizing them, in order to obtain concepts of water and management models that help us to solve some of the current and future problems related to this resource, and to fulfill efficiency, equity and sustainability objectives.

Water as an Economic Resource: Prices, Markets, Goods

While the idea of water as an *economic resource* is not new, it has been strengthened by the fourth principle of the Dublin Conference (ICWE, 1992): "Water has an economic value in all its competing uses and should be recognized as an economic good… Past failure to recognize the economic value of water has led to wasteful and environmentally damaging uses of the resource. Managing water as an economic good is an important way of achieving efficient and equitable use, and of encouraging conservation and protection of water resources." This point has been interpreted by many authors, experts, agencies, organizations, corporations, etcetera, in the sense of water as one more element (Gray, 1983), an *input,* in an economic system, a "resource" that is not different or should not be considered different than others in terms of its conceptualization, treatment and management, while setting aside some particular characteristics. Thus, water, is an *economic* resource in the more formal sense of the term. And more extreme concepts are empty of other relevant aspects. The problem with this vision stems from the interpretation (sometimes implicit) of *economics*, and particularly its meaning in the design of water policies. We consider this concept of the resource to be derived from concrete ways to value, manage and use it, and therefore, from the "tools" considered most appropriate for said purpose.

The most generalized (we could say orthodox) interpretation of water as a resource encompasses techno-economic concepts, criteria, tools, etcetera. The water's value is basically economic, which is or ought to be reflected in prices (see Ward & Michelsen, 2002: 443). As in the case of other in a system, water ought to have prices that reflect its situation (supply-demand) at a particular moment and, when applicable, total costs. Prices (see, for example, Dinar, 2000; Van der Zaag & Savenije, 2006; Rogers, De Silva, & Bathia, 2002; World Bank, 2004) are what ensure its efficient use, in theory. They are what counteract an inadequate or inefficient use (in primarily economic terms). This is based on the idea that treating water as a "free" resource leads to excessive and inefficient consumption as well as environmental problems. That is, a lack of prices and market mechanisms is mistakenly (as we will see) considered to lead to economic and ecological problems. In this sense, references to Hardin's "tragedy of commons" (1968) to explain some of the problems in the water sector are not uncommon.

In this context, the market (water markets) is governed by one main (and considered better) mechanism to allocate scarce water among purposes and users who compete with each other (see, for example, MacDonnell, 2004; Glennon, 2005; Henderson & Akers, 2008; Ward & Michelsen, 2002; Zilberman & Schoengold, 2005; Rogers ., 2002; Libecap, 2009, 2010; Briscoe, 2011; Fonseca, 1998; World Bank, 2004). Thus, a further step is taken, and now it is not only a resource (an *input*) but also a (see MacDonnell, 2004; Serageldin, 2010; Mitchell, 1984). And here lies the key to the economistic interpretation of the fourth Dublin principle— the statement that water is an leads to treating it as a to be allocated by the market and, thus, a product. At this level, we are not only faced with the question of efficiency, of allocating it for the most beneficial uses, the most valuable purposes (in economic terms). In addition, a business opportunity arises, in which it is seen as a source of numerous (and certain) benefits by large companies and investors who are aware of its strategic importance in this century (see, for example, Goldman Sachs, 2008; Morgan Stanley, 2012; Serageldin, 2010). We could say that the narrowest view of water as an serves as a basis or argument for treating it as a product, as an element that "belongs" (or should belong) to the market, subjected to its principles; going beyond arguments about its technical, ecological and economic efficiency to ideas about obtaining benefits.

Using this line of argument, private ownership is logically the most supported form of ownership (see, for example, Libecap, 2009). For the market to function well, water rights should be well defined, legally recognized and guaranteed (legally and judicially) by the State. This means individual control of the resource is given more priority and is more highly valued than other forms of control, such as communal (cooperatives) or state (centralized). The supra-individual level should never interfere, or interfere as little as possible, in individual (rational) decisions about the use and allocation of water. Thus the individual (holder of private rights) is raised to a key position, individualism is placed above collectivism, individuality over collectivity (see also Ingram & Brown, 1998: 123-124). General and social interests lose to individual interests, although the former appear much more often as an argument in favor of some of the decisions that support water markets, private property… The old idea that individual economic action will generate collective benefits (or prevent social costs) is carried into water management and water policies. Thus, through the market, not only property owners and water users benefit but also the society as a whole, by fostering a more beneficial use in overall economic, social and environmental terms (as is said, by promoting conservation and sustainability). In fact, unlike the past, the need to integrate environmental factors into water policies is expressly recognized today (Gleick, 1998, 2000), where sustainability is explicitly specified as a goal (GWP, 2000). Nonetheless, orthodox economic science (for example, Adler, 2008, 2008/09, 2012) and various official organizations support solutions that defend markets, as mentioned earlier.

In sum, this interpretation of water as an — considered to be stricter or more extreme— is based on elements such as prices, markets, private property, efficiency, individual control…In other words, with this interpretation, economics implies that water should have prices that are well-determined by the market or by administrative mechanisms (fee systems).

Water as an economic resource: managing scarcity

Another interpretation of the fourth Dublin principle, of water as an has nothing to do with the economistic perspective that we analyzed in the previous section (prices, private property and markets). That is, such a concept does not go along with concrete "tools." A sufficient explanation of this is provided by Robbins' classic definition of generalized acceptance in economic science. According to this author, the economy will take care of the study of "human behavior as a relationship between ends and scarce means which have alternative uses" (Robbins, 1994: 85). The key to this definition, as is known, lies in the scarcity of the medium, such that means that individuals use the resources they have to satisfy certain needs or to attain other particular ends. Extending this idea, an resource would be considered a resource. Thus, the economy would take care of studying the best way to allocate the available (scarce) resources to achieve certain objectives (Mochón, 1994: 4). The economy (specifically the micro-economy) is, in general terms, conceived of as the science of choice in the face of scarcity (Frank, 2002: 24).

Thus, scarcity is the basic component of this interpretation of water as an , and therefore, the need to make decisions about its (best) use and/or allocation. Obviously, the aims (alternatives) are not given but rather are socially defined, although some agreement on certain overall objectives may exist, such as proper use, conservation…as reflected by many international documents and agreements (for example, ICWE, 1992; GWP, 2000). And also, no reference is made to tools or concrete means to achieve those aims.

This interpretation is centered on scarcity and the need for effective management, it is the "other" interpretation of the fourth Dublin principle, according to several authors (see, for example, Savenije & Van der Zaag, 2002; Savenije, 2002; Brown, 1997; Hellegers & Perry, 2006; McNeill, 1998; Ali, 2011).

Do traditional communities manage water as an *economic resource*?

A negative view of traditional water management is not uncommon. It is said to use archaic and backward systems, with technically and economically inefficient allocation and distribution mechanisms, and users who are attached to their traditions and excessively conserve, who do not recognize the (economic) value of water or the elements in the modern management of this good, etcetera. In too many cases, this has meant ignoring such systems, undervaluing them and substituting their organizational structures and procedures with modern ones (see also Chartres & Varma, 2011: 152-153). Nevertheless, is it true that traditional and indigenous communities, which have based their economies on water, do not recognize it or manage it as an ?

If we consider what has been collected in the extensive amount of literature (see, for example, Maass & Anderson, 1978; Tang, 1992; Guillet, 1992; Sengupta, 1991; Lam, 1998; Siy, 1982) about those systems, written from the social science perspective (past and present), it can be said, in general, that they do not deny (as is sometimes assumed) the economic and productive importance of water, but rather, in general, its scarcity is recognized and it is managed carefully. Furthermore, it is crucial that these communities have this resource or access to it, in the strictest sense. Being able to irrigate the soil means producing food for their own consumption and/or to sell. Protecting water, defending it, "adoring" it, conserving it, is a (rational) survival strategy. And trying to improve its use, to use it more "efficiently," is also part of this strategy. This suggests that the character of water as a scarce resource is not rejected and, therefore, it needs to be carefully managed for productive, social and environmental ends. In addition, communal and traditional irrigation systems have a long and diverse history of managing scarcity (see, for example (Brown, 1997; Jinapala & Somaratne, 2002; Hellegers & Perry, 2006; Ingram & Brown, 1998; McNeill, 1998; Toro-Sánchez, 2007), but with a collective model (participatory, in modern terms), a model that also integrates economic, social, environmental and cultural aspects. If this were not the case, the longevity of many of these systems and their economic, social and ecological sustainability could not be understood (see Walker & Salt, 2012: 58).

The official international discourse on water often discusses integration in relation to the view of integrated, holistic or comprehensiveness management (GWP, 2000; see also Rahaman & Varis, 2005). Meanwhile, this concept of water and its management exists, generally, in indigenous and traditional systems. In other words, it is considered to be a multidimensional element (see also Mehta, 2000; Wateau, 2011) in the sense that the holistic (a whole) vision includes infrastructure and ecological (or biological), economic, cultural and social aspects. On the other hand, as has been seen, in the atomistic and economistic view of our own Western culture (water as an , as an) the economic discourse and business criteria dominate, and the individual (not the group or community) are at the center, playing the leading role.

As opposed to managing water as a separate or independent resource, integrated management can be seen in cases (and there are many) in which ecosystems have been managed, in which other natural resources play a key role and are determinants of the availability of water (what Ávila-García (2006) calls "territorial matrix", the water-land-forest). Carefully managing forest regions is especially important because they directly affect water availability; springs and rivers begin in these areas and run through them. Traditional and indigenous farmers know that caring for the forests is key to maintaining the supply of water in their territories and communities, and therefore have integrated them into management practices (see, for example, Taniyama, 2004; Rivadeneira & Peralta-Proaño, 2009).

Sustainable water management can be seen in different practices and rules, as well as different elements involved in traditional and indigenous irrigation. For example, the top-to-bottom distribution of water— following the spatial locations of channels and farms— has adapted well to environments with steep slopes, reducing loss or enabling the use of water (when produced) for irrigation of lower terrain. This calls into question technical concepts of efficiency (see Guillet, 2006; Boelens & Vos, 2012). Even the reticence towards increasing irrigation zones, which has been observed in an infinite number of cases (see, for example, Maass, 1994; Maass & Anderson, 1978; Trawick, 2001a; Batista-Medina, 2001), can be interpreted as having positive ecological effects (its connection to a specific territory inhibits the tendency to look for more water), in addition to social, economic and systemic benefits (preventing the collapse of the irrigation system). It is important to keep in mind that limiting irrigation zones is a way to adjust the "supply" and the "demand" of water, by affecting the latter (managing demand), to ensure a minimum amount for all who have the right to use it. This mechanism also avoids conflicts (between "old" and "new" irrigators). Meanwhile, where a connection between the water and the land or a territory does not exist (or has been limited), private property and markets have reduced the sustainability of irrigation zones when conditions have been adequate (high productive value of water, commercial farming…). This generates conflicts as well as economic problems (many farmers without the minimal amount of water needed to irrigate their land) and ecological problems (overexploitation of aquifers) (see, for example, Budds, 2012; Poncet, Álvarez-Latorre, & Reyes- Serrano, 2011; Toro-Sánchez, 2007).

In addition to these concrete mechanisms (among many others), we should highlight the implications of certain values or behaviors related to religious beliefs, legends, myths…in the use and consumption of water (see, for example, Maliva & Missimer, 2012; Bark, Hatton-MacDonald, Connor, Crossman, & Jackson, 2011; Jinapala & Somaratne, 2002; Vargas, 2006; Ávila-García, 2006; Angchok & Singh, 2006; Park & Ha, 2012). In other words, in many traditional and indigenous systems the symbolic value of water directly or indirectly translates into sustainable practices. The fact that water is not considered a mere external or independent resource (as occurs in our society) to be appropriated and dominated, but rather is part of "us," encompassed by the spiritual and divine (water as a divine gift) or conceived of as a vital resource in a broad sense, leads to its treatment and use in an ecologically careful and respectful manner. As Peña mentions (1999: 109; 2012a) when talking about the irrigation channels ("acequias") in New Mexico, an authentic environmental ethic can be described in which farmers are not owners (individual) or mere producers or users but rather authentic "guardians" of a resource that they have inherited from the past (from nature, ancestors and gods) and which should also be treated with care for future generations (Ingram & Brown, 1998: 124).

We also cannot neglect the importance of the positive ecological effects of these systems. Many studies indicate that traditional and indigenous irrigation has not only enabled production and, thus, the survival of communities and groups in highly disparate environments (sometimes quite extreme) but also, as an unintentional effect, they have created and maintained spaces and territories rich in flora and fauna (for example, Martínez-Saldaña, 2012; Brown & Rivera, 2000; Peña, 1999; Peña, 2012b; Rivera, 1996). In other words, they have been generators and maintainers of life, of biodiversity. The water that runs, infiltrates, or is "lost" from the channels feeds plants and animals and recharges aquifers, or it returns to nearby surface watercourses (see Fernald, Guldan, & Ochoa, 2010). These authentic "ecological flows" have commonly been viewed by the modern techno-science perspective as losses, inefficiencies, and wasteful and unsustainable practices, etc.

International documents about water are raising questions about equity and security in terms of access to water, particularly considering the most disadvantaged groups in society. In general, both of these questions are also present in farmer or indigenous irrigation systems (see Boelens & Dávila (Eds.), 1998; Whiteley, Ingram, & Perry (Eds.), 2008; Mabry (Ed.), 1996; Mabry & Cleveland, 1996). Furthermore, both objectives are priorities in many cases. Mechanisms and rules are designed and implemented so that everyone with the right to water has access in an equitable and secure manner, without ignoring efficiency and productivity. For example, the adscription system, or uniting water with the land, which is present in an infinite number of irrigation systems, presumes that every farmer with terrain in the irrigation zone has access to a portion (proportional) of the available water. All of them, together, share in the abundance and, particularly, in the scarcity of water. This not only presumes equitable access to a fundamental resource but also secure access, ensuring that everyone can thereby produce food. And also not to be overlooked is that equity is one of the elements that makes systems stable, in other words, it contributes to making them socially sustainable (see also Trawick, 2001a: 14; Trawick, 2001b: 373). In fact, where it is not present, for whatever reason, opportunism and internal conflicts stand out.

