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Dynamic Water Quality Modelling Of Tannery Effluents – Bogotá River (Colombia)

Tania Fernanda Santos Santos

Luis Alejandro Camacho

WATER QUALITY MODELLING OF TANNERY EFFLUENTS (CR, SULFUR, CL) UPPER BOGOTÁ RIVER BASIN (COLOMBIA)

TANIA FERNANDA SANTOS[1], LUIS A. CAMACHO[1].

(1):*Departamento de Ingeniería Civil y Ambiental. Facultad de Ingeniería. Universidad de los Andes. Colombia*

ABSTRACT

In this research the extension of a dynamic water quality model in order to simulate the impact caused by tannery effluents with high contents of sulphides, chlorides and chromium is presented. The model subroutines, designed and implemented in MATLAB/SIMULINK in this work, were coupled to a dynamic water quality model applied within the project framework “Dynamic water quality modeling of the Bogotá river”, UNAL-EAAB [1]. The implemented Chromium (Cr) subroutine describes the behavior of the heavy metal transport and chemical reaction in the water column. Also the speciation of Cr^3 and Cr^6 and the fractions of dissolved and particulate Cr are determined in order to compute water-sediment interactions under anoxic and anaerobic conditions depending on the oxidation state of Cr. The sulphides model can represent the behavior of H_2S (Sulphides), Sulphates and Sulphites based on a speciation and chemical equilibrium model depending on the pH. As a study case application, the results along a 20 km stretch of the Bogotá River - Colombia between the municipalities of Villapinzón and Chocontá are presented and analyzed. Within this reach the river temporal water quality dynamics caused by spatial and temporal variations of non-treated tannery effluents is very high. The dynamic model is calibrated in the studied reach using field data and laboratory analyses of water samples taken during two measurement campaigns carried out under different hydrological conditions. Additionally, model verification is performed with an independent data series. With the proposed model satisfactory values of the Nash determination coefficient were obtained during calibration and verification phases in the range of R^2 0.74 to 0.97. Finally, the calibrated model is used as part of a decision support tool, simulating the impact on the river water quality of different treatment scenarios for the tannery effluents.

INTRODUCTION

As a consequence of the current human activities and population growth in the cities, and because of treated and non-treated effluent discharges, the river water quality has decreased substantially. These wastewaters can affect public health, limiting the use of water and impacting landscape and ecosystems.

Following a rigorous calibration and verification protocol, mathematical models can predict water quality under different both hydrological and pollution load scenarios [2]. Additionally, it is possible to analyze the impact that an effluent discharge will have on the river water quality in order to assess if the standards for the different water uses along the river basin are maintained.

This research focus is on the dynamic water quality conditions that result on a river downstream of tannery effluents varying in space and time. The dynamic model AMQQ developed in UNAL-EAAB project [1] was extended in order to incorporate the toxic tannery effluent determinands e.g. Chromium, Sulfur and their transport and fate.

In this article first the conceptual and mathematical constructed model of Chromium and Sulfur species is presented, secondly the model utility and its prediction capacity is shown through the calibration and verification results obtained in the upper Bogotá river basin.

MODEL DESCRIPTION

The water quality model of tannery effluents was developed coupling the Aggregated Dead Zone (ADZ) solute transport model by Beer and Young [6], the Multilinear discrete lag-cascade model (MDLC) developed by Camacho and Lees [7], and the Quality Simulation Along River Systems, QUASAR model Whitehead *et. al.*[8]; Camacho[9]; and Lees *et al.*[10]. The dynamic unsteady flow model for conventional determinands AMQQ ADZ-MDLC-QUASAR, UNAL and EAAB [1] implemented in SIMULINK of MATLAB, provides a means of assessing current environmental impacts of pollutants on the water quality of the Bogotá river, and constitutes a potential starting point for a decision support system for the planning and management of sanitation alternatives.

The river is modeled as a series of incompletely mixed reactors to characterize transport phenomena i.e. advection, dispersion and dead zones, and physical, chemical and biological transformations of each water quality conventional determinand *i.e*. organic matter, nutrients, oxygen, pathogens, suspended and dissolved solids.

The tannery process is characterized by the use of chemicals as Sulphur (S) in the deharing process and Chromium (Cr) in the subsequent tannery process, in order to stabilize the animal skin and transform it into leather. As a result, the process generates effluents with these substances. In river waters, their behavior is different to conventional determinands and both can be found in particulate or dissolved form. In addition, in the environment S and Cr have different species that determine the possible chemical and physics reactions in the water column i.e., oxidation-reduction, sorption, precipitation, volatilization.

Chromium model.

