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Predictive modeling to determine oxygen and ozone doses applicable to *in situ* remediation of polluted water bodies

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Abstract

This work shows the results for the first time of calibrating and validating a mathematical model, capable of predicting the amounts of O_3 and O_2 necessary to reduce pollution levels in a lake based on the chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total nitrogen (TN), total phosphorus (TP) and fecal coliforms (FC) concentrations. The model was designed to treat a natural or artificial lake as though it were an aerated lagoon operating as an idealized continuous flow complete-mix reactor. The O_3 yield constant for eliminating the non-biodegradable fraction of COD and for deactivating fecal coliforms were laboratory derived and calibrated with field values. Based on the field parameters, the model accurately predicted a reduction in BOD_5, COD, TN, TP and FC of 53%, 51%, 39%, 42% and 98%, respectively. The model proved to be effective in predicting O_2 and O_3 demand and time of recovery of a polluted water body.

1. Introduction

In situ treatment has gained great relevance in recent years, since these techniques have proven to be an important complement in meeting the demand of wastewater treatment plants (Schönach *et al* 2017). One of the most commonly used method is hypolimnetic oxygenation (Anawar and Chowdhury 2020), which is performed either by injecting oxygen or air at the bottom, or by extracting water from the hypolimnion to saturate it with oxygen and then injecting it back to the bottom (side stream supersaturation) (Gerling *et al* 2014). This technique has shown some degree of efficacy, but still exhibits certain limitations. For example, hypolimnetic oxygenation can only prevent the release of phosphorus and other reduced compounds from sediments, but does not attack pollution entering the water body (Schönach *et al* 2017). In addition, the injection of air or oxygen alone does not attack all pollutants, since organic matter must be in a biodegradable form in order to completely degrade (Ouldali *et al* 1989, Shammas *et al* 2009). Other substances such as recalcitrant organic compounds, pathogens, dyes, and various toxic substances cannot be efficiently removed from the water column by oxygen injection alone either.

To overcome limitations encountered in applying a single type of treatment, several authors have suggested using two or more remediation techniques at the same time (Anawar and Chowdhury 2020). Recently, Tabla-Hernandez *et al* (2020) reported the implementation of an oxygen and ozone injection system in a highly polluted urban lake. Ozone was included as part of the treatment because it has been used to target a wide range of pollutants (Shi and McCurry 2020). Furthermore, ozone can improve the organoleptic properties of water (color and taste) and is able to reduce turbidity through destabilization of colloidal particles (Malik *et al* 2017). However, the most important feature of this gas is its capacity

to produce biodegradable organic compounds from non-biodegradable substances (Ulucan-altuntas and Ilhan 2018). Subsequently, the purpose of oxygen is to stimulate the growth of an aerobic biota, which will complete the oxidation of biodegradable organic matter until it eventually mineralizes (H_2O and CO_2) (Welander *et al* 1997).

Injecting ozone (O_3) has proven to be an excellent complement to cover oxygen (O_2) deficiencies; nevertheless, it is not widely implemented in polluted water bodies and the required doses for a polluted lake are still unknown. This manuscript is therefore the first to present the *Waterlife* mathematical model. This model has been calibrated and validated by laboratory and field tests to predict what will happen when this same treatment is applied in other bodies of water with similar characteristics. To this end, mathematical equations and constants were used to calculate the oxygen demand of a natural lake as if it were a continuous flow aerated artificial lagoon and the ozone demand was calculated based on experimental data.

2. Methodology

2.1. Study site

Lake Valsequillo is an artificial water reservoir built in the year 1946 and located in the state of Puebla, Mexico. It covers approximately 3153 ha and has an average depth of 11.8 meters. Its main inflows are the Atoyac and Alseseca Rivers with an annual flow of approximately 6.7 $m^3\ s^{-1}$ and 0.8 $m^3\ s^{-1}$, respectively. The reservoir is hydrodynamically divided by the San Baltazar Tetela peninsula into two zones (east and west). More information related to the study site is presented further in text S1 (available online at stacks.iop.org/ERL/17/014038/mmedia) (figure 1).