Final Reflections

As has been seen in the text above, the second interpretation of water management as an can be found in a limitless number of indigenous and farmer systems in different parts of the world, and so can some of the basic principles of Integrated Water Resources Management. At the fringes of the concept (*economic resource*), creating confusion and undoubtedly some rejection, are the transcultural and historical studies by various social scientists and historians that have told us that, in some cases, traditional systems have been managing water as an (that is, resource) for centuries. And if we consider the longevity of many of these systems, which have often endured in extreme environments, this management has been generally quite effective.

But these systems have been, and are today, up against a lack of knowledge, a lack of understanding and disapproval on the part of experts, technicians and those responsible for water policies. The application of those water policies has often resulted in eliminating these systems or creating serious problems. In other words, "modern" management models have been introduced in numerous cases based on the stricter idea of water as an and on Western techno-science, cases in which a resource considered to be scarce and vital was being carefully, sustainably and equitably management with reasonable efficiency.

In light of this, increasingly more voices have been raised in favor of correcting this water policy and the related interventions, to learn from indigenous and traditional systems, studying them, supporting them, recognizing them and taking them into account (see for example Mabry & Cleveland, 1996: 228; Chartres & Varma, 2011; 152-153), as has been done, for example in the Irrigation Communities in Spain (see Giménez-Casalduero & Palerm-Viqueira, 2007). And this does not mean overvaluing them, thinking each and every one functions correctly in every way, thereby falling into a sense of romanticism (see also Mehta, 2000: 14-16; Wateau, 2011: 264; Bakker, 2007: 444; Chalaune, 2009: 104-106). But rather, it seems to be clear that many lessons can be learned from them, to benefit the present and future of this highly threatened resource, which is vital to everyone. These systems also continue to be a valid management option in many cases. We cannot ignore their contributions to sustainable water management and to water ecosystems, or their economic and social functions. They have helped and continue to help sustain numerous indigenous and farming communities. They have even supported regional and national economies if we consider that small and medium farmers and the irrigation systems they use represent a good portion of agricultural production (see Mabry, 1996: 6).

What has been presented here is not intended to oppose the market, or private property and prices… These mechanisms are part of toolbox, which can work under certain circumstances, while in other circumstances these tools could be problematic, difficult to implement …. (see ver Savenije, 2002; Aguilera, 2002; Henderson & Akers, 2008; Zilberman & Schoengold, 2005; Bauer, 1997; Van der Zaag & Savenije, 2006; Dellapenna, 2000, 2009, Draper & Sehlke, 2005). But there are others that are not in the water economy textbooks or university classrooms, nor are they in government offices or institutions and organizations. They have been (and still are) out "there", in arid zones, and semi-arid and temperate regions, in the mountains and valleys, in places near and far…

References

Adler, J. H. (2008). Water Marketing as an Adaptive Response to the Threat of Climate Change. *Hamline Law Review*, *31*(3), 730-754.

Adler, J. H. (2008/2009). Warming Up' to Water Markets Regulation. *Winter*, *31*, 14-17.

Adler, J. H. (2012). Water Rights, Markets, and Changing Ecological Conditions. *Environmental Law*, *42*, 93-113.

Aguilera, F. (2002). *Los mercados de agua en Tenerife*. Bilbao: Bakeaz.

Ali, M. H. (2011). *Practices of Irrigation & On-Farm Water Management*. Volume 2. New York: Springer.

Angchok, D., & Singh, P. (2006). Traditional Irrigation and Water Distribution System in Ladakh. *Indian Journal of Traditional Knowledge*, *5*(3), 397-402.

Ávila-García, P. (2006). El valor social y cultural del agua (pp. 233-248). En V. Vásquez García, D. Soares-Moraes. A. de la Rosa-Regalado (Eds.). *Gestión y cultura del agua. Tomo II*. México, DF: Instituto Mexicano de Tecnología del Agua, Colegio de Postgraduados.

Bakker, K. (2007). The "Commons" *versus* the "Commodity": Alter-Globalization, Anti-Privatization and the Human Right to Water in the Global South. *Antipode*, *39*(3), 430-455.

Bark, R., Hatton-MacDonald, D., Connor, J., Crossman, N., & Jackson, S. (2011). Water Values (pp. 17-27). In CSIRO. *Water, Science and Solutions for Australia*. Melbourne: Commonwealth Scientific and Industrial Research Organization (CSIRO).

Batista-Medina, J. A. (2001). *El agua es de la tierra. La gestión comunal de un sistema de riego del nordeste de La Palma (Los Sauces)*. Madrid: Ministerio de Educación, Cultura y Deporte.

Bauer, C. J. (1997). Bringing Water Markets Down to Earth: The Political Economy of Water Rights in Chile, 1976-1995. *World Development*, *25*(5), 639-656.

Boelens, R., & Vos, J. (2012). The Danger of Naturalizing Water Policy Concepts: Water Productivity and Efficiency Discourse from Field Irrigation to Virtual Water Trade. *Agricultural Water Management*, *108*, 16-26.

Boelens, R., & Dávila, G. (Eds.) (1998). *Buscando la equidad. Concepciones sobre justicia y equidad en el riego campesino*. Assen, Países Bajos: Van Gorcum.

Briscoe, J. (2011). Water as an Economic Good: Old and New Concepts and Implications for Analysis and Implementation (pp. 61-65). In P. A. Wilderer (Ed.). *Treatise on Water Science (vol. I)*. Amsterdam: Elsevier.

Brown, F. L. (1997). Water Markets and Traditional Water Values: Merging Commodity and Community Perspectives. *Water International*, *22*(1), 2-5.

Brown, J. R., & Rivera, J. A. (2000). Acequias de Común: The Tension between Collective Action and Private Property Rights. In *Constituting the Commons: Crafting Sustainable Commons in the New Millennium. Eighth Biennal Conference of the International Association for the Study of Common Property*. Bloomington, Indiana, May 31-June 4.

Budds, J. (2012). La demanda, evaluación y asignación del agua en el contexto de escasez: un análisis del ciclo hidrosocial del valle del río Ligua, Chile. *Revista de Geografía Norte Grande*, *52*, 167-184.

Chalaune, P. (2009). Water, Wealth and Power: A Case Study from Upper Mustang of Nepal. *Occasional Papers in Sociology and Anthropology*, *11*, 104-125.

Chartres, C., & Varma, S. (2011). *Out of Water. From Abundance to Scarcity and How to Solve the World's Water Problems* (pp. 152-153). New Jersey: FT Press.

Draper, S. E., & Sehlke, G. (2005). Free Markets - A Stimulus or Impediment for Integrated Water Resources Management? In *2005 World Water and Environmental Resources Congress*, Anchorage, Alaska.

Gray, J. A. (1983). Water: A Resource Like Any Other? *Canadian Water Resources Journal*, *8*(4), 35-41.

Dellapenna, J. W. (2000). The Importance of Getting Names Right: The Myth of Markets for Water. *William & Mary Environmental Law and Policy Review*, *25*(2), 317-377.

Dellapenna, J. W. (2009). The Market Alternative (pp. 373-388). In J. W. Dellapenna & J. Gupta (Eds.). *The Evolution of Law and Politics of Water*. Berlin: Springer.

Dinar, A. (2000): Political Economy of Water Pricing Reforms (pp. 1-25). In A. Dinar, (Ed.). *The Political Economy of Water Pricing Reforms*. Washington, DC: The World Bank, Oxford University Press.

Fernald, A. G., Guldan, S. J., & Ochoa, C. G. (2010). Hydrological Impacts of Traditional Community Irrigation Systems in New Mexico. *Rural Connections*, May, 33-36.

Fonseca, C. (1998). El valor económico del agua. *Contexto*, *1*, 34-38.

Frank, R. H. (2002). *Microeconomía y conducta*. Madrid: McGraw-Hill.

Giménez-Casalduero, M., & Palerm-Viqueira, J. (2007). Organizaciones tradicionales de gestión del agua: importancia de su reconocimiento legal para su pervivencia. El caso de España. *Región y Sociedad*, *19*(38), 3-24.

Gleick, P. H. (1998). Water in Crisis: Paths to Sustainable Water Use. *Ecological Applications*, *8*(3), 571-579.

Gleick, P. H. (2000). The Changing Water Paradigm. A Look at Twenty-First Century Water Resources Development. *Water International*, *25*(1), 127-138.

Glennon, R. (2005). Water Scarcity, Marketing, and Privatization. *Texas Law Review*, *83*, 1873-1902.

Goldman Sachs (2008). *The Essentials of Investing in the Water Sector*. Goldman Sachs Global Investment Research. Recuperado de www.goldmansachs.com.

Guillet, D. (1992). *Covering Ground. Communal Water Management and the State in the Peruvian Highlands*. Ann Arbor, USA: The University of Michigan Press.

Guillet, D. (2006). Rethinking Irrigation Efficiency: Chain Irrigation in Northwestern Spain. *Human Ecology*, *34*(3), 305-329.

GWP (2000). *Integrated Water Resources Management*. Background Papers, 4. Estocolmo: Global Water Partnership. Technical Advisory Committee (TAC).

GWP (2010). *Integrated Water Resources Management*. Global Water Partnership. Recuperado de www.gwp.org.

Hardin, G. (1968). The Tragedy of the Commons. *Science*, *162*, 1243-1248.

Hellegers, P., & Perry, C. J. (2006). Can Irrigation Water Use Be Guided by Market Forces? *Water Resources Development*, *22*(1), 79-86.

Henderson, J., & Akers, M. (2008). Can Markets Improve Water Allocation in Rural America? *Economic Review (Federal Reserve Bank of Kansas City)*, *Fourth Quarter*, 97-117.

ICWE (1992). *The Dublin Statement on Water and Sustainable Development*. International Conference on Water and the Environment, Dublín, Irlanda, enero 26-31.

Ingram, H., & Brown, F. L. (1998). Valores mercantiles y comunitarios del agua: un estudio de caso en el suroeste de los Estados Unidos (pp. 123-130). En R. Boelens & G. Dávila (Eds.). *Buscando la equidad. Concepciones sobre justicia y equidad en el riego campesino*. Assen: Van Gorcum.

Jinapala, K., & Somaratne, P. G. (2002). Relevance of Cultural Knowledge and Practices for Efficient Water Management in Today's Context. Benchmark Conditions in Ruhuna River Basins in Sri Lanka (pp. 189-198). In K. Imbulana, P. Droogers, & I. W. Makin (Eds.). *World Water Assessment Programe. Sri Lanka Case Study. Ruhuna Basins*. Colombo, Sri Lanka: IWMI.

Lam, W. F. (1998). *Governing Irrigation Systems in Nepal. Institutions, Infrastructure, and Collective Action*. Oakland: ICS Press.

Libecap, G. D. (2009). The Tragedy of the Commons: Property Rights as Solutions to Resource and Environmental Problems. *The Australian Journal of Agriculture and Resource Economics*, *53*, 129-144.

Libecap, G. D. (2010). Water Woes. Using Markets to Quench the Thirst of the American West. *The Milken Institute Review*, *Fourth Quarter*, 59-68.

Mabry, J. B. (1996). The Ethnology of Local Irrigation (pp. 3-30). In J. B. Mabry (Ed.). *Canals and Communities. Small-Scale Irrigation Systems*. Tucson: The University of Arizona Press.

Mabry, J. B., & Cleveland, D. A. (1996). The Relevance of Indigenous Irrigation. A Comparative Analysis of Sustainability (pp. 227-260). In J. B. Mabry (Ed.). *Canals and Communities. Small Scale Irrigation.* Tucson: The University of Arizona Press.

MacDonnell, L. (2004). Water as Commodity. *Southwest Hydrology*, March/April, 16-18.

Maliva, R., & Missimer, T. (2012). *Arid Lands Water Evaluation and Management* (pp. 871-879). Berlin: Springer.

Martínez-Saldaña, T. (2012). Water Rituals on the Bravo/Grande River: A Transnational Political and Ecological Inheritance. *Journal of Political Ecology*, *19*, 57-69.

McNeill, D. (1998)."Water as an Economic Good. *Natural Resources Forum*, *22*(4), 253-261.

Maass, A. (1994). Estructuras de poder y cohesión social en los sistemas de regadío del oeste de los Estados Unidos y el Levante español (pp. 41-51). En J. Romero & C. Giménez (Eds.). *Regadíos y estructuras de poder*. Alicante: Instituto de Cultura Juan Gil-Albert.

Maass, A., & Anderson, R. L. (1978). …*And the Desert Shall Rejoice. Conflict, Growth, and Justice in Arid Environments.* Cambridge, USA: MIT Press.

Mehta, L. (2000). *Water for Twenty-First Century: Challenges and* Misconceptions. Brighton: Institute of Development Studies.

Mitchell, B. (1984). The Value of Water as Commodity. *Canadian Water Resources Journal*, *9*(2), 30-37.

Mochón, F. (1994). *Economía. Teoría y política*. Madrid: McGraw-Hill.

Morgan Stanley (November, 2012). *Water: The Next Big Commodity Wave?* Fidelity Investment Managers. Recuperado de https://www.morganstanleyfa.com/public/projectfiles/4d1056d8-af1a-4925-b68f-5871ad26d67b.pdf

Park, W.B., & Ha, K. (2012). Spring Water and Water Culture on Jeju Island. *Ground Water*, *50*(1), 159-165.

Peña, D. G. (1999). Cultural Landscapes and Biodiversity. The Ethnoecology of an Upper Rio Grande Watershed Commons (pp. 107-132). In V. Nazarea (Ed.). *Ethnoecology. Situated Knowledge/Located Lives*. Tucson: University of Arizona Press.

Peña, D. G. (2012a). Water, Place, Resilience, and Democracy. *New Clear Vision*. Recuperado de www.newclearvision.com.

Peña, D. G. (2012b). *Acequia: An Indigenous Tradition of Water Democracy*. Primer Congreso de Acequias de Colorado, San Luis, Colorado, octubre de 2012.

Poncet, Y., Álvarez Latorre, P., & Reyes-Serrano, H. F. (2011). Transformations Sociales, Transformations Spatiales: L'évolution du Système D'irrigation du Limarí (Chili). *Sécheresse*, *22*(4), 253-259.

Rahaman, M. M., & Varis, O. (2005). Integrated Water Resources Management: Evolution, Prospects and Future

Challenges. *Sustainability: Science, Practice, & Policy*, *1*(1), 15-21.