Chromium (Cr) is the only toxic element that is regulated for different species (Cr^3 and Cr^6) due to the toxicity of each oxidation state [11]. This characterization is performed by differences in the chemical, toxicological and epidemiological two species behavior. The Cr^6 is a powerful epithelial irritant and carcinogen determinand; it is toxic to plants, aquatic animals and bacteria. In contrast, the Cr^3 in low concentrations is generally known as a benign and organic micronutrient. For this reason, the model includes the more stable and prevalent two forms of Chromium in the environment. Cr^6 compounds are highly soluble and mobile species compared with Cr^3 [12].

The model includes three compartments: water, aerobic and anaerobic sediments; moreover, for each of the compartments the Cr^3 and Cr^6 particulate and dissolved fractions are determined to define the portion of each species that will be affected by the processes of sedimentation, diffusion, resuspension and precipitation.

The conceptual model with the reactions expected between Cr^3 and $Cr^6$is shown in Figure 1.

This model is coupled with the AMQQ model in order to integrate the toxic and conventional determinands models. To determine the gain or loss of oxide reduction reactions between Cr^3 and Cr^6, two models that estimated the Cr^3 and Cr^6 speciation according to pH were designed. The models are based on the chemical equilibrium principle and experimental analyzes presented in MINTEQ tool [13]. The possible existing forms of Cr^3 & Cr^6 in the environment have been studied to obtain the dependence on pH in aquatic environments with unique H_2O and OH agents [14], [12].The Cr^3form that could be oxidized to Cr^6 is $Cr(OH)_3$ and the Cr^6 forms that could be reduced to Cr^3 are $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{-2}$ [11], [14].

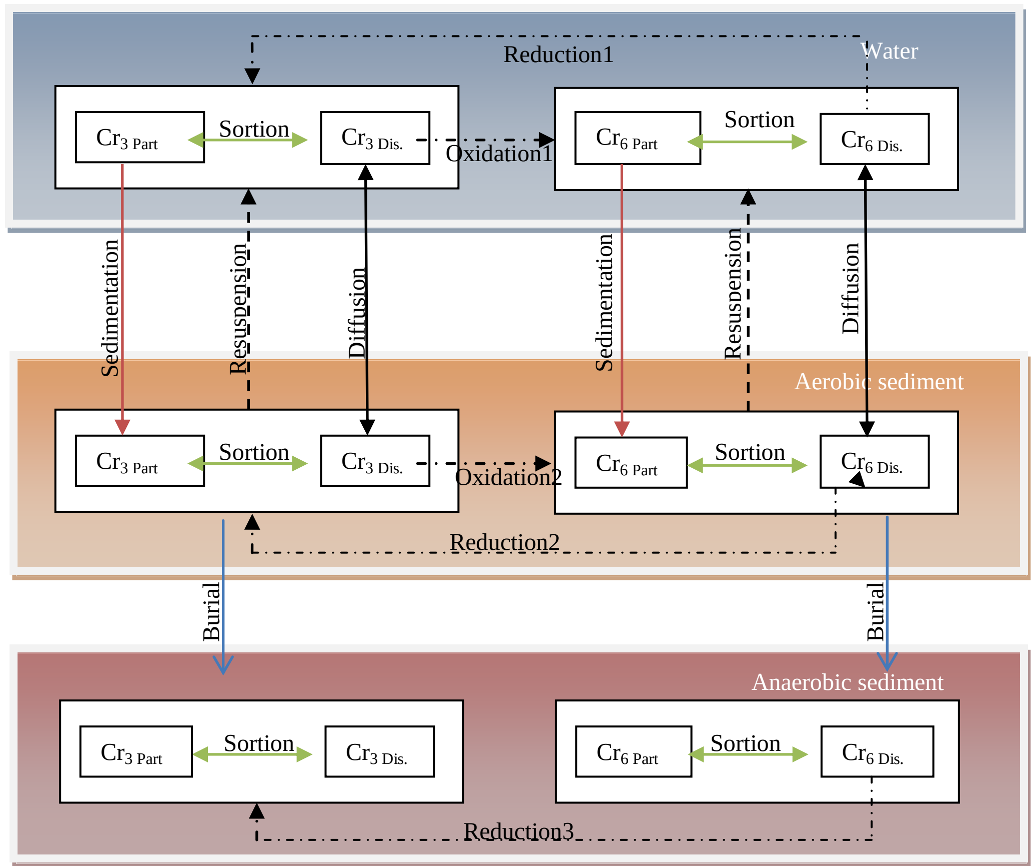

Figure 1. Conceptual model Cr^3 and Cr^6. Source:Santos[15].