2.2. Conceptual model

In 2018, three Mobile Water Decontamination Units (MWDU) for ozone and oxygen injection, built by Dellepere Enterprises Corp, were introduced to the Lake Valsequillo. The MWDUs are capable of injecting 120 g $O_3\ h^{-1}$ and 250 Kg $O_2\ h^{-1}$ as microbubbles (90 $\pm$ 10 μm in diameter) at an adjustable depth ranging from 2 to 10 m (depending on the lake's bathymetry). They are also able to cruise at two knots of speed while delivering the treatment. These units were operating for 12 months (November 2018–November 2019) and the results of 5 months of operation (November 2018–April 2019) were reported in Tabla-Hernandez *et al* (2020). Prior to bringing the MWDUs to Lake Valsequillo, a laboratory-level experiment was conducted to determine the amount of ozone required to reduce several physicochemical and bacteriological parameters in order to comply with agricultural irrigation water quality standards for the water in the Valsequillo reservoir (Tabla-Hernández *et al* 2018). To model the lake as intended in this paper, some general considerations are presented in text S2.

2.3. Water quality measurement

The physicochemical parameters of the water quality measured were BOD_5, COD, TN, TP, FC, dissolved oxygen (DO) and Temperature (T). The sampling was carried out during the dry season for 5 months (from November 2018 to March 2019). All water samples were collected at a constant depth of 2.5 m. The methodology, the location of the sampling sites and the equipment used are discussed in greater detail in tables S1 and S2.

2.4. Design equations

The most commonly used models in bioprocess design are based on equilibrium equations, combined with kinetic equations of substrate consumption and product formation (Oliveira-Esquerre *et al* 2003). The model developed to determine the oxygen and ozone demand at the Valsequillo Lake is stochastic (deterministic), since the parameters are presented in terms of exact and non-random values (Leduc and Ouldali 1990). In biological processes, the theoretical oxygen demand is usually estimated based on the BOD_5 (Shammas *et al* 2009). Similarly, this study presents a model built mainly from the oxygen demand as a function of BOD_5. Nonetheless, it also takes into consideration other important parameters such as COD, total nitrogen concentration, fecal coliform concentration, and total phosphorus through a combination of mathematical relationships related to artificial aeration, constants obtained in the laboratory and equations proposed by the authors in this paper (table S3).

2.4.1. Amount of oxygen needed for Lake Valsequillo

2.4.1.1. Calculation of the actual oxygen demand rate (AOR)

This is the stoichiometric ratio between oxygen consumption, substrate removal and new cell generation (Shammas *et al* 2009). For this calculation, the equation proposed by Tchobanoglous *et al* (2003) was used, since it not only considers the production of heterotrophic biomass but also that of nitrifying biomass (equation (1)) (supp material). This equation includes the amount of oxygen required to oxidize BOD_5 and to reduce nitrogen susceptible to nitrification (ion ammonium, NH_4^+ or total nitrogen).

*2.4.1.2. Calculation of the performance coefficients (*A, B, C *and* D*)*

Coefficients A and C relate the amount of oxygen consumed with the reduction of the substrate (BOD_5), while coefficients B and D relate the amount of oxygen consumed with the biomass formed. Since the exact composition of the biodegradable organic matter entering the lake is unknown, to calculate coefficient A (equation (1.1)) (supp material), an