Rivadeneira, G., & Peralta-Proaño, J. (2009). *Derechos colectivos en la gestión del agua en Ecuador*. Cochabamba, Bolivia: Programa de Investigación Interdisciplinaria y Capacitación Interactiva sobre Gestión Local del Agua y Políticas Hídricas en la Región Andina.

Rivera, J. A. (1996). Irrigation Communities of the Upper Rio Grande Bioregion: Sustainable Resource Use in the Global Context. *Natural Resources Journal*, *36*, 731-760.

Robbins, L. (1994) [1935]. The Nature and Significance of Economic Science (pp. 83-110). In D. Hausman, D. *The Philosophy of Economics. An Anthology*. Cambridge: Cambridge University Press.

Rogers, P., De Silva, R., & Bathia, R. (2002). Water is an Economic Good: How to Use Prices to Promote Equity, Efficiency, and Sustainability. *Water Policy*, *4*, 1-17.

Savenije, H. (2002). Why Water in Not an Ordinary Economic Good, or Why the Girl is Special. *Physics and Chemistry of the Earth*, *27*, 741-744.

Savenije, H., & Van der Zaag, P. (2002). Water as an Economic Good and Demand Management. Paradigms with Pitfalls. *Water International*, *27*(1), 98-104.

Sengupta, N. (1991). *Managing Common Property. Irrigation in India and the Philippines*. Nueva Delhi: Sage.

Serageldin, I. (2010). *Water - An Increasingly Hot 'Commodity'*. Fidelity Investment Managers. November 2010. Recuperado de www.fidelityworldwide.com.

Siy, R. Y. (1982). *Community Resource Management. Lessons from the Zanjera*. Quezon City: University of Philippines Press.

Tang, S. Y. (1992). *Institutions and Collective Action. Self-Governance in Irrigation*. San Francisco, USA: ICS Press.

Taniyama, S. (2004). Water Use in the Asian Monsoon Region: Water is the Common Property of the Whole Community. *Paddy Water Environment*, *2*, 113-114.

Toro-Sánchez, F. J. (2007). El uso del agua en Níjar: implicaciones ambientales del modelo actual de gestión. *Revista de Estudios Regionales*, *83*, 145-176.

Trawick, P. (2001a). Successfully Governing the Commons: Principles of Social Organization in an Andean Irrigation System. *Human Ecology*, *29*(1), 1-25.

Trawick, P. (2001b). The Moral Economy of Water: Equity and Antiquity in the Andean Commons. *American Anthropologist*, *103*(2), 361-379.

Van der Zaag, P., & Savenije, H. (2006). *Water as an Economic Good: The Value of Prices and the Failure of Markets*. Delft: UNESCO-IHE Institute for Water Education.

Vargas, R. (2006). *La cultura del agua. Lecciones de la América Indígena*. Montevideo: UNESCO-Programa Hidrológico Internacional para América Latina y el Caribe.

Walker, B., & Salt, D. (2012). *Resilience Practice. Building Capacity to Absorb Disturbance and Maintain Function*. Berlin: Springer.

Ward, F. A., & Michelsen, A. (2002). The Economic Value of Water in Agriculture: Concepts and Policy Applications. *Water Policy*, *4*, 423-446.

Wateau, F. (2011). Water, Societies and Sustainability: A Few Anthropological Examples of Non-Market Water Values. *Policy and Society*, *30*, 257-265.

Whiteley, J. M., Ingram, H., & Perry, R. W. (Eds.) (2008). *Water, Place, & Equity*. Cambridge: The MIT Press.

World Bank (2004). *Water Resources Sector Strategy. Strategic Directions for World Bank Engagement*. Washington, DC: The World Bank, International Bank for Reconstruction and Development.

Zilberman, D., & Schoengold, K. (2005). The Use of Pricing and Markets for Water Allocation. *Canadian Water Resources Journal*, *30*(1), 47-54.

Institutional address of the author

Dr. José Antonio Batista-Medina

Universidad de La Laguna
Facultad de Geografía e Historia
Campus de Guajara
Apdo. 456
38200 San Cristóbal de La Laguna, Santa Cruz de Tenerife, España
Teléfono: +34 (922) 317 744
jbatisme@ull.es

Marcos Springs, San Andrés y Sauces, Canary Islands, Spain. Managed as Collective Property.

Photo: José Antonio Batista Medina.

Technical Note

Estimation of Monthly Runoff in Humid Climates Using Regression Models

• Daniel Francisco Campos-Aranda •
Profesor jubilado de la Universidad Autónoma de San Luis Potosí
*Autor de correspondencia

Abstract

Campos-Aranda, D. F. (March-April, 2015). Estimation of Monthly Runoff in Humid Climates Using Regression Models. *Water Technology and Sciences* (in Spanish), 6(2), 113-130.

Mathematical modeling of the rainfall-runoff relationship (RRR) is indispensable when temporal and spatial data are scarce. Ungauged basins is one example of a lack of data at sites of interest. And future records of induced or natural hydrological changes in a basin is an example of data that cannot be measured. In both cases, the use of a regional RRR model makes it possible to perform the needed evaluations. The simplest model for estimating monthly runoff volume is a monthly polynomial regression, which can model a linear or curved RRR. In addition, this method can include the delay in monthly runoff by averaging antecedent precipitation. The present study fitted a monthly regression model to the joint set of precipitation and runoff data from the Tancuilin and El Cardon hydrometric stations in Partial Hydrological Region 26 (Lower Panuco River), with records containing 33 an 37 years respectively. The study found that the monthly coefficients of the regression models can be regionalized based on the average runoff coefficient. The comparisons performed show that regionalized regression models provide an excellent estimation of monthly runoff, accurately reproducing average monthly values. They also provide a good approximation of the dispersion in small and medium basins located in humid climates.

Keywords: Linear regression, linear correlation coefficient, transport factor, monthly average runoff coefficient, statistical parameters, confidence interval of prediction, determination coefficient of prediction.

Resumen

Campos-Aranda, D. F. (marzo-abril, 2015). Estimación del escurrimiento mensual en climas húmedos con base en modelos de regresión. Tecnología y Ciencias del Agua*, 6(2), 113-130.*

La modelación matemática de la relación precipitación-escurrimiento (RPE) es indispensable debido a la escasez de datos tanto espacial como temporal. El establecimiento de la RPE en cuencas sin aforos es un ejemplo de la ausencia de datos en sitios de interés, y la estimación del registro futuro debido a cambios hidrológicos en la cuenca, inducidos o naturales, es un ejemplo de datos no factibles de medir. En ambos casos, contar con un modelo de la RPE regional permitirá realizar las evaluaciones necesarias. Para la estimación del volumen escurrido mensual, el modelo más simple que se puede establecer es la regresión polinomial mensual, la cual puede modelar una RPE lineal o curva. Además, tal planteamiento puede incluir el retraso mensual del escurrimiento, al promediar la precipitación antecedente. En este estudio se ajustó el modelo de regresión mensual a los datos conjuntos de precipitación y escurrimiento de las estaciones hidrométricas Tancuilín y El Cardón, de la Región Hidrológica 26 Parcial (Bajo Río Pánuco), con registros de 33 y 37 años, respectivamente. Se encontró que es posible regionalizar los coeficientes mensuales de los modelos de regresión con base en su coeficiente de escurrimiento promedio. Los contrastes realizados muestran que los modelos de regresión regionalizados permiten una excelente estimación del escurrimiento mensual, pues reproducen fielmente sus valores promedio mensuales y conducen a una buena aproximación de su dispersión, en cuencas pequeñas y medianas de climas húmedos.

***Palabras clave**: regresión lineal, coeficiente de correlación lineal, factor de transporte, coeficiente de escurrimiento promedio mensual, parámetros estadísticos, intervalo de confianza de la predicción, coeficiente de determinación de la predicción.*

Received: 16/07/2013
Accepted: 02/12/2014

Introduction

Modeling the rainfall-runoff relationship (RRR) can address several practical needs, for example, to evaluate water resources, forecast floods or estimate the impact of discharges on water quality. The primary reason for the need to use a RRR is the limitations related to hydrological measuring techniques, since we cannot currently measure all the physical processes involved in a basin because of existing spatial and temporal limitations in measuring capabilities. Therefore, available measurements always need to be extrapolated, for example, in ungauged basins where measurements do not exist or for the future which cannot be measured, in order to estimate the impact of induced or probable hydrological changes (Beven, 2001).

A basic way to classify different RRR modeling approaches is to distinguish between global and distributed models. Global models treat basins as units, with state variables corresponding to average values for the area. Distributed models divide the basin into elemental areas, or a grid composed of squares, with state variables associated with each one of the elements. A second distinction that can be made is between *deterministic* and *stochastic* models. Deterministic models produce a single response for each simulation performed using a series of inputs and parameters, whereas stochastic models permit a degree of randomness or uncertainty in the responses according to the variability in the input variables, parameters or boundary conditions (Beven, 2001). Other more detailed or exhaustive classifications of RRR models can be found in Haan, Johnson and Brakensiek (1982), Singh (1995), and Sene (2010).

Conceptual and *black box* models have proliferated the most since the use of RRR modeling began in the 1960s. Conceptual models use simplified mathematical representations of the main hydrological processes that occur in a basin, while black box models are entirely mathematical and based only on a basin's input and output measurements, without considering internal processes that transform rainfall into runoff (Jones, 1997; Shaw, Beven, Chappell, & Lamb, 2011).

Mimikou and Rao (1983), and Anderson and Burt (1985) report that the appropriate RRR model for a particular practical application depends primarily on the following factors: (1) time scale used for the modeling, (2) existence of measurements of the physical parameters of the basin, (3) type of hydrological data available and their reliability, and (5) time and human resources dedicated to the application. They also indicate that simple models are most appropriate when the time scale is large, such as one month.

When using RRR models to evaluate water resources, the following estimates can be performed: (1) deducing the value of missing records in a registry, (2) enlarging a registry from a gauging station before beginning operations, (3) calculating inputs into reservoirs when hydrometric stations are suspended, and (3) predicting monthly runoff in a sub-region in basins with and without gauges, along with the use of a model to predict monthly precipitation.

El *objetivo* de este trabajo consiste en expThe *objective* of this work is to present a detailed description of the general polynomial regression model with monthly periods, or "memory," where rainfall is an input and runoff is modeled as a response. For calibration purposes, the model is applied to the basins in Partial Hydrological Region 26 (Lower Panuco River) which have two hydrometric stations ¾Tancuilin in the state of San Luis Potosi, and El Cardon in the state of Veracruz. This work also indicates how to *regionalize* the fit parameters of the monthly regression models based on the average runoff coefficient.

The comparisons performed show that the regional regression models provide a good approximation of monthly runoff in small and medium basins in humid climates.

Theoretical Supporting Concepts

General regression model

This model was proposed and applied by Mimikou and Rao (1983) and may be the simplest mathematical model that can be used to reproduce monthly RRR, albeit linear or curved. Its expression is:

$$V_{i,j} = \sum_{k=0}^{K} \beta_{j,k} \cdot \left(\frac{P_{i,j} + P_{i,j-1} + \cdots + P_{i,j-m}}{m+1} \right)^{k} \qquad (1)$$

where $V_{i,j}$ is monthly runoff for the *nth* year, with *i* ranging from 1 to *n*, which is the size of the set of records processed, and *j* is the number of the month, where 1 = January and 12 = December. It is useful to express $V_{i,j}$ in equation (1) in millimeters, which is equal to dividing its value, in thousands of cubic meters ($10^3 \cdot m^3$), by the area of the basin *A* ,in km². $P_{i,j}$ is the monthly precipitation *representative* of the basin, in millimeters. *K* and *m* are the parameters of the model and $\beta_{j,k}$ are the regression coefficients of the model, which are obtained with the least squares fit of the residuals. Sugawara (1992) indicates that even in basins with a good rainfall station network, the weighting factors used to obtain $P_{i,j}$ should not be based on their geometric properties but rather on meteorological conditions, and can be estimated by finding the best reproduction of observed runoff.

Selection of the Model's Parameters

Los parámetros *K* y *m* definen la estructura del modelo. El primero determina su *orden* como ecuación de regresión polinomial y el segundo su *memoria* con respecto a la precipitación mensual. Entonces, para estimar el valor de *K* se debe establecer la *relación funcional* entre el escurrimiento y la precipitación de cada mes; el primero como la variable dependiente en las ordenadas y la segunda como la variable independiente en las abscisas. Como tal relación pueden ser lineal o curva, en el primer caso *K* = 1 Parameters *K* and *m* define the structure of the model, where *K* determines the *order* of polynomial regression equation and *m* the memory corresponding to monthly precipitation. To estimate the value of *K*, the *functional relationship* needs to be established between runoff and precipitation for each month, where runoff is the dependent variable on the *y*-axis and precipitation is the independent variable on the *x*-axis. This relation can be linear (where $K = 1$) or curved (where $K > 1$). Mimikou and Rao (1983) indicate that it is uncommon to find different *K* values for each month, and therefore this parameter is considered to be a characteristic of the basins which describes the monthly behavior of the RRR.

When a monthly functional relationship has a large dispersion, the relation between $V_{i,j}$ and the average precipitation for months *j*, *j*-1, . . . , *j*-*m* should be determined, where *m* indicates the memory of the process for month *j*. For small basins, $m = 1$ is usually sufficient to improve the relationship. Mimikou and Rao (1983) reported that when the functional relationship is not improved by using the average of the monthly precipitation and that of the preceding month, then the use of the model defined by equation (1) is not recommended to reproduce the RRR.