Solving the Cr^3 chemical equilibrium equations system (1) with the premise that the sum of all Cr^3 forms portion is 1, it is possible to obtain the concentration of each Cr^3 form according to pH,

Reaction	pK	Equilibrium equation	
$Cr^{3+} + H_2O = Cr(OH)^{2+} + H^+$	pK_2=3.85	$L_2 = \frac{K_2 L_1}{[H^+]}$	
$Cr^{3+} + 2H_2O = Cr(OH)^+_2 + H^+$	pK_3=10.06	$L_3 = \frac{K_3 L_1}{[H^+]}$	
$Cr^{3+} + 3H_2O = Cr(OH)_3 + 3H^+$	pK_4=18.70	$L_4 = \frac{K_4 L_1}{[H^+]^3}$	Eq.(1)
$Cr^{3+} + 4H_2O = Cr(OH)^-_4 + 4H^+$	pK_5=27.87	$L_5 = \frac{K_5 L_1}{[H^+]^4}$	
$3Cr^{3+} + 4H_2O = Cr_3(OH)^{5+}_4 + 4H^+$	pK_6=8.4	$L_6 = \frac{K_6 L_1^3 (Cr_3)^2}{[H^+]^4}$	

where de pK_x (x between 1 to 6) are the chemical equilibrium constants, L_x (between 1 to 6) are the fractions of each Cr_3 form [14] defined as: L_1 is Cr^{3+}/Cr3, L_2 is $Cr(OH)^{2+}$/Cr3, L_3 is $Cr(OH)^+_2$/Cr3, L_4 is$Cr(OH)_3$/Cr3, L_5 is $Cr(OH)^-_4$/Cr3 andL_6 is $Cr(OH)^{5+}_4$/Cr3.

In the same way, solving the Cr^6 chemical equilibrium equations system (2) is possible to obtain the concentration of each Cr^6 form according to pH, where de K_x (x between 7 to 9) are the chemical equilibrium constants, D_x(between 1 to 4) are the fractions of each Cr6 form [12] defined as D_1 is $HCrO_4^-$/Cr6, $D_2$is H_2CrO_4/Cr6, $D_3$is CrO_4^{2-}/Cr6 and $D_4Cr_2O_7^{2-}$/Cr6.

Reaction	K	Equilibrium equation
$H_2CrO_4 = H^+ + HCrO_4^-$	$K_7=10^{-0.75}$	$D_2 = \frac{[H^+]D_1}{K_7}$
$HCrO^-{}_4 = H^+ + CrO_4^{2-}$	$K_8=10^{-6.45}$	$D_3 = \frac{K_8 D_1}{[H^+]}$
$2HCrO^-{}_4 = Cr_2O_7^{2-} + H_2O$	$K_9=10^{2.2}$	$D_4 = K_9 D_1^2 Cr_6$

Eq.(2)

As an example, following the conceptual model for Cr coupled with the transport model AMQQ, the resulting differential equation of Cr_3in water is:

Cr_{3w}=Transport +Resuspension 1– Sedimentation 1+/- Diffusion 1- Oxidation1 + Reduction1

$$\frac{dCr_{3w}(t)}{dt} = \frac{1}{Tr}\left(e^{-kCr3t}Cr_{3i}(t-\tau) - Cr_{3w}(t)\right) + \frac{1}{Hw}\left[\left(vr_1 * Cr_{3s}(t)\right) - \left(vs_1 * Cr_{3w}(t) * Fp_{3w}\right)\right] + \frac{1}{Hw}\left[vd_1\left(Cr_{3s}(t) * Fd_{3s} - Cr_{3w}(t)Fd_{3w}\right) - \left(vo_1 * Cr_{3w}(t) * Fd_{3w} * L_4\right)\right] + \frac{1}{Hw}\left[\left(vre_1 * Cr_{6w} * Fd_{6w} * (D_1 + D_3 + D_4)\right)\right]$$

Eq. (3)

where the sub-index *w* means water, and *s* aerobic sediment; *Tr* is the hydraulic retention ADZ mixing time; *Hw* is the water depth; vr_1 is the resuspension velocity; vs_1 is the settling velocity; vd_1 is the diffusion velocity; vo_1 is the oxidation velocity; vre_1 is the reduction velocity; Fp_{3w} is the Cr^3 particulate fraction in water; Fd_{3w} is the Cr^3 dissolved fraction in water; and Fd_{6w} is the Cr^6 dissolve fraction in water

Sulfur model

The sulfurs are present in the environment in various chemical forms i.e. Sulphides (S^{2-}, H_2S, HS^-), Sulphates (SO_4) and Sulphites (SO_3). All plants, animals and bacteria metabolize sulfur to synthesize amino acids. Sulphides can be assimilated biologically as Sulfates.