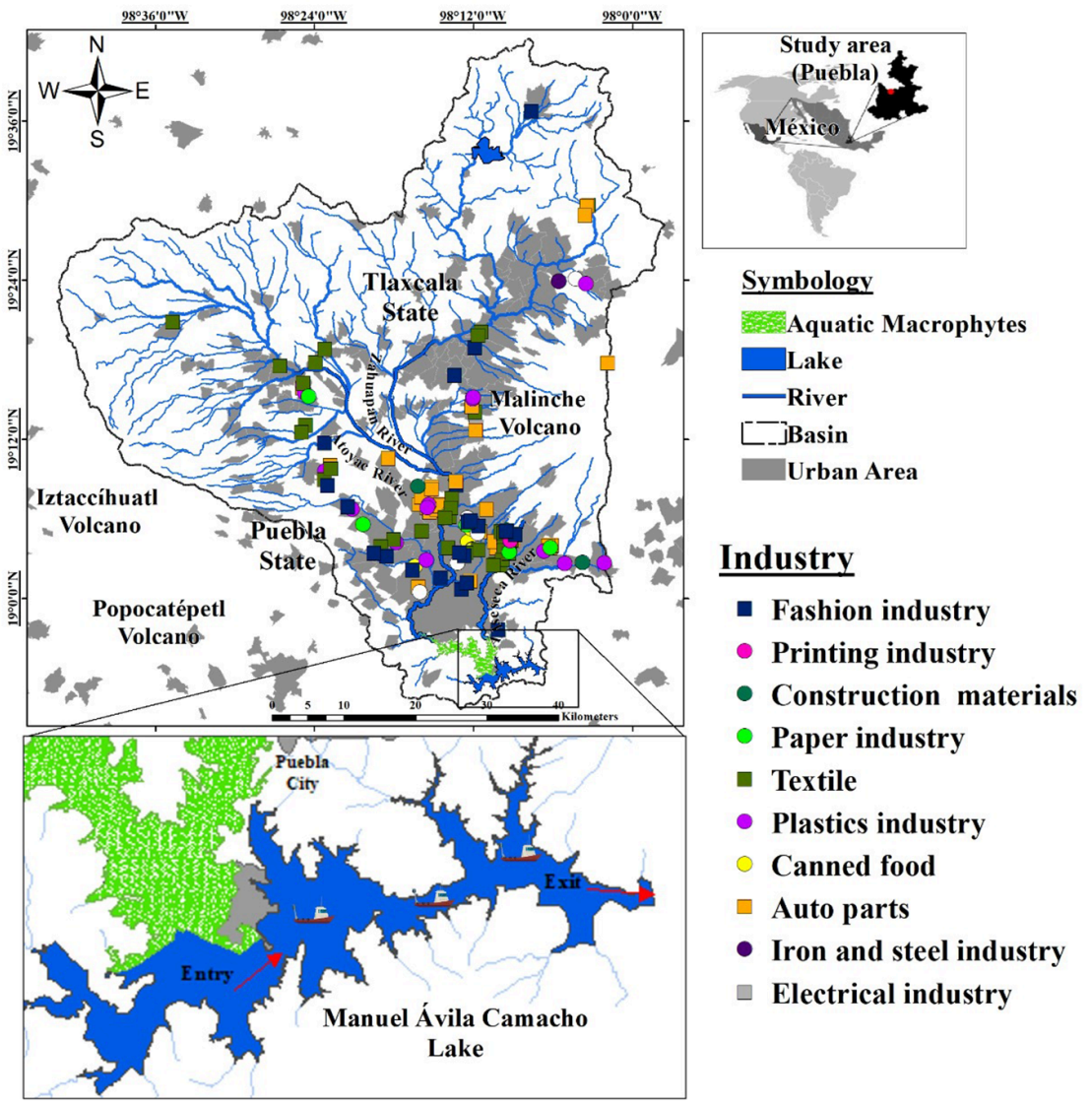

Figure 1. Study area map illustrating the entry and exit of the water and the zone of treatment in the Valsequillo reservoir, Puebla, México.

initial composition similar to that of glucose was assumed, as proposed in Tchobanoglous *et al* (2003). For coefficient *B* (equation (1.2)) (supp material), the condensed formula of a heterotrophic bacterium ($C_5H_7NO_2$), was considered (Hoover and Porges 1952). To calculate coefficient *C* (equation (1.3)) (supp material), the sum of the two nitrifying reactions in the presence of nitrosomas and nitrobacter bacteria was considered (Wezernak and Gannon 1967). Finally, coefficient *D* (equation (1.4)) (supp material) is calculated similarly to coefficient *B* but bearing in mind that this coefficient represents the nitrifying biomass.

2.4.1.3. Calculation of heterotrophic (P_{x,bio_H}) *and nitrifying* ($P_{x,bioN}$) *biomass*

Total biomass production refers to the number of cells produced from the substrate removed. These are heterotrophic or nitrifying in nature and are directly proportional to the removal of BOD_5 and ammonia nitrogen, respectively. The heterotrophic biomass production is obtained from equation (1.5) (supp material), while the nitrifying biomass is obtained from equation (1.6) (supp material). To calculate both biomasses, the yield of each must be calculated using the stoichiometric ratios described in equations (1.7) and (1.8) (supp material).

2.4.1.4. Calculation of the standard oxygen demand rate (SOR)

This number represents the corrected AOR according to the physical conditions of the medium where the oxygen injection is carried out, namely: the salinity of the water, the temperature, the height above sea level where the treatment is implemented, the type of aerators used, the kinetic constant of oxygen transfer (and hence the size of the oxygen bubble) and lastly the desired concentration of dissolved oxygen in the lake (operating concentration) (equation (2)) (supp material).