Regression Coefficients and Correlation of the Functional Relationship

When *K*= 1, equation (1) is a straight line, where $\beta_{j,0}$ is the y-axis at the origin and $\beta_{j,1}$

is the slope of the line, whose least squares fitting of the residuals are expressed as (Draper & Smith, 1998; Ryan, 1998; Montgomery, Peck, & Vining, 2002; Campos-Aranda, 2003):

$$\beta_{j,1} = \frac{\sum_{i=1}^{n} P_{i,j} \cdot V_{i,j} - n \cdot \overline{P}_j \cdot \overline{V}_j}{\sum_{i=1}^{n} \left(P_{i,j}\right)^2 - n \cdot \left(\overline{P}_j\right)^2} \tag{2}$$

$$\beta_{j,0} = \overline{V}_j - \beta_{j,1} \cdot \overline{P}_j \tag{3}$$

In the above equations, $P_{i,j}$ is the monthly precipitation when $m = 0$ and can be the average of the said month and the previous month, when $m = 1$. $\overline{P}_j$ and $\overline{V}_j$ are average monthly precipitation and runoff values, both in millimeters. The quantitative measurement of the functional relationship between rainfall and runoff is obtained from the linear correlation coefficient (r_{xy}), which determines the degree of association or dependence between the two variables, with 0 for totally dispersed points and 1 when they are all along a straight line. This is expressed as:

$$\left(r_{xy}\right)_j = \frac{\sum_{i=1}^{n}\left(P_{i,j} - \overline{P}_j\right) \cdot \left(V_{i,j} - \overline{V}_j\right)}{\left[\sum_{i=1}^{n}\left(P_{i,j} - \overline{P}_j\right)^2 \cdot \sum_{i=1}^{n}\left(V_{i,j} - \overline{V}_j\right)^2\right]^{1/2}} \tag{4}$$

When the functional relationship between rainfall and runoff is curved ($K>1$), a parabolic ($K = 2$) or cubic ($K = 3$) *polynomial regression* model will need to be fitted, whose solution is obtained with the matrix proposed by Draper and Smith (1998), Ryan (1998), Montgomery *et al.* (2002) and Campos-Aranda (2003), as well as the determination coefficient ($R^2 = r_{xy}^2$), which indicates how much of the variability of the dependent variable is explained by the polynomial regression.

Confidence Interval of the Predictions

An important application of the RRR, or linear regression model, is to predict the values of the dependent variable (V_j) that correspond to a certain specific value of the regressor variable (P_j). This includes its probable variability interval, which is associated with a particular confidence level (usually 95%). The interval of each prediction is obtained from the statistic of the Student's *t*-distribution, relative to a level of significance α = 5% and $\nu = n - 2$ degrees of freedom with a two-tailed test. It is expressed as (Draper & Smith, 1998; Ryan, 1998; Montgomery *et al.*, 2002):

$$\hat{V}_j \mp t_{\alpha,\nu}\left[CMR_j\left(1 + \frac{1}{n} + \frac{\left(P_j - \overline{P}_j\right)^2}{var(P_j)}\right)\right]^{1/2} \tag{5}$$

in which:

$$RMS_j = \frac{1}{n-2}\sum_{i=1}^{n}\left(V_{i,j} - \hat{V}_{i,j}\right)^2 \tag{6}$$

$$var(P_j) = \sum_{i=1}^{n}\left(P_{i,j} - \overline{P}_j\right)^2 \tag{7}$$

RMS_j is the residual mean square and *var* (P_j) is the variance of the monthly precipitation. $\hat{V}_j$ and $\hat{V}_{i,j}$ are estimates of monthly runoff obtained with equation (1). The computational algorithm proposed by Zelen and Severo (1972) was used To calculate $t_{\alpha,\nu}$, expressed as:

$$t_{\alpha,\nu} = x_p + \frac{g_1(x_p)}{\nu} + \frac{g_2(x_p)}{\nu^2} + \frac{g_3(x_p)}{\nu^3} + \frac{g_4(x_p)}{\nu^4} \tag{8}$$

$$g_1(x) = \left(x^3 + x\right)/4$$

$$g_2(x) = \left(5x^5 + 16x^3 + 3x\right)/96$$

$$g_3(x) = \left(3x^7 + 19x^5 + 17x^3 - 15x\right)/384$$

$$g_4(x)=\left(79x^9+776x^7+1482x^5-1920x^3-945x\right)/92160$$

where x_p is the normal standardized variable, whose levels of significance (α) at 10, 5 and 1% are 1.64485, 1.95996 and 2.57583, with a two-tailed test; v are the degrees of freedom. In equation (5), if the first addend is suppressed (that is, the one, then the expression is obtained for the confidence interval of the mean response or regression line, thereby eliminating an amount equal to RMS_j (Haan, 1977; Ryan, 1998; Draper & Smith, 1998; Montgomery *et al.*, 2002). The confidence intervals of the mean response are indicated with a dotted line and those related to the prediction with a solid line.

Predictive Capacity of the Linear Regression

The main hypotheses or premises inherent in the linear regression are: (1) the relationship between $V_{i,j}$ and $P_{i,j}$ is linear; (2) the errors or *residuals* $\left(e_{i,j}=V_{i,j}-\hat{V}_{i,j}\right)$ have a mean of 0 and a constant variance; (3) the errors are not correlated, and; (4) the errors have a normal distribution. The analysis of the residuals enable verifying the above hypothesis. In addition, atypical or disperse values can be detected by studying scaled residuals, that is, observations that are separate from the rest of the data and that affect the quality of the fit of the regression line. A logical scaling consists of dividing the residuals ($e_{i,j}$) by the root square of the RMS$_{j,}$ which is the same as standardizing the residuals which now have a mean of zero and a variance close to 1. A standardized residual over 2 or 3 indicates a potential atypical value. The scaling can be improved by dividing the residuals by the exact standard deviation of the n-th residual, which results in the *studentized residuals*, which is generally expressed as (Draper & Smith, 1998; Montgomery *et al.*, 2002):

$$r_{i,j}=\frac{e_{i,j}}{\sqrt{RMS_j\left(1-h_{ii}\right)}} \tag{9}$$

The RMS_j is obtained using equation (6) and h_{ii} is the n-th element on the main diagonal in the Hat Matrix, which gets its name because it transforms the vector of observed magnitudes (y_i) into a vector of estimated values ($\hat{y}_i$), as shown in equation (10). The variable h_{ii} measures the influence of the n-th point in the fit. For a simple linear regression, the values vary from $1/n$ to 1, at end points, which strongly influence the fit (Clarke, 1994). In matrix notation, the solution of the linear regression obtained by the least squares of the residuals for the vector of the estimated values is:

$$\hat{\mathbf{y}}=\mathbf{X}\hat{\beta}=\mathbf{X}\left(\mathbf{X}'\mathbf{X}\right)^{-1}\mathbf{X}'\mathbf{y}=\mathbf{Hy} \tag{10}$$

Then, matrix $\mathbf{H}=\mathbf{X}(\mathbf{X'X})^{-1}\mathbf{X'}$ has n rows and n columns, it is symmetric ($\mathbf{H'}=\mathbf{H}$) and is idempotent ($\mathbf{HH}=\mathbf{H}$). The elements on the main diagonal can be calculated using the following equation:

$$h_{ii}=\mathbf{x'}_i\left(\mathbf{X}'\mathbf{X}\right)^{-1}\mathbf{x}_i \tag{11}$$

where $\mathbf{x'}_I$ is the nth row in matrix $\mathbf{X}$. For the particular case of a linear regression with only one regressor ($x_i=P_{i,j}$), the expression of h_{ii} corresponds to the two last addends in equation (5), that is (Montgomery *et al.*, 2002):

$$\left(h_{ii}\right)_j=\frac{1}{n}+\frac{\left(P_{i,j}-\overline{P}_j\right)^2}{var(P_j)} \tag{12}$$

in which $var(P_j)$ is calculated with equation (7). A third type of scaled residuals is *eliminated residuals* ($e_{(i)}$) or *PRESS residuals*, which takes its name because it enables calculating this statistic. The PRESS residuals are obtained by eliminating the n-th observation, fitting the regression model to the $n - 1$ remaining data and calculating the y_i corresponding to the omitted observation, whose expression is (Montgomery *et al.*, 2002):

$$[e_{(i)}]_j = [y_i - \hat{y}_{(i)}]_j = \frac{e_{i,j}}{1-\left(h_{ii}\right)_j} \qquad (13)$$

The *PRESS* statistic (Prediction Error Sum of Squares) is defined as the sum of the squared PRESS residuals and measures how well the regression model predicts new data. Its formula is (Montgomery *et al.*, 2002):

$$PRESS_j = \sum_{i=1}^{n}\left[\frac{e_{i,j}}{1-\left(h_{ii}\right)_j}\right]^2 \qquad (14)$$

An important application of the PRESS statistic is the comparison of regression models. In general, a model with a lower PRESS is preferable to one with a higher value. In addition, the PRESS statistic can be used to calculate an indicator similar to the determination coefficient (R^2) for predictions, whose expression is (Montgomery *et al.*, 2002):

$$(R^2_{predic})_j = \left[1 - \frac{PRESS_j}{var(V_j)}\right]\cdot 100 \qquad (15)$$

The denominator $var(V_j)$ is calculated using equation (7). The R^2_{predic} statistic numerically determines the predictive capacity of the regression model, defining the percentage of the variability that will be explained when predictions are made, as compared to the percentage of the variability in the original data explained by the least squares fit [$R^2 = 100\cdot(r_{xy})^2$].

Monthly Precipitaiton Transport Factor

The rain gauge station with monthly precipitation records considered representative of precipitation in the basin is designated as the *base rain gauge station*. In small basins, this station usually is not located near its center of gravity (cg) and therefore its annual mean precipitation value (MAP_{base}) is different than that which is estimated for the basin (MAP_{basin}); for example, with annual mean isohyet curves exactly at its *cg*. Thus, the transport or corrective factor (*Cf*) for monthly precipitation for the base station is:

$$Cf = \frac{MAP_{basin}}{MAP_{base}} \qquad (16)$$

Average monthly Runoff Coefficients

Mimikou and Rao (1983) used the monthly average runoff coefficient (*Ce*) to establish relationships with regressions coefficients, which are valid within a geographic region. Campos-Aranda (2013) found that the *Ce* are similar among sub-regions or geographic areas. Therefore, the *Ce* will be used to *regionalize* the results from the monthly models. Having defined the area *A* of the basin, in km^2 (that is, in millions of m^2) and the corrective factor (*Cf*), then the formula for each *Ce* will be:

$$\left(Ce\right)_j = \frac{\overline{V}_j}{A\cdot Cf\cdot \overline{Pb}_j} \qquad (17)$$

where $\overline{V}_j$ is the average monthly runoff volume in thousands of m^3 and $\overline{Pb}_j$ is the monthly average precipitation at the base station, in millimeters.

Processed Hydrological Information

Tancuilin Hydrometric Station

General Characteristics

This station is located in the lower basin of the Panuco River (Hydrological Region 26) in the state of San Luis Potosi. The area of the basin is 321 km^2, the MAP_{basin} is 2950 millimeters (INEGI, 1980) and it has

Table 1. General characteristics and available records from the hydrometric and rain gauge stations processed.

Hydrometric Rain Gauge	Code	North Latitude	WG Longitude	Start of registry	End of registry	Incomplete or missing years
Tancuilín	26291	21° 23′	98° 52′	July, 1960	December, 2002	1995, 1996, 2000
Tancuilín	24084	21° 23′	98° 52′	January, 1961	October, 2012	1986-2001 (1985)
El Cardón	26286	21° 23′	98° 28′	June, 1960	December, 2002	1995, 1998, 1999, 2000
El Cardón	30046	21° 23′	98° 28′	September, 1960	November, 2012	1994,1997-2000
San Martín Chalchicuautla	24009	21° 21′	98° 40′	January, 1961	November, 2012	1964-1969 (1968,1993)
Chapulhuacanito	24122	21° 14′	98° 46′	September, 1972	November, 2012	1977, 1985 (1978)

only one rain gauge station (with the same name), located at the gauging site. Figure 1 shows the location of both stations and the corresponding basin. All the hydrometric information used from this station came from the *BANDAS* system (IMTA, 2002). The rain gauge information was obtained from the offices of the National Water Commission (Conagua, Spanish acronym) in San Luis Potosi. Table 1 shows the incomplete and missing years for both stations.

Deduction of Missing Monthly Data

For all the rain gauge stations, the missing monthly data were considered equal to the *mode* of the available total registry, obtained by fitting a two-parameter Gamma distribution (Campos-Aranda, 2005). For the Tancuilin hydrometric station, 1961 to 1994 was determined to be the longest common period containing monthly runoff and rainfall records, with 1985 missing (33 years). This rainfall registry results in an MAP_{basin} of 240.9 mm, and therefore Cf is 1.3164.

Homogeneity tests

The statistical quality of the annual runoff and rainfall values from the set of registries was evaluated by the Von Neumann (VN) test, which is a general test that detects non-randomness versus non-specified deterministic components. In addition, two persistence tests were applied [Anderson (PA) and Sneyers (PS)] as well as two trend tests [Spearman (TS) and Kendall (TK)]. The Cramer test (PC) for differences in means was also applied, with two sub-periods equal to half of the registry (one at the beginning and one at the end). Lastly, the Bartlett variability test (VB) was applied by dividing each registry into three or four sub-periods depending on the size of the registry (WMO, 1971; Ruiz-Maya, 1977; Buishand, 1982; Campos-Aranda, 2005).

For the common registries from the Tancuiolin hydrometric and rain gauge stations, the results from the seven statistical tests (Table 2) indicate they are homogeneous, that is, they do not have deterministic components.

Functional Relationships

Figures 2 through 5 show the functional relationships for the months of January, February and July. These are shown to be linear, as well as the rest of the months. Table 3 presents the correlation coefficients (r_{xy}) and their corresponding determination coefficients (R^2, R^2_{predic}) obtained from the linear fitting of the least squares of the residuals (equations (4) and (15)). Dispersed values were not eliminated from any of the fits and, therefore, the number (n) of pairs was always 33.