In the tanning process the Sulfur comes from the use of Sodium Sulphide and Sodium Hydrosulfide and in the deharing process from the hair degradation. The discharges with these substances originate important environmental impacts. Under alkaline conditions, sulfur prolonged its dissolved state, but when the effluent pH drops below 9.5, the production of hydrogen sulphide is started and increased by the presence of acid in the effluent, generating odors and the risk of inhaling the toxic gas H_2S.

The possible reactions between the Sulfur forms that occur by bacteria actions are summarized in the conceptual model presented in Figure 2.

According to the Sulfur conceptual model, where it is expected that the sulphites and sulphides are transformed into sulphates, the differential equations describing the behavior in water including the transport process are formulated. As an example in this article, the differential equation of sulphates was obtained (see Eq 4). The Sulphate concentration (SO_4) is calculated in terms of the transport (*Tr* is the hydraulic retention ADZ mixing time and τ is the advective ADZ delay time), plus the reaction from SO_3 (in terms of the S_3 rate) and the Sulphite-Sulphate reaction given by the S_4 rate, less the reaction from Sulphate to Sulphide (S_1 rate), see Eq (4).

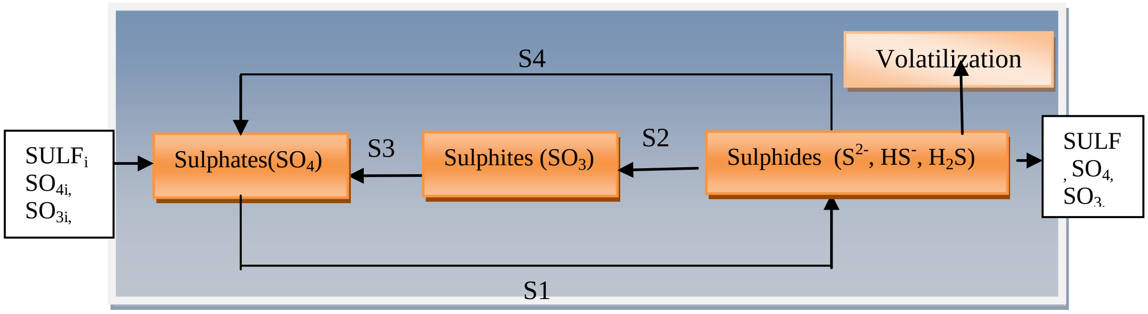

Figure 2. Sulfur conceptual model.

SO_4=Transport+Reaction (SO_3-SO_4)+ Reaction (Sulphites-SO_4)- Reaction (SO_4-Sulphites)

$$\frac{dSO_4(t)}{dt} = \frac{1}{T_r} e^{-k_{SO4}t}\left(SO_{4i}(t-\tau) - SO_4(t)\right) + \left[S_3 * SO_3(t) + S_4 * Sulf.(t) - S_1 SO_4(t)\right] \quad \text{Eq. (4)}$$

BOGOTA RIVER UPPER BASIN.

A comprehensive research in the upper basin of the Bogotá River was carried out, along a reach located at 5 km downstream of the town of Villapinzón, located at 2662 meters above sea level. In this reach, the river receives the untreated municipal wastewater of 6000 inhabitants in Villapinzón. Downstream, 170 tanneries in a corridor of 10 km are located with a total processing capacity of about 100.000 skins per month. In addition, only 20 industries have some wastewater treatment process, therefore producing highly intermittent and polluted wastewater with chlorides, chromium, BOD, COD, suspended solids, sulfur, nitrogen, and fats and oils to the Bogota River. The length of the study reach is about 4.5 km and is characterized by sequences of pools and rapids with lower flow rates of about 2.5 m^3/s. As a consequence, this reach has a high dynamic hydraulic and water quality behavior.

To understand the dynamic water quality condition of the river, field visits, hydraulic tracers, and flow gauging measurements were performed. Subsequently, sample stations were defined in order to capture the dynamic water quality behavior by continuous conductivity measurements over long periods of time. Four sample stations were defined (Figure 3).

Field data

In order to obtain the relevant information and field data to calibrate and verify the developed solute transport and water quality model (AMQQ) extended to tannery effluents, three water quality campaigns were performed under high (2.33 m^3/s), medium (1.33 m^3/s) and low flow (0.55 m^3/s). Hydrometric measurements, *in situ* measurements of conductivity (see Figure 4), pH, temperature and dissolved oxygen, and water sampling for laboratory analysis of all water quality determinands were carried out following the water mass. The first samples in each station (see black circles) are used to calibrate the model in steady state mode. The following samples taken during the contamination event are used to characterize the river dynamics, water quality processes and to calibrate the AMQQ dynamic model extended to represent the effect of tannery effluents.