2.4.1.5. Corrected oxygen saturation concentration ($C_{\bar{S},TH}$)

Equation (2.1) (supp material) shows the corrected oxygen saturation concentration with respect to altitude, injection depth and the percentage of injected oxygen that can escape. Since the percentage of oxygen saturation changes according to the altitude above sea level, this variable has been taken into consideration (equations (2.2) and (2.3)) (supp material). Additionally, the relationship between barometric pressure and water depth is included in equation (2.4) (supp material) (Lee and Ye 2013).

2.4.1.6. Oxygen transfer correction factor (α)

The oxygen transfer correction factor is the ratio of the oxygen transfer diffusion constant between polluted water and clean water (tap water). This value depends on the number of particles present in the lake water, but also on the aeration device used. For conventional diffusers, this value lies between 0.4 and 0.8; for mechanical aerators, it is between 0.6 and 1.0; and for advanced diffusers, whose bubble size ranges between micro and nano bubbles, it is greater than 1.0 (Mazzei 2018).

2.4.1.7. Salinity-surface tension factor (β)

This factor is the ratio of the saturation concentration of dissolved oxygen in contaminated water with respect to clean (tap) water (equation (2.7)) (supp material). The higher the concentration of dissolved particles in the lake water, the lower the saturation concentration of dissolved oxygen (Tchobanoglous *et al* 2003). In addition, other variables necessary to correct the oxygen demand were taken into consideration. These considerations are discussed further in text S3.

2.4.1.8. Calculation of phosphorus uptake by bacteria

The amount of phosphorus taken up by heterotrophic bacteria is dependent on the chemical composition of the bacteria found in a contaminated water body (Hoover and Porges 1952). The molecular formula used to represent the organic fraction of a cell is $C_{60}H_{87}O_{23}N_{12}P$. This composition is valid for both heterotrophic and nitrifying bacteria (Sherrard and Schroeder 2014). Hence, in this model, the reduction of phosphorus in the water column is based on the biomass generated during the aeration process (equation (3.1)).

2.4.2. Amount of ozone required in Lake Valsequillo

This model considers ozone demand as a function of those parameters that best represent ozone decay kinetics, i.e. chemical oxygen demand (COD) and fecal coliform concentration (FC). Therefore, the ozone demand will be calculated by equation (4) (supp material), which is a function of the non-biodegradable fraction of COD, whose yield (Z) was calculated in the laboratory and has a value of 0.004 g O_3/g COD for the Valsequillo lake. Additionally, for ozone demand as a function of Fecal coliform concentration (equation (5)) (supp material), a yield (W) of 1.3×10^{-9} g O_3/CFU will be considered (Tabla-Hernández *et al* 2018). Since the Z and W yields are experimental values, they will be the starting values for the modeling, but can then be modified after calibrating with the field values.

2.5. Model calibration and verification

Calibration and verification of predictive mathematical models are done based on the values collected on site. Additionally, for the calibration to be correct, the system must be working in stationary mode (i.e. without variations with respect to time) (Leduc and Ouldali 1990). To meet both conditions, the ozone and oxygen injection was conducted in Lake Vasequillo between 2018 and 2019. The main monitoring was done in the steady state period (i.e. during dry season and with a constant flow of water).

The algorithm was written in Excel software (License: 10037FFE93ECA64D) (supp material); all design equations, performance constants, stoichiometric ratios, hydraulic and water quality values of Lake Vasequillo before and after treatment were recorded. The algorithm was used to adjust the constants A, Z, W, X and Y_N according to the amount of ozone and oxygen injected into the lake during 5 months of operation.

Finally, a sensitivity analysis was performed to test the reliability of the model. To do so, different values to those obtained after calibrating the A, Z, W, X and Y_N coefficients were assigned. This was done with the purpose of finding the range of values in which the non-fixed variables (SOR, DO_3 (COD), DO_3 (FC) and (P_E)) did not deviate beyond 10% of the the proposed safety factor.

2.5.1. Statistical analysis

The normality and homogeneity of the variance of the data groups were verified using the Shapiro–Wilk and Levene tests, respectively. The differences between the concentration levels of each physicochemical parameter were determined by using one-way analysis of variance and the Kruskal–Wallis test for parametric and non-parametric data, respectively. Tukey's test and Dunn's method were performed with a significance level of $p = 0.05$ for parametric and non-parametric data, respectively. All analysis were performed using Sigma Plot 12.0 (Systat Software Inc., San Jose, CA, USA).