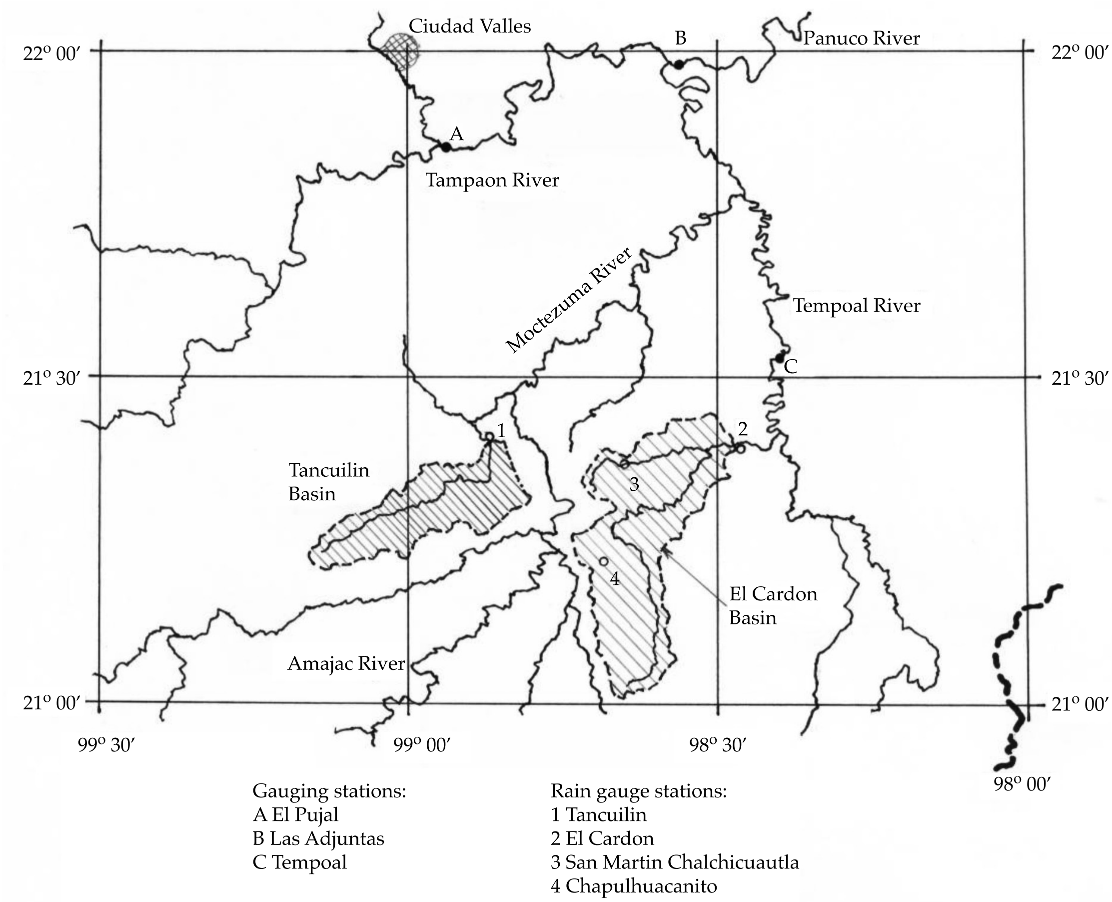


Figure 1. Location of the basins and rain gauges in the Tancuilin and El Cardon hydrometric stations, within Partial Hydrological Region 26 (Lower Panuco River).

Table 2. Description of registries, characteristic magnitudes and results from the homogeneity tests.

Hydrometric (m³) rain gauge (mm)	Registry period (years)	Statistical Parameters*				Statistical tests							
		M	SD	Cv	r_1	VN	PA	PS	TK	TS	PC_1	PC_2	VB
Tancuilín	1961-1994 (33)	453 444.7	200 813.2	0.443	-0.026	H	H	H	H	H	H	H	H
Tancuilín	1961-1994 (33)	2 240.9	519.5	0.232	0.092	H	H	H	H	H	H	H	H
El Cardón	1961-1997 (37)	391 219.3	183 543.9	0.469	0.179	H	H	NH	H	H	H	H	H
El Cardón (original)	1961-1997 (37)	1 228.7	317.4	0.258	0.240	H	H	NH	H	H	H	H	H
El Cardón (integrado)	1961-1997 (37)	1 580.9	353.2	0.223	0.134	H	H	H	H	H	H	H	H
San M. Chalchicuautla	1961-1997 (37)	1 471.4	361.8	0.246	0.351	NH	NH	NH	H	H	H	H	H
Chapulhuacanito	1973-1997 (25)	1 908.1	455.4	0.239	-0.167	H	H	H	H	H	H	H	H

* Legend:

M *arithmetic mean in* m³ or mm.

SD Standard deviation in m³ or mm.

Cv Coefficient of variation, dimensionless.

r_1 first-order serial correlation coefficient, dimensionless.

H homogenous.

NH not homogeneous.

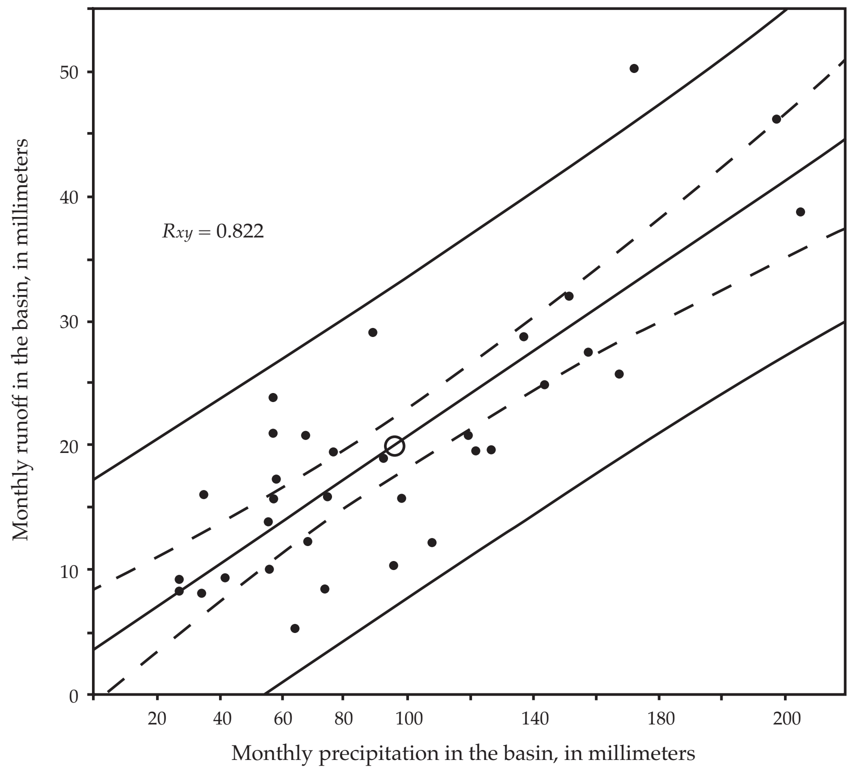


Figure 2. Functional rainfall-runoff relationship for the month of January in the Tancuilin hydrometric station.

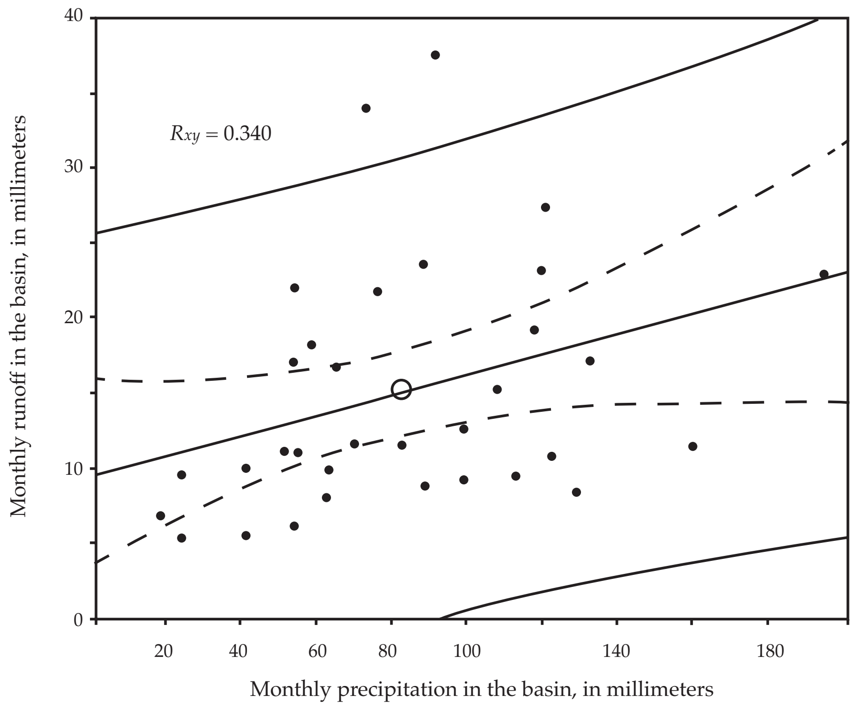


Figure 3. Functional rainfall-runoff relationship for the month of February in the Tancuilin hydrometric station.

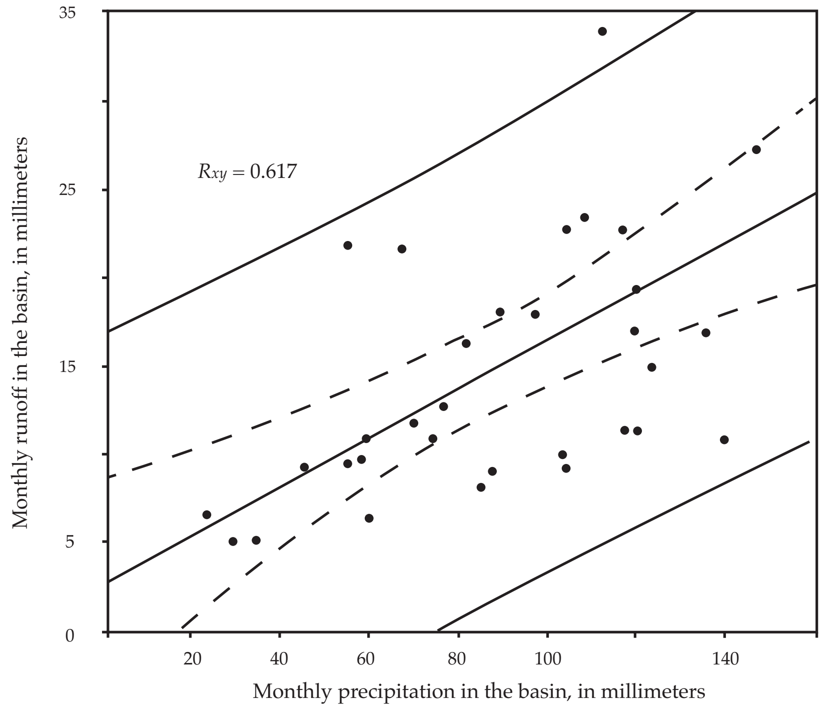


Figure 4. Functional rainfall-runoff relationship for the month of February in the Tancuilin hydrometric station.

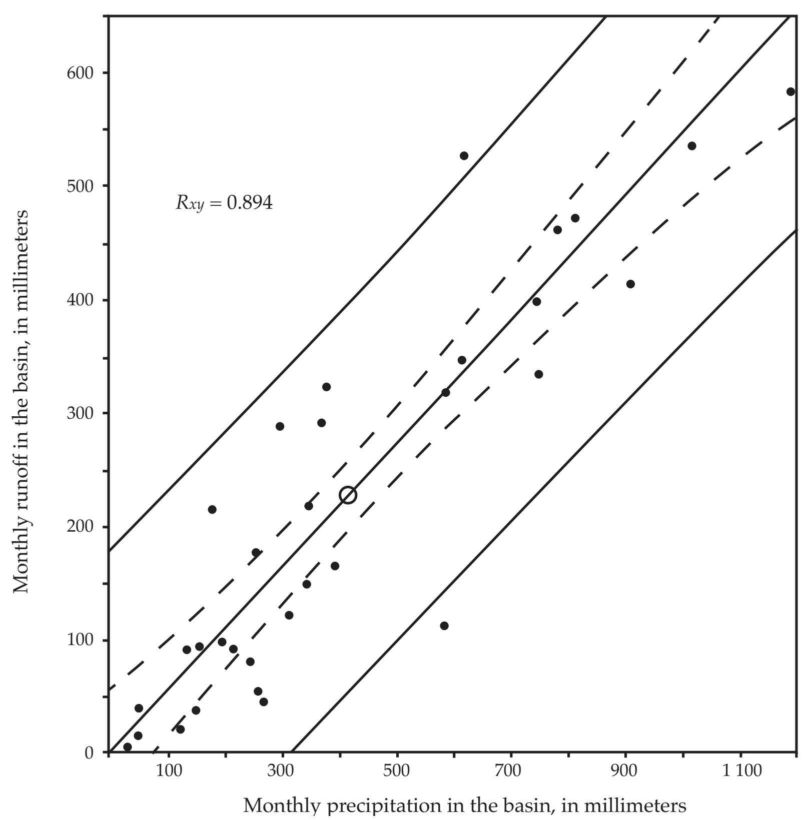


Figure 5. Functional rainfall-runoff relationship for the month of July in the Tancuilin hydrometric station.

Table 3. Monthly correlation coefficients (r_{xy}) and determination (R^2) coefficient between monthly runoff and rainfall in the hydrometric stations indicated.

Hydrometric station	J	F	M	A	M′	J	J′	A′	S	O	N	D
Tancuilín (r_{xy} con $m = 0$)	0.822	0.340	0.712	0.567	0.581	0.727	0.894	0.799	0.761	0.473	0.589	0.124
Tancuilín (r_{xy} con $m = 1$)	-	0.617	-	0.614	0.517	-	-	-	-	0.556	0.366	0.635
Tancuilín (R^2)	0.676	0.380	0.507	0.375	0.337	0.529	0.799	0.638	0.580	0.309	0.347	0.404
Tancuilín $(R^2)_{predic}$	0.630	0.286	0.403	0.250	0.161	0.407	0.771	0.586	0.509	0.176	0.003	0.263
El Cardón (r_{xy} con $m = 0$)	0.717	0.367	0.814	0.604	0.569	0.886	0.856	0.830	0.893	0.711	0.638	0.617
El Cardón (r_{xy} con $m = 1$)	-	0.734	-	0.722	0.547	-	-	-	-	0.482	0.581	0.755
El Cardón (R^2)	0.514	0.539	0.662	0.521	0.324	0.785	0.732	0.688	0.797	0.505	0.407	0.570
El Cardón $(R^2)_{predic}$	0.312	0.494	0.602	0.420	0.217	0.736	0.691	0.636	0.772	0.322	0.103	0.526

Table 4. Regression coefficients ($\beta_{j,k}$) for monthly models corresponding to the hydrometric stations indicated.