3. Results

3.1. Model output values

Table 1 shows the results of modeling Lake Valsequillo with a treatment flow (Q) of 648 000 m^3 d^{-1}, equivalent to the inflow from the two main rivers (Alseseca and Atoyac Rivers).

Table 1. Concentration values of the calibrated constants and the fixed variables of the mathematical model.

Fixed variables			
Parameter	Units	Original values	Calibrated value
B	g O_2/g biomass	1.4	—
C	g O_2/g biomass	4.6	—
D	g O_2/g biomass	1.4	—
$P_{x,\mathrm{bio_H}}$	g biomass m^{-3}	2.4	—
$N_{x,\mathrm{I}}$	g m^{-3}	11.5	—
$N_{x,\mathrm{E}}$	g m^{-3}	7.0	—
Q	m^3 d^{-1}	648 000.0	—
S_0 (BOD_0)	g m^{-3}	10.7	—
S (BOD)	g m^{-3}	5.0	—
Y	g $\mathrm{biomass_{(H)}}$/g substrate	0.4	—
$C_{\bar{S},\mathrm{TH}}$	g m^{-3}	8.5	—
$C_{\mathrm{S,TH}}$	g m^{-3}	7.3	—
F_a	m	0.8	—
P_d	mm Hg	1140.0	—
α	—	1.2	—
β	—	0.9	—
F	%	10.0	—
C_{L}	g m^{-3}	2.0	—
θ	—	1.1	—
$C_{s,20}$	g m^{-3}	9.1	—
O_t	%	85.0	—
$P_{\mathrm{at,H}}$	mm Hg	760.0	—
HASL	mm Hg	2000.0	—
Injec. depth	m	5.0	—
T	°C	22.0	—
P_{I}	g m^{-3}	2.6	—
$\mathrm{nbCOD_0}$	g m^{-3}	25.3	—
$\mathrm{COD_0}$	g m^{-3}	36.0	—
nbCOD	g m^{-3}	12.4	—
$\mathrm{FC_I}$	CFU/100 ml	3107.0	—
FC	CFU/100 ml	45.2	—
Coefficient calibration			
A	g O_2/g substrate	1.1	1.0
Y_{N}	g de $\mathrm{biomass_{(N)}}$/g NH_4^+	0.1	0.2
$P_{x,\mathrm{bio_N}}$	g biomass m^{-3}	0.5	1.2
Z	g O_3/g COD	4.0×10^{-3}	1.0×10^{-3}
W	g O_3/CFU	1.3×10^{-9}	4.3×10^{-10}
X	g P/g biomass	2.0×10^{-2}	0.3
Calculation of variables from the calibration of the coefficients			
AOR	Kg O_2 h^{-1}	612	575
SOR	g O_2 h^{-1}	798	750
DO_3 (COD)	g m^{-3}	464.4	120
P_{E}	g m^{-3}	2.54	1.5
DO_3 (FC)	g O_3 d^{-1}	1074.6	120

The lake is located at 2000 m above sea level, with a temperature (T) of 22 °C: it has an average injection depth of 5 m, a bubble size in the order of micrometers (α) and a safety factor (F) of ±10%. Based on these parameters, the mathematical model estimates a reduction in BOD_5, COD, TN, TP and FC of 53%, 51%, 39%, 42% and 98%, respectively. All these reduction percentages estimated by the model are statistically significant ($p < 0.05$) (table S4) (supp material). The corrected oxygen saturation concentration ($C_{\bar{S},\mathrm{TH}}$) was lower than the oxygen concentration at standard conditions ($C_{s,20}$), that is 8.5 ± 0.3 and 9.08 g m^{-3} (fixed value obtained from Tchobanoglous *et al* (2003)), respectively. This difference was mainly due to the height above sea level at which the oxygen injection was carried out (2000 m above sea level, masl).

3.2. Model calibration

The main values adjusted to the different variables of the model are the amount of oxygen and ozone injected into Lake Valsequillo during 5 months of operation and the reduction percentages of the different physicochemical parameters recorded in the field (Tabla-Hernandez *et al* 2020). The first variable calibrated was coefficient A, which establishes the amount of oxygen required per unit of substrate (BOD_5). The initial proposed value of A was 1.07, which yielded a SOR of 798 kg O_2 h^{-1}; since this amount does not correspond to the 750 kg O_2 h^{-1} that were injected by the three decontamination units (MWDU), the 1st iteration was performed around this coefficient to adjust it to the actual dosage resulting in an A value of 1.01. In addition to this constant, constant Y_{N} was also calibrated. The iteration changed the value from 0.123 to 0.28 g $\mathrm{biomass_{(N)}}$/g NH_4^+ and thus the amount of nitrifying biomass produced ($P_{x,\mathrm{bio_N}}$) went from 0.56 to 1.27 g biomass m^{-3}. Calibrating both constants resulted in adjusting SOR to the 750 kg of oxygen that were injected per hour with the three MWDUs.

The 3rd variable calibrated with the field values was variable Z, which measures ozone demand as a function of the fraction of non-biodegradable COD. The starting value was 0.004 g O_3/g COD (Tabla-Hernández *et al* 2018). Since the Z yield is an experimental value, this was the starting value and was adjusted according to the non-biodegradable COD ($\mathrm{nbCOD_0}$). From this value, the ozone demand ($\mathrm{DO_{3(COD)}}$) calculated by the model was 1393.2 g O_3 h^{-1}, which does not correspond to the amount injected into Lake Valsequillo (360 g O_3 h^{-1}). Therefore, this coefficient was adjusted to match the actual ozone dose, yielding a new value of 0.00103 g O_3/g COD. The 4th iteration was done to calibrate the W coefficient, which relates the amount of ozone needed to deactivate each Colony-forming unit of fecal coliforms ($\mathrm{DO_{3(FC)}}$). To remove 99% of the fecal coliforms in the lake, the model calculated an ozone demand of 1074 g O_3 h^{-1} to reduce 99% of the FC concentration. This value is greater than the 360 g of ozone injected per hour. Adjusting this dose changed the value of W by an order of magnitude increasing from 1.3×10^{-9} to 4.36×10^{-10} g O_3/CFU.

Finally, the X coefficient was calibrated, which correlates the grams of phosphorus captured per cell produced (biomass unit). The starting value of this coefficient is theoretical (equation (3.1)) (supp material), so it was adjusted according to the values recorded on site. After performing the iteration required to obtain a decrease in phosphorus concentration by 43%, the value of X was modified by one order of magnitude, going from 0.022 to 0.3 g P/g biomass.

3.3. Sensitivity analysis

During the sensitivity analysis, different values were assigned to the coefficients that were calibrated to find the range of values in which the most important output variables (SOR, DO_3 (COD), DO_3 (FC), and (P_E)) did not deviate beyond the proposed safety factor (F) of $\pm$10%. The range of reliable values of the studied coefficients was found to be as follows: coefficient A ($0.7 \leqslant 1.01 \leqslant 1.35$); coefficient Y_N ($0.048 \leqslant 0.28 \leqslant 0.1$); coefficient X ($0.040 \leqslant 0.3 \leqslant 0.26$); coefficient Z ($0.00094 \leqslant 0.001033 \leqslant 0.00113$) and coefficient W ($3.93 \times 10^{-10} \leqslant 4.36 \times 10^{-10} \leqslant 4.8 \times 10^{-10}$). On the other hand, the treated water flow was 648 000 m^3 d^{-1}. From the sensitivity analysis, it can be inferred that this value could be increased to 706 500 m^3 d^{-1}, without exceeding the safety factor of 10%. This means that between 7.5 and 8.1 m^3 s^{-1} could be treated with the same installed air and ozone injection capacity (i.e. three MWDU units).

4. Discussion

Since the difference between the proposed initial value and the calibrated value of coefficient A is very low, it can be inferred that the predominant composition of biodegradable organic matter in this type of aquatic system does not differ much from the initial theoretical composition ($C_6H_{12}O_6$). This means that to calculate the oxygen demand in other bodies of water with similar characteristics to the lake under study, the reported value can be used to apply the model without having to know the chemical composition of the organic matter.