Hydrometric station (regression coefficient)	J	F	M	A	M′	J	J′	A′	S	O	N	D
Tancuilín ($\beta_{j,0}$)	3.730	2.679	5.284	5.008	9.499	-32.355	3.866	-3.011	-31.244	-38.410	9.360	-4.007
Tancuilín ($\beta_{j,1}$)	0.168	0.140	0.102	0.151	0.113	0.496	0.538	0.525	0.725	0.563	0.407	0.313
El Cardón ($\beta_{j,0}$)	3.634	-0.706	2.349	-4.696	-4.690	-39.655	-4.466	-10.540	-57.188	-13.817	16.926	1.699
El Cardón ($\beta_{j,1}$)	0.234	0.271	0.175	0.303	0.215	0.411	0.431	0.359	0.664	0.676	0.219	0.299

Table 5. Monthly average runoff coefficient (*Ce*) for the hydrometric stations indicated.

Hydrometric station	J	F	M	A	M′	J	J′	A′	S	O	N	D	Annual
Tancuilín	0.207	0.185	0.162	0.180	0.152	0.414	0.548	0.518	0.672	0.730	0.465	0.383	0.466
El Cardón	0.300	0.289	0.219	0.191	0.182	0.267	0.411	0.311	0.493	0.592	0.405	0.426	0.351

For the Tancuilin hydrometric station, the lowest values of r_{xy} are observed in February, April and May and from October through December. To define the lowest value of r_{xy} that is statistically different than zero, a test based on the Student *t*-distribution was applied (Yevjevich, 1972) with a significance level α of 5%, resulting in a value of $r_{xy} = 0.34$ for $n = 33$. The values of r_{xy} obtained in February and December are not statistically different than zero. Therefore, for these months and the rest of those with low r_{xy} values, $m = 1$ will be used to improve the correlation.

Figure 4 shows the new functional relationship for February, whose r_{xy} is now 0.617. In December a notable improvement in the correlation is also observed, and a considerable improvement is seen even in April and October; unlike May and November. In the figures, the confidence limits of the mean response are drawn with dotted lines and the predictions (equation (5) with solid lines.

Regression and Runoff Coefficients

Having defined the memory of the model for each month, Table 4 shows the regression coefficients obtained by fitting the least squares of the residuals of equation (1) (equations (2) and (3)), with $n = 33$ from the Tancuilin gauging station.

For simultaneous monthly runoff and precipitation in Tancuilin, the application of equation (17) resulted in the *Ce* values shown in Table 5. These values correspond to the average of the 33 years and have been indicated in the functional relationships (Figures 2, 3 and 5) by a circle above the regression line.

El Cardon Hydrometric Station

General Characteristics

This station is located in the Temporal River system in Hydrological Region 26 (lower Panuco), in the state of Veracruz. The area of the basin is 609 km^2 and the MAP_{basin} is 1 750 millimeters (INEGI, 1980). The basin contains two rain gauge stations and a rain gauge is located in the gauging station. Figure 1 shows the basin and the location of its rain gauge stations. The hydrometric information was taken from the *BANDAS* SYSTEM (IMTA, 2002) and the rain gauge information was obtained from the San Luis Potosi division of Conagua. The years 1961 to 1997 ($n = 37$) represented the common period for the monthly rainfall and runoff data, since the hydrometric registry from 1998 to 2000 is incomplete. According to the available precipitation registries (see Table 1) and the Thiessen polygons, the percentages of the basin area corresponding to each rain gauge are 20% for El Cardon from 1961 to 1972 and 80% for San Martin Chalchicuautla for the same period. The percentages from 1973 to 1997 were 20% for El Cardon, 30% for San Martín Chalchicuautla and 50% for Chapulhuacanito. The integrated registry has a MAP_{basin} of 1 580.9 mm, and therefore Cf is 1.1070.

Deduction of Missing Data

As has already been indicated, the missing monthly data at these three rain gauge stations were taken to be equal to the *mode* estimated with all the available data for the corresponding month and with a two-parameter Gamma function (Campos-Aranda, 2005). For San Martín Chalchicuautla, the missing years were estimated with a linear regression model based on the annual values and values from the El Cardon station, with 31 data pairs. An r_{xy} of 0.820 was obtained without eliminating disperse values. The model was used to calculate missing annual values from 1968 and 1993 and the relation with the magnitude of El Cardon was determined. Each relation found was applied to the monthly values to obtain rainfall in San Martín Chalchicuautla for the same year. This procedure was also used to estimate missing monthly values for the year 1978 in Chapulhuacanito based on the registry from San Martín Chalchicuautla. A correlation of 0.819 was identified with 23 data pairs. The missing runoff volume in December, 1995 was estimated based on the mode of 37 values, including the year 2001.

Homogeneity Tests

Table 2 presents the results from applying the statistical tests to the annual runoff volume in the El Cardon station and to the four annual precipitation volumes used to estimate the regime that was representative of monthly rainfall in the basin corresponding to the gauging station mentioned. Slight persistence was found in the original precipitation registry in El Cardon. This was detected using only the Sneyers test. According to the three initial tests, persistence was present in the registry from San Martín Chalchicuautla. This station could not be substituted, nevertheless since its registry is small it is not expected to have a notable impact on the registry created for the basin.

Functional Relationships

Figures 6, 7 and 8 show the functional relationships for the months of January,

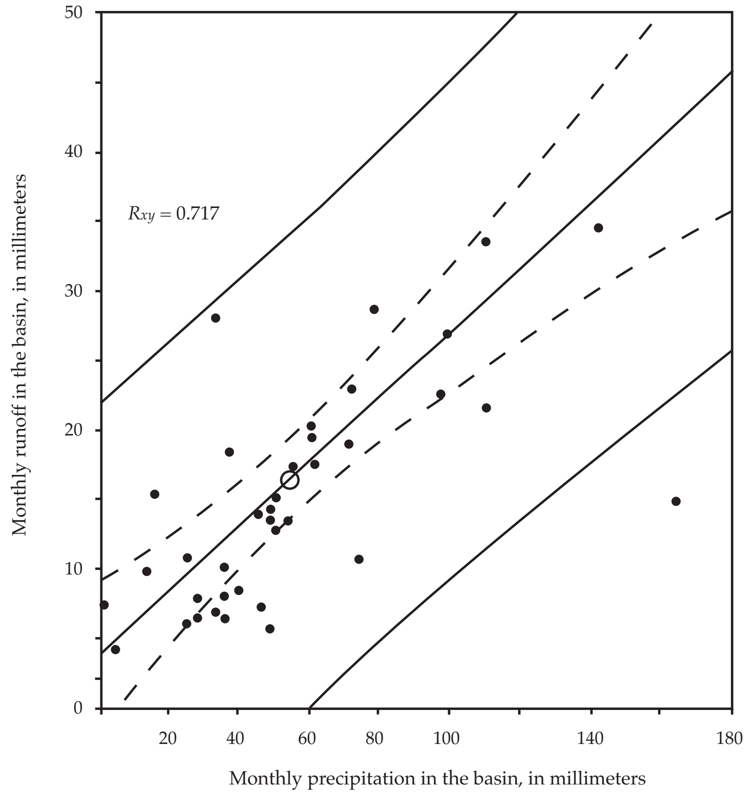


Figure 6. Functional rainfall-runoff relationship for the month of January in the El Cardon hydrometric station.

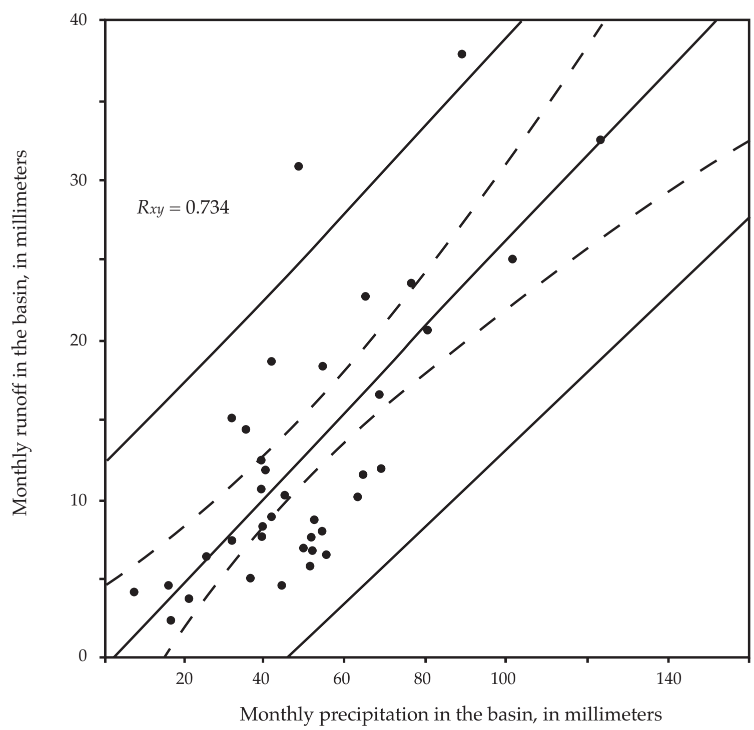


Figure 7. Functional rainfall-runoff relationship for the month of February in the El Cardon hydrometric station.

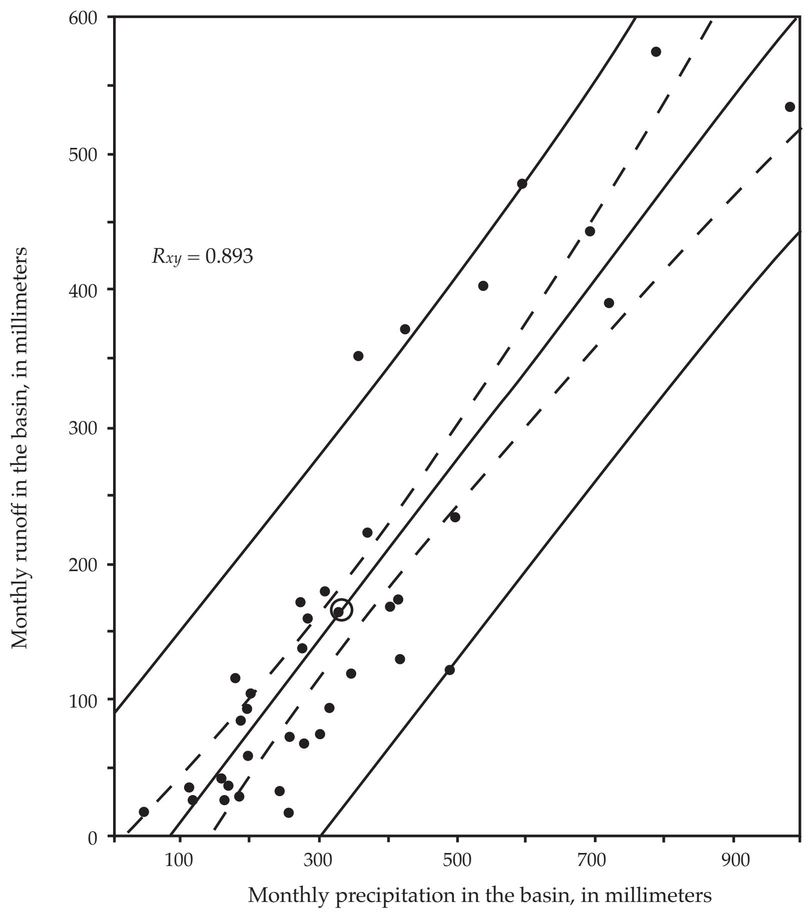


Figure 8. Functional rainfall-runoff relationship for the month of September in the El Cardon hydrometric station.

February and September. Linear models were defined for these months as well as for the rest of the months. Table 3 shows the monthly values of r_{xy}, where the lowest magnitudes can be observed in February, April, May and October through December. For n = 37 and α = 5%, r_{xy} was determined to be statistically different than zero and larger than 0.32 (Yevjevich, 1972). Therefore, all the r_{xy} corresponding to El Cardon are acceptable, but could be improved with $m = 1$. This would be achieved only in February, April and December.

Regression and Runoff Coefficients

Table 4 shows the regression coefficients corresponding to the monthly models defined for El Cardon gauging station. Lastly, Table 5 shows the respective runoff coefficients estimated with equation (17), which have been indicated in the functional relationships (Figures 6 and 8) by a circle above the regression line.

Analysis of the Results

General Comments

The monthly correlation coefficients (r_{xy}) shown in Table 3 range from a maximum of 0.894 during the rainy season to a minimum of 0.569 during the month of May. These magnitudes can be considered acceptable only to continue the regional analyses and illustrate the application of the regional regression models to estimate monthly runoff. Nevertheless, the values of r_{xy} should be over 0.92 for all the months, as found by Mimikou and Rao (1983), to obtain more congruent results or less dispersion than what will be shown herein.

In the results in Table 3, the two following deficiencies are implicit: (1) for the Tancuilin hydrometric station, its only rain gauge station is not located within the basin; and (2) in the El Cardon hydrometric basin, the two rain gauge stations available are located in the lower third of the area, therefore no rainfall registries are available for the mountainous region (Figure 1).

Although the basins in which the Tancuilin and El Cardon gauging stations are located are nearby, they have quite different estimated annual mean precipitations, with values of 2 950 and 1 750, respectively, This is reflected by the magnitudes of the monthly average runoff coefficients (*Ce*) shown in Table 5.

Regionalization of the Results

Figures 9 and 10 present the graphs of the relationships between the monthly average runoff coefficients (*Ce*) and the y-axis at the origin ($\beta_{j,0}$), as well as the slope ($\beta_{j,1}$) of the functional relationships determined for the Tancuilin and El Cardon hydrometric stations. The graph of Ce_j versus $\beta_{j,0}$ presents a large dispersion and its linear relationship has a linear correlation coefficient (r_{xy}) of 0.593, with 22 data pairs, when eliminating June and September in the El Cardon station registry. An r_{xy} of 0.698 is obtained by also eliminating November in El Cardon and June in Tancuilin, with virtually the same linear equation, which is:

$$\beta_{j,0} = 13.467 - 47.426 \cdot Ce_j \qquad (7)$$

Meanwhile, the graph of Ce_j versus $\beta_{j,1}$ presents and excellent linear relationship, with an r_{xy} of 0.920 with 22 data pairs when

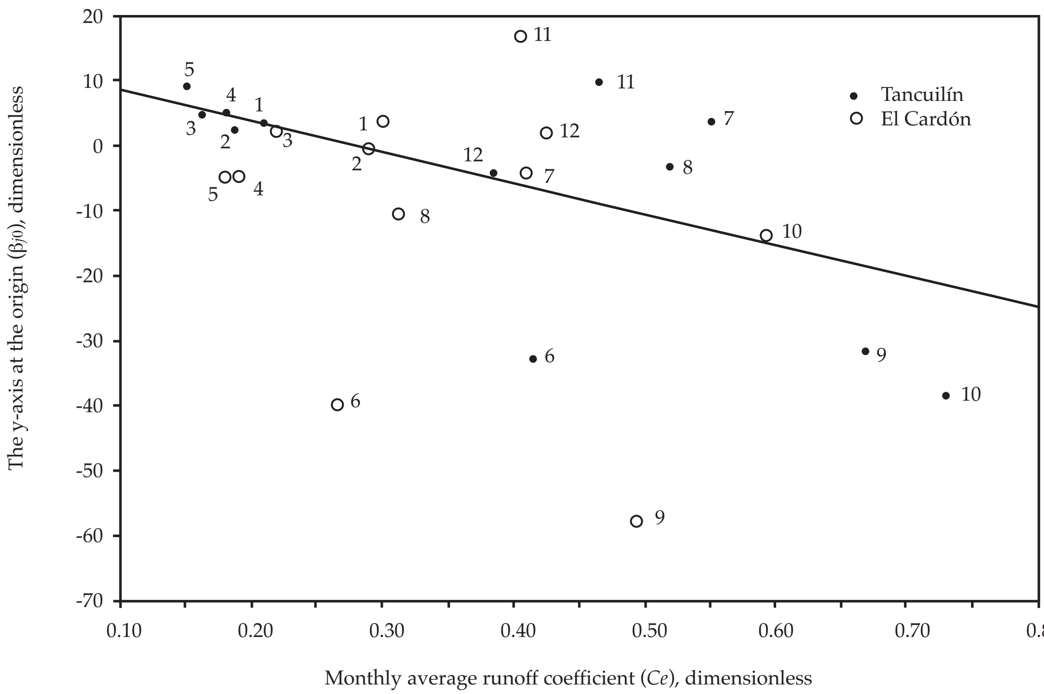


Figure 9. Regional dispersion diagram of the y-axis at the origin ($\beta_{j,0}$) of the regression models.

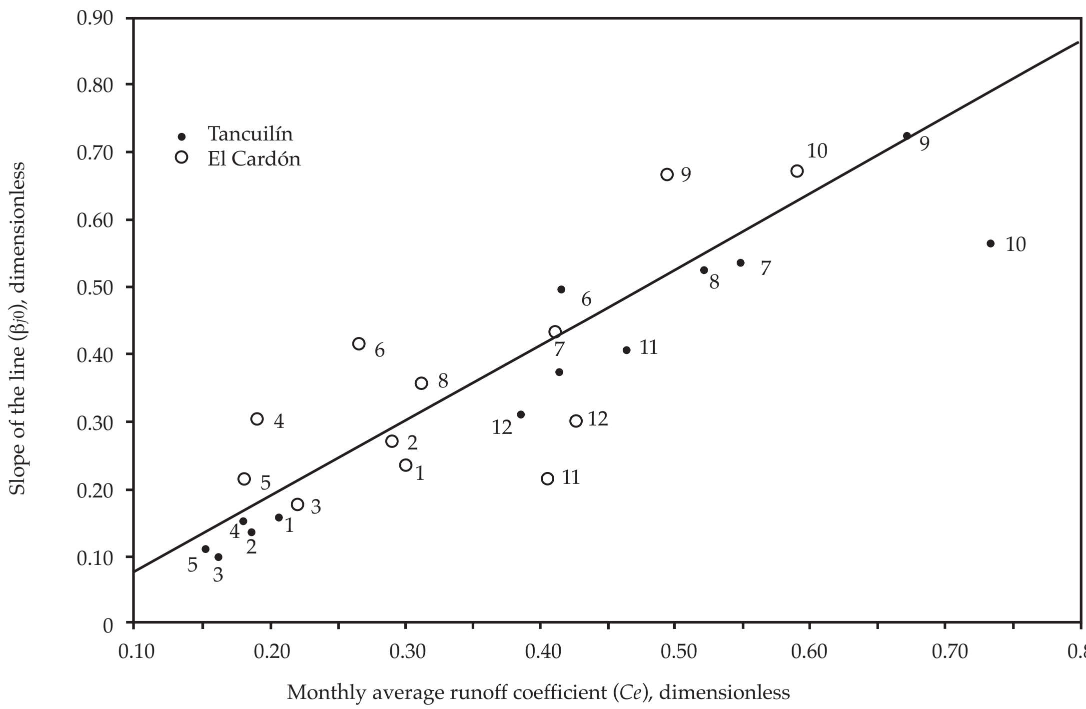


Figure 10. Regional dispersion diagram of the *slope* ($\beta_{j,1}$) of the regression models.

Cuadro 6. Valores observados y estimados en miles de m[3] de la media aritmética (M) y la desviación estándar (DE) del escurrimiento mensual en las estaciones hidrométricas Tancuilín y El Cardón.

Hydrometric Station	Statistical parameter	J	F	M	A	M'	J	J'	A'	S	O	N	D
Tancuilín	M_{obs}	6 345	4 841	4 573	6 458	12 131	52 447	72 621	64 739	127 327	66 605	23 914	11 444
	M_{est}	7 233	6 427	6 021	6 953	12 932	52 313	72 682	64 572	129 798	102 822	22 202	14 504
	SD_{obs}	3 450	2 569	2 618	5 192	10 884	58 628	58 119	50 743	98 732	57 232	29 139	11 114
	SD_{est}	3 341	1 958	2 697	3 527	7 603	36 847	55 827	42 043	74 275	44 208	20 494	8 881
El Cardón	M_{obs}	10 144	7 818	7 087	9 740	15 672	44 428	57 772	42 034	100 379	59 292	22 483	14 405
	M_{est}	9 751	8 661	8 708	101 746	17 604	44 627	56 070	41 612	99 238	51 477	19 776	15 667
	SD_{obs}	7 417	5 246	5 459	10 444	19 071	53 090	52 477	37 066	91 583	59 615	14 183	10 052
	SD_{est}	6 850	4 112	5 364	4 480	8 590	30 268	44 348	26 905	63 683	37 228	17 277	11 218

eliminating October in Tancuilin and November in El Cardon. This relationship is expressed as:

$$\beta_{j,1} = -0.0332 + 1.116 \cdot Ce_j \qquad (8)$$

This has two interesting aspects: (1) there is practically no *y*-axis at the origin and (2) its slope is virtually equal to that of Ce_j.

Comparison of the Regional Model

The proposal adopted was to use the *regional relationships* defined by equations (7) and (8) to obtain the regression coefficients for each monthly model, with known values of Ce_j (Table 5). Each monthly model is applied to the available precipitation period to estimate the monthly runoff volume. Next, the monthly means and standard deviations of estimated and observed runoff are quantified. Table 6 presents the results obtained.

For the Tancuilin gauging station, the model slightly overestimates the mean from January to March, as well as in October, while the correspondence is excellent for the rest of the months. With respect to the dispersion, larger differences in standard deviation values are inferred for the months with low linear correlation coefficients (Table 3), which are February, April, May and October through December. In the El Cardon gauging station, some of the estimates of the mean are slightly higher than those observed, and they are deficient during the rainy period. Most of the differences among the standard deviations occur during months with lower linear correlation coefficients (Table 3), which are April and May. These differences are smaller for the rest of the months, and there are even some months in which the estimated dispersion is larger than the observed dispersion, such as November and December.

Conclusions

First: The simplicity of the rainfall-runoff model does not imply that it is approximate, especially when modeling monthly runoff in humid climates. This was shown through the use of a regional linear regression model applied over months. The order (K) of the model is a characteristic of the basin and specifies the behavior of the rainfall-runoff relationship. It is linear when $K = 1$ and non-linear or curved when $K > 1$, thereby approximately representing the order of the curvature. The memory parameter (m) is a characteristic of each month and is equal to 1, or larger in months when runoff is delayed.

Second: The monthly regression model provides good estimates, even when applied to a basin whose only rain gauge station is located outside the basin, as in the case of the Tancuilin gauging station. With respect to the El Cardon hydrometric station (corresponding to a medium basin), even though it contains two rain gauge stations the distribution is not optimal (Figure 1). The poor representativeness of precipitation in both basins is reflected by the functional relationships, whose linear correlation coefficients were under 0.80 for half of the months.

Third: When all the monthly linear correlation coefficients are higher than 0.92, less dispersed results than those shown in Figures 9 and 10 will be obtained. This is relative to the regionalization of the regression coefficients. These magnitudes are obtained in small and medium basins in humid climates with rain gauge stations located in the basin and a nearly optimal distribution.

Fourth: The results of this study show that monthly regression models can be regionalized and result in estimates similar to monthly runoff volume, even in basins without an optimal rain gauge station network. The results presented in Table 6 show that the monthly regression model reliably reproduces the mean values, with estimates close to the observed standard deviations.

Acknowledgements

The author thanks Armando Rocha Hernández, engineer and head of the Weather Forecasting Center of the Local San Luis Potosi Divison of Conagua, for providing all the rain gauge information processed. We also appreciate the suggestions by the anonymous reviewer, which helped us to expand the work into topics not covered, such as confidence intervals of the predictions and predictive capacity of the regression.

References

Anderson, M. G., & Burt, T. P. (1985). Chapter 1: Modelling Strategies (pp. 1-13). In *Hydrological Forecasting*. Chichester, England: John Wiley & Sons, Ltd.

Beven, K. J. (2001). Chapter 1: Down to Basics: Runoff Processes and the Modelling Process (pp. 1-23). In *Rainfall-Runoff Modelling. The Primer*. Chichester, England: John Wiley & Sons, Ltd.

Buishand, T. A. (1982). Some Methods for Testing the Homogeneity of Rainfall Records. *Journal of Hydrology*, *58*, 11-27.

Campos-Aranda, D. F. (2003). Capítulo 5: Ajuste de curvas (pp. 93-127). En *Introducción a los métodos numéricos: software en Basic y aplicaciones en Hidrología Superficial*. San Luis Potosí, México: Editorial Universitaria Potosina.

Campos-Aranda, D. F. (2005). Capítulo 4: Análisis de la precipitación (pp. 97-120, 267-281). En *Agroclimatología Cuantitativa de Cultivos*. México, DF: Editorial Trillas.

Campos-Aranda, D. F. (octubre-diciembre, 2013). Coeficientes de escurrimiento promedio mensuales: comportamiento y aplicación en la estimación de la disponibilidad. Revista digital *Tláloc*, *61*, 24.

Clarke, R. T. (1994). Theme 4.9: Influence, Consistency and Leverage (pp. 141-146). In *Statistical Modelling in Hydrology*. Chichester, England: John Wiley & Sons, Ltd.

Draper, N. R., & Smith, H. (1998). Chapter 3: Fitting Straight Lines: Special Topics (pp. 79-114). In *Applied Regression Analysis*. Third edition. New York: John Wiley and Sons.

Haan, C. T. (1977). Chapter 9: Simple Linear Regression (pp. 180-196). In *Statistical Methods in Hydrology*. Ames, USA: The Iowa State University Press.

Haan, C. T., Johnson, H. P., & Brakensiek, D. L. (1982). *Hydrologic Modeling of Small Watersheds* (533 pp.). ASAE Monograph No. 5. Michigan, USA: St. Joseph.

IMTA (2002). *Banco Nacional de Datos de Aguas Superficiales (BANDAS).* 8 CD's. Jiutepec, México: Comisión Nacional del Agua, Secretaría de Medio Ambiente y Recursos Naturales,Instituto Mexicano de Tecnología del Agua.

INEGI (1980). *Carta de precipitación total anual: México*. Aguascalientes, México: Instituto Nacional de Estadística, Geografía e Informática.

Jones, J. A. A. (1997). Chapter 6: Modelling Runoff Processes (pp. 171-210). In *Global Hydrology: Processes, Resources and Environmental Management*. Harlow, England: Pearson Education Limited.

Mimikou, M., & Rao, R. (January, 1983). Regional Monthly Rainfall-Runoff Model. *Journal of Water Resources Planning and Management*, *109*(1), 75-93.

Montgomery, D. C., Peck, E. A., & Vining, G. G. (2002). Capítulo 4: Comprobación de la adecuación del modelo (pp. 117-153). En *Introducción al análisis de regresión lineal*. México, DF: Compañía Editorial Continental.

Ruiz-Maya, L. (1977). Capítulo 9: Condiciones paramétricas del análisis de varianza (pp. 233-249). En *Métodos estadísticos de investigación*. Madrid: Instituto Nacional de Estadística.

Ryan, T. P. (1998). Chapter 14: Linear Regression (pp. 14.1-14.43). In H. M. Wadsworth, Jr. (Ed.). *Handbook of Statistical Methods for Engineers and Scientists*. Second edition. New York: McGraw-Hill.Second edition.

Shaw, E. M., Beven, K. J., Chappell, N. A., & Lamb, R. (2011). Chapter 12: Catchment Modelling (pp. 280-321). In *Hydrology in Practice*. Fourth edition. London: Spon Press.

Singh, V. P. (1995). Chapter 1: Watershed Modeling (pp. 1-22). In *Computer Models of Watershed Hydrology*. Highlands Ranch, USA: Water Resources Publications.

Sene, K. (2010). Chapter 4: Hydrological Forecasting (pp. 101-140). In *Hydro-meteorology. Forecasting and Applications*. Dordrecht, The Netherlands: Springer.

Sugawara, M. (1992). Chapter 5: On the Weights of Precipitation Stations (pp. 59-74). In J. P. O'Kane (Ed.). *Advances in Theoretical Hydrology*. Amsterdam: Elsevier Science Publishers.

WMO (1971). Annexed III: Standard Tests of Significance to be Recommended in Routine Analysis of Climatic Fluctuations (pp. 58-71). In *Climatic Change*. Technical Note No. 79, WMO-No. 195. Secretariat of the WMO. Geneva: World Meteorological Organization.

Yevjevich, V. (1972). Chapter 11: Correlation and Regression (pp. 232-276). In *Probability and Statistics in Hydrology*. Fort Collins, USA: Water Resources Publications.

Zelen, M., & Severo, N. C. (1972). Chapter 26: Probability Functions (pp. 925-995). In M. Abramowitz & I. A. Stegun (Eds.). *Handbook of Mathematical Functions*. New York: Dover Publications, Inc.