A similar conclusion can be drawn from coefficient (Y_N), since its value did not differ considerably, increasing from 0.123 to 0.280 g biomass$_{(N)}$/g NH_4^+. However, this small variation was sufficient for the model to estimate an increase in nitrifying biomass, which can be interpreted as the existence of other forms of nitrogen removal, other than the nitrification process proposed in the model. There are several mechanisms that could account for nitrogen loss during oxygen injection into a water body: (a) gaseous ammonia escaping to the atmosphere, (b) nitrogen precipitation by assimilation of NH_4^+ in biomass, (c) biological denitrification, and (d) sedimentation of insoluble particulate nitrogen (Middlebrooks and Pano 1983, Shammas *et al* 2009). Additionally, during treatment, the conversion of organic nitrogen compounds into NH_4^+ (ammonification), driven by the oxidation of organic nitrogen by ozone, may have occurred. It is likely that one or more of the above mechanisms other than nitrification were present; if so, that phenomenon would be quantified in the increase of the Y_N value. Therefore, the model is better able to predict total nitrogen removal using a value of 0.280 g biomass$_{(N)}$/g NH_4^+ than the theoretical value originally proposed.

Unlike the two previous constants, the performance constant (Z) increased its value by one order of magnitude after calibration. Constant Z was originally obtained in the laboratory, simulating the conditions of ozone injection in water from Lake Valsequillo. Under these laboratory conditions, the injection depth is practically zero, since the injection was carried out in one-liter bottles (Tabla-Hernández *et al* 2018). As a result, part of the injected ozone escaped to the atmosphere without reacting with the different pollutants contained in the water samples, increasing the ozone demand per unit of COD removed and thus the value of Z. On the other hand, during the implementation of the treatment on site, ozone was injected at a depth between 5 and 10 m, having enough time to react throughout the entire water column. This difference in implementation could be reflected in the variation between the initial value and the calibrated value of Z. In other words, the effect of the depth of ozone injection is already considered in the value Z (0.00103). Moreover, the originally proposed constant W, which measures the amount of ozone required as a function of Fecal coliform concentration, was obtained in the same way as constant Z. It was therefore not surprising that this value also increased by an order of magnitude after calibration. Thus, during this process, the original value was also adjusted to the conditions of the treatment implementation on site, namely the injection depth and half-life time of ozone in the lake water.

It is worth noting that Tabla-Hernandez *et al* (2020) determined that no residual ozone concentrations were detected at any time during the treatment nor significant variations in the initial bromide concentrations, therefore no bromate was generated. Hence, the value of the Z coefficient is not affected by ozone loss to the atmosphere.

The constant that presented the greatest variation after calibration was X, which expresses the amount of phosphorus captured by the biomass generated during the treatment. The value of the original variable was obtained from the stoichiometric ratio, which states that for every gram of bacteria, there are 0.022 g of phosphorus embedded in them. During calibration, however, value X was adjusted to 0.3 g P/g biomass. The difference in phosphorus uptake capacity could be due to the type of bacteria present in Lake Valsequillo. Organisms capable of capturing

more than 30% of their total biomass in the form of phosphorus are polyphosphate-accumulating organisms (PAOs). This type of bacteria thrives in systems where oxygen concentration varies with time. For example, the enhanced biological phosphorus removal process is a variation of the activated sludge process discovered in 1959, which involves subjecting microorganisms to anaerobiosis (in the presence of available organic matter) and alternating it with aerobic or anoxic conditions (with little available organic matter) (Dorofeev *et al* 2020).

PAOs release phosphorus under anaerobic conditions and absorb it again at a higher rate under aerobic conditions (Saia *et al* 2017); this process depicts a type of microbial existence known as cyclic metabolism. The value of the coefficient suggests that there could be a high concentration of PAOs in Lake Valsequillo, which began to actively capture phosphorus after the oxygen was injected. This interpretation is plausible since different studies have reported that PAOs are widely distributed in aquatic ecosystems, especially those that receive high phosphorus concentrations (Saia *et al* 2017). Another phenomenon that may have occurred is the precipitation of phosphorus due to the indirect interaction of ozone, as it can oxidize organic phosphorus thus releasing reactive phosphorus (PO_4^{-3}). The latter, in turn, is free to mix with alkaline or alkaline earth metals such as calcium, which is found in high concentrations in the Lake Valsequillo (Martinez-Tavera *et al* 2021). If this is the case, this phenomenon would be quantified in constant X, which means that to use the value of 0.3 g P/g biomass to model another water body, the concentration levels of alkalinity measured as calcium carbonate must be similar to those of Lake Valsequillo.