Dirección del autor

Dr. Daniel Francisco Campos Aranda

Profesor jubilado de la Universidad Autónoma de San Luis Potosí
Genaro Codina 240, Colonia Jardines del Estadio
78280 San Luis Potosí, San Luis Potosí, México
campos_aranda@hotmail.com

Discussion

Technical notes and technical articles are open to discussion according to the following guidelines:

- The discussion will be written in the third person.
- The writer of the discussion shall use the term “commentator” when referring to oneself and the term “author” when referring to the one responsible for the technical note or article.
- The discussion shall be sent within 12 months of the last day of the quarter in which the a technical article or note was published.
- The length of the discussion may be extended by written request from the commentator.
- The discussion is to be presented according to the Guide for Collaborators published in this journal (omitting data referring to the length and abstract). In addition, the bibliographical citation of the technical notes or articles to which the discussion refers shall be included.
- The maximum length of the discussion is 4 journal pages (approximately 10 cuartillas, including figures and tables).
- The figures and tables presented by the commentator shall be progressively marked with Roman numbers and when citing those generated by the author the original numeration should be respected.
- The editors will suppress data that does not pertain to the subject of the discussion.
- The discussion will be rejected if it contains topics addressed by other sources, promotes personal interests, is carelessly prepared, raises controversy involving already established facts, is purely speculative or falls outside the purpose of the journal.
- The discussion will be published along with commentaries from the author or authors to which it refers.
- The discussion will be directed by the editor in chief.

Puente de Dios Waterfall, San Luis Potosi, Mexico.

Photo: Isarain Chávez.

Guide for Collaborators

The journal ***Water Technology and Sciences*** invites specialists to collaborate with original, unpublished technical articles or notes **related to water, resulting from investigations and provide original contributions**, based on the disciplines of hydrology, hydraulics, water management, water and energy, water quality, and physical, biological and chemical sciences as well as political and social sciences, among other disciplines, according to the guidelines stated below.

PREPARATION OF THE ARTICLE

FORMAT

Font: Palatino throughout the entire document (body of text, tables and figures).

Font Size: Use 8, 9, 10 and 20 points, according to the following table:

8 points (Palatino)	9 points (Palatino)
• Tables. • Figures. • Acknowledgements.	• Name of authors. • Institution of authors. • Abstract. • *Abstract* and *keywords*. • Institutional address of the authors.
10 points (Palatino)	**20 points capital letters (Palatino)**
• Body of the text. • Title of the work in Spanish.	• Title of the work in English.

Line Spacing: double-spaced.

Page Numbers: all pages shall be numbered.

Length

***Technical article*:** **30 pages** (numbered), including figures and tables.

***Technical note*:** **10 pages** (numbered), including figures and tables.

CONTENS

Title

The article shall present significant contributions to scientific and technological knowledge pertaining to the specialty. It shall be based on finished works or those that have completed a development cycle. It shall show results from a series of experiences over 1 year or more of investigations and be supported by an adequate bibliographical review. **The basic structure of the text shall contain an introduction, the development and the conclusions**. The classic layout is preferable: abstract, introduction, methodology, results, discussion, conclusion and references.

Title

The title, **written in Spanish and English**, shall be informative and not exceed 12 words.

Abstract

The abstract, **written in Spanish and English**, shall be concise and provide a broad overview of the investigation (objective, method, results and conclusions) without exceeding 250 words.

Key Words

Eight words or key phrases (maximum) shall be provided **in Spanish and English** that facilitate the identification of the information.

Footnotes

Not admitted. The information is to be incorporated into the text.

Acknowledgements

To be included after the text and before the references.

Tables

- One page for each table.
- A list of all the tables cited shall be presented after the references.

Figures

- One page for each figure.
- All the names of the figures shall be included after the tables.
- They should be high-resolution (300 dpi).

Note: When the article is approved by the publication, the author shall send each figure in JPG format with high-resolution (300 dpi).

References

- The entire bibliography must be referenced in the main body of the text.
- In the case of addressing scientific and technological topics that are common domain, works that denote the knowledge of the authors about the state-of-art shall be cited.
- Avoid self-citations to the extent possible
- APA format shall be used as a basis.

Some examples of references in APA format are:

Complete Books

Last name, A. A. (Year). Title of work. city published: Publisher.
Last name, A. A. (Year). Title of work. Consulted at http://www.xxxxx
Last name, A. A. (Year). Title of work. doi:xxxxx
Last name, A. A. (Ed.). (year).City published: Publisher.

Book Chapters

Last Name, A. A., & Last Name, B. B. (Year).. Title of chapter or entry. In A. Last Name, B. Last Name & C. Last Name (Eds.), Title of book (pp. xxx-xxx). Place: Publisher.
Last Name, A. A., & Last Name, B. B. (Year).. Title of chapter or entry. In A. Last Name, B. Last Name & C. Last Name (Eds.), Title of book (pp. xxx-xxx). Consulted at http://www.xxxxxxx

Newspaper Article or Note Consulted Online

Last Name, A. A., & Last Name, B. B. (Year). Title of article. Title of publication, issue (number), pp. Consulted at http://www.xxxxxxx

That is: Last Name, A. A., & Last Name, B. B. (Year). Title of article. Title of publication, 1(2), 5-17, pp. Consulted at http://www.xxxxxxx

Printed Newspaper Article or Note

Last Name, A. A., & Last Name, B. B. (Year). Article Title. Title of publication, 8(1), 73-82.

Newspaper Article Publication with DOI

Last Name, A. A., & Last Name, B. B. (Year). Article Title. Title of publication, 8(1), 73-82, doi:xxxxxx

Conferences or Symposiums

Collaborator, A. A., Collaborator, B. B., Collaborator, C. C., & Collaborator, D. D. (Month, year). Title of collaboration. In E. E. President (Presidency), Title of symposium. Symposium held at the conference by Name of Organization, Place.

Language

Spanish or English

Separation of numbers and use of decimal points

In *Tecnología and Ciencias del Agua*, the separation between thousands is denoted with a blank space. A decimal point is used to separate whole numbers from fractions. In this regard, refer to Diccionario panhispánico de dudas, edited by the Real Academia Espyearla and the Asociación de Academias de la Lengua Espyearla, in 2005, with respect to numeric expressions: "**the Anglo-Saxon use of the period is accepted, normal in some Hispano-American countries…: π = 3.1416.**".

Delivery of Article

Send the article in *Word* with the name of the authors and institutional address to **revista.tyca@gmail.com**, with copy to Elizabeth Peña Montiel, elipena@tlaloc.imta.mx.

General Information

The review process will begin once the material is received, during which time the manuscript could be rejected. If the text is suitable for review, having fulfilled the Editorial Policy and the Editorial Committee having determined so, it will proceed to the review stage.

Depending on the review process, the text may be accepted without changes, with minor changes, with extensive changes or rejected.

Once a work is published, the main author has the right to two journals and ten offprints free of charge.

In there are any questions, please write to Helena Rivas López, hrivas@tlaloc.imta.mx or Elizabeth Peña Montiel, elipena@tlaloc.imta.mx

Citations within the body of the text

Type of citation	First appearance in text	Subsequent appearances	Format in parenthesis, first citation in text	Format in parenthesis, subsequent citing in text
Work by one author	Last name (Year)	Last name (Year)	(Last name, year)	(Last name, year)
Work by two authors	Last name and Last name (Year)	Last name and Last name (Year)	(Last name & Last name, Year)	(Last name & Last name, Year)
Work by three authors	Last name, Last name and Last name (Year)	Last name *et al*. (Year)	(Last name, Last name, & Last name, year)	(Last name of first author *et al*., year)
Work by four authors	Last name, Last name, Last name and Last name (Year)	Last name *et al*. (Year)	(Last name, Last name, Last name, & Last name, year)	(Last name of first author *et al*., year)
Work by five authors	Last name, Last name, Last name, Last name and Last name (Year)	Last name *et al*. (Year)	(Last name, Last name, Last name, Last name, & Last name, year)	(Last name of first author *et al*., 2008)
Work by six or more authors	Last name of first author *et al*. (Year)	Last name of first author *et al*. (Year)	(Last name of first author *et al*., Year)	(Last name of first author *et al*., year)
Groups (easily identified with abbreviations) such as authors	Complete name of institution (Acronym, year)	Acronym (Year)	(Complete name of institution [acronym], year)	(Institution, year)
Groups (without abbreviations) such as authors	Complete name of institution (year)	Complete name of institution (year)	(Complete name of institution, year)	

Editorial Policy

Mission

Disseminate scientific and technical knowledge and advances related to water through the publication of previously unpublished articles and technical notes that provide original contributions.

Our Principles

- Impartiality
- Objectivity
- Honesty

Our Values

- Knowledge
- Experience
- Thematic expertise

Contents

Interdisciplinary, composed of previously unpublished articles and technical notes related to water, that result from research and provide original scientific and technological contributions or innovations, developed based on the fields of knowledge of diverse disciplines.

Topics Covered

Interdisciplinary, related to water, with priority topics in the following knowledge areas:

- Water and energy
- Water quality
- Physical, biological and chemical sciences
- Hydro-agricultural sciences
- Political and social sciences
- Scientific and technological development and innovation
- Water management
- Hydrology
- Hydraulics

Type of Contributions

Technical article: scientific document that addresses and communicates, for the first time, results from a successful investigation or innovation, whose contributions provide and increase current knowledge about the topic of water.

Technical note: text that addresses advances in the field of hydraulic engineering and professional practices in the field of water, while not necessarily making an original contribution in every case it must be a previously unpublished work.

Some of the articles submitted to the review process can result in being published as notes and vice versa. This will occur through a proposal and process of mutual agreement between the authors and the editor responsible for the topic. The article and the note have nearly the same structure (abstract, introduction, methodology, results, discussion, conclusion, references).

Review Process

The journal is governed by a rigorous review process which establishes that each article be analyzed separately by three reviewers who recommend its acceptance, acceptance with minor changes, acceptance with extensive changes, rejection or acceptance as a technical note with the required changes.

At least one of three reviewers will be sought from a foreign institution.

The reviewers may not belong to the same institution as the authors proposing the article for publication.

When the decisions are opposing or inconsistent, the involvement of other reviewers or the members of the Editorial Committee may be requested.

On occasion, the approval of an article will be decided by two reviewers in addition to the opinion of the editor of the corresponding topic or, the editor in chief.

A rejected article will not be accepted for a new review process.

The review process will be performed in such a way that neither the authors nor the reviewers know the names of the other party.

The review process is performed by high-level specialists and experts who are national and internationally renowned in their professional fields and have the ability to reliably evaluate, in a timely manner, the quality as well as the originality of contributions, in addition to the degree of scientific and technological innovation in the topic under which it is submitted for possible publication.

This participation is considered a professional contribution and will be performed as a courtesy.

The reviews have a "Guide for the Reviewer" provided by the journal's Editorial Department.

Final Ruling

The ruling resulting from the review process is not subject to appeal.

Authors

Works are published from authors of any nationality who present their contributions in Spanish; nevertheless, we all accept works in Spanish or English.

Responsibility of the Authors

Submitting a proposal for the publication of an article commits the author not to simultaneously submit it for consideration by other publications. In the event an article has been submitted to another media for eventual publication, the author agrees to do so with the knowledge of the Editorial Department, which will suspend the review process and inform the Editorial Committee of the decision by the authors.

Collaborators whose articles have been accepted will formally cede the copyright to ***Tecnología y Ciencias del Agua***.

The authors are responsible for the contents of the articles.

The author is responsible for the quality of the Spanish used. If the writing is deficient the work will be rejected. ***Water Technology and Sciences*** will only be responsible for the editorial management.

The author commits to making the changes indicated by the editor of the topic in the time frame establish by the editor. In the event these indications are not met, the article will be removed from the review process and be classified as rejected.

The author shall be attentive to resolving the questions and proposals presented by the editors and the editorial coordinator.

Each author shall approve the final printed proofs of their texts.

It is suggested that authors consult the "Guide for Collaborators."

Readers

Academics, investigators, specialists and professionals interested in the analysis, investigation and search for knowledge and solutions to problems related to water.

Reception of Articles

The reception of articles and notes is ongoing.

Time period

Bimonthly, appearing in the second month of the period.

Subscription and Distribution

The journal is distributed through paid and courtesy subscriptions.

Open Access

Water Technology and Sciences, previously ***Hydraulic Engineering in Mexico***, provides a digital version of all the material published since 1985.

Special editions and issues

Water Technology and Sciences will publish special numbers independently or in collaboration with other journals, professional associations or editorial houses with renowned prestige and related to water resources.

In addition, it will publish articles by invitation, acknowledging the professional advances of prominent investigators.

In both cases, the quality of the technical continents and scientific contributions will be reviewed.

Water Technology and Sciences is registered in the following national and international indices and abstracts:

• Thomson Reuters Science Citation Index® (ISI) • Expanded Thomson Reuters Research Alert® (ISI) • Índice de revistas mexicanas de investigación científica y tecnológica del Consejo Nacional de Ciencia y Tecnología (Conacyt) (2013-2018) • Sistema de Información Científica Redalyc (Red de Revistas Científicas de América Latina y El Caribe, España y Portugal), Universidad Autónoma del Estado de México • EBSCO (Fuente Académica Premier NISC; Geosystems, como Marine, Oceanographic and Freshwater Resources) • ProQuest (Cambridge Scientific Abstracts) • Elsevier (Fluid Abstracts: Process Engineering; Fluid Abstracts: Civil Engineering) • CAB Abstracts, CAB International • Latindex (Sistema Regional de Información en Línea para Revistas Científicas de América Latina, el Caribe, España y Portugal), Universidad Nacional Autónoma de México • Periódica (Índice de Revistas Latinoamericanas en Ciencias), Universidad Nacional Autónoma de México • Catálogo Hela (Hemeroteca Latinoamericana), Universidad Nacional Autónoma de México • Actualidad Iberoamericana, CIT-III, Instituto Iberoamericano de Información en Ciencia y Tecnología.

Other Sources

The journal can also be found archived in Google scholar.

Contents

Technical articles

Technical notes

Contenido

Artículos técnicos

Notas técnicas

IMTA
Instituto Mexicano de Tecnología del Agua

http://www.imta.gob.mx/tyca