The reduction of P and N predicted by the model also modified its ratio (N/P). This ratio is very important, since it impacts the concentration of cyanobacteria in lakes (known to threaten the ecosystem balance). When this happens, one of the parameters becomes the limiting agent for phytoplankton bloom development (Montalvo *et al* 2021) and may inhibit the growth of opportunistic invasive algal communities. Likewise, the rest of the phosphorus and nitrogen that enters phytoplankton productivity is transferred to the higher trophic chains of zooplankton and fish, as well as aquatic macrophytes and littoral vegetation. Therefore, a natural control flow in the dynamics of these variables is achieved (Luna-pabello and Aburto-casta 2014).

With respect to the amount of oxygen injected into Lake Valsequillo, table S5 (suppl material) shows the results reported in different water bodies around the world using different injection techniques (surface and hypolimnetic). The oxygen flow rate reported by other authors varies between 1.0×10^{-2} and 1.8×10^{-7} kg O_2 m^{-3} d^{-1}. The oxygen flow rate used in the current modeling falls within this range (6.0×10^{-5} kg O_2 m^{-3} d^{-1}). This value highlights the fact that oxygen injection is able to turn a water body into a kind of wastewater treatment plant (like an aerated lagoon), without having to substantially increase the amount of oxygen injected compared to existing techniques. Another comparative advantage of this oxygenation technique is the wide range of pollutants that can be targeted, since, although several pollutants can be reduced by hypolimnetic oxygenation, its main objective is preventing the release of phosphorus from sediments. On the other hand, combining ozone with oxygen can reduce a wide range of pollutants by targeting them throughout the water column without having to wait for them to reach the sediments.

Regarding the recovery time of the lake, the model predicts that the projected reduction of pollutants would occur after 123 d of treatment. Notwithstanding, this time is only valid when the lake operates as a batch type reactor, i.e. without any inflow, but when operating as an idealized continuous flow complete mix reactor (with inflow and outflow of water) the projected time to reduce the pollutants to target levels will be regulated by the hydraulic retention time (321 d).

During the feasibility analysis, some variables were taken into consideration: the volume of treated water, the total organic load in the lake, the acquisition cost of the technology, the operation and maintenance costs and the lifetime of the equipment reported by the manufacturer. The feasibility analysis of this type of technology shows that the treatment is cost-effective. The cost of the treatment is 0.019 USD m^{-3}. This is consistent with other studies that report that among all the techniques available for recovering contaminated bodies of water, aeration is the most affordable one (Schönach *et al* 2017).

Finally, some considerations and recommendations are presented when using the mathematical model in another body of water:

(a) The model does not predict the concentration of disinfection by-products, therefore some compounds, such as bromates and aldehydes, must be monitored periodically during treatment.
(b) In order to use the mathematical model in another body of water, the initial concentration levels of BOD_5, COD, TN, TP and FC must be measured. In addition, the non-fixed variables (α and β) must be measured in the laboratory or obtained by literature review. Finally, the temperature and height above sea level at which the body of water is located must be known variables before implementing the model.
(c) The model was built under steady state conditions and therefore represents idealized conditions. However, the model does not consider other aspects such as the nutrient cycle, so when applying the model to another body of water, these aspects should be taken into consideration.

(d) The amounts of ozone injected into the lake were below the reported lethal doses of various organisms found in these types of water bodies (table S6, supplementary material). Nonetheless, before implementing this treatment elsewhere, it is recommended to be aware of the different sensitivities of living organisms to ozone.

5. Conclusions

The mathematical model presented here was originally developed with values obtained in the laboratory and later calibrated and validated with previously published field values. The model was shown to be an effective tool in predicting oxygen and ozone demand to reduce different physicochemical pollutants in a contaminated water body. The comparison between the oxygen demand estimated by the model and the data reported in the scientific literature is consistent. The results of this work show that it is possible to achieve a certain degree of recovery in a water body in a relatively reasonable time by injecting oxygen and ozone in the form of microbubbles throughout the water column. This model can be used in other water bodies with similar characteristics to Lake Valsequillo to predict the recovery time of a lake using MWDU or other similar technologies.

Author contributions

Jacobo Tabla-Hernandez: writing-original draft, data curation, conceptualization, investigation. Alejandro V Dellepere: conceptualization, supervision, project administration, writing-review and editing, investigation. Ernesto Mangas-Ramírez: formal analysis, methodology, investigation, writing-review and editing.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

To our knowledge, we have no conflicts of interest to declare.

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