Calibration was performed using the Shuffle Complex Evolution SCE-UA, Duan *et al*. [3] methodology and the GLUE Generalised Likelihood Estimation Uncertainty, Binley and Beven and [4] methodology based on the analysis of Monte Carlo simulations (MC). Parametric model uncertainty and parameters identifiability were carried out using the MCAT tool Monte Carlo Analysis Toolbox, Lees and Wagener [5]. Once calibrated and verified the model was used to simulate different scenarios and analyses of tannery effluents treatments and their impact on the river water quality.

Geographical position Bogotá River Basin map	Study reach. 5 sample stations

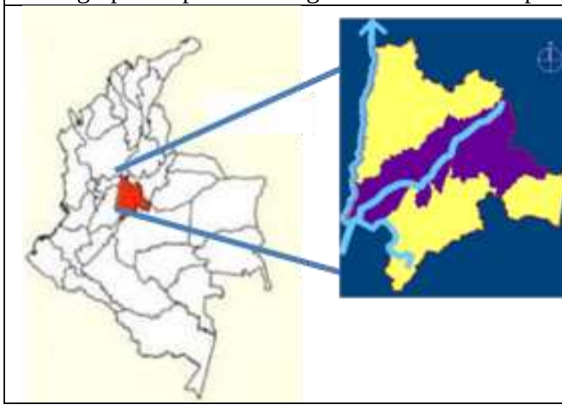

Figure 3. Bogotá river Basin map, four samples stations.

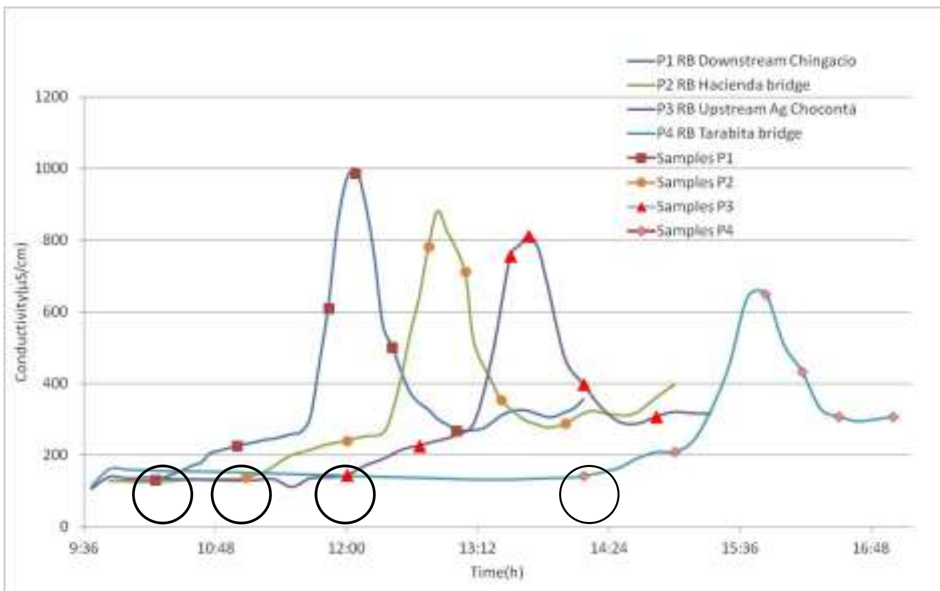

Figure 4. Conductivity measurements in four sample stations.
Campaign May 6, 2009.Q= 1.33 m^3s^{-1}

Calibration and verification results

The implemented chromium and sulfur model was satisfactorily calibrated and verified. Nash determination coefficients R^2 of 0.74 and 0.97 for the flow conditions of 0.55 and 1.33 m^3/s respectively were obtained during calibration. As an example, in Figure 5 the behavior of the tannery effluents in verification mode using data of campaign 2 is presented. The Cr^3 and Cr^6 models simulations and field data plots are shown in Figure 5a. The Cr^3 model result is very close to the observed data, showing the excellent results of the model. However, the Cr^6 model shows a concentration increase in a small range (0.001). According to the laboratory analyses Cr^6 concentrations are less in all samples than the detection limit (0.05 mg/l). In Figure 5b the behavior of sulphides, sulphates and sulphites is shown. The detection limit to sulphides and sulphites is 0.2 mg/l. In all samples the concentration was less than this value. The sulphates model results are considered excellent showing the increase concentration expected along each sample station.

a.

b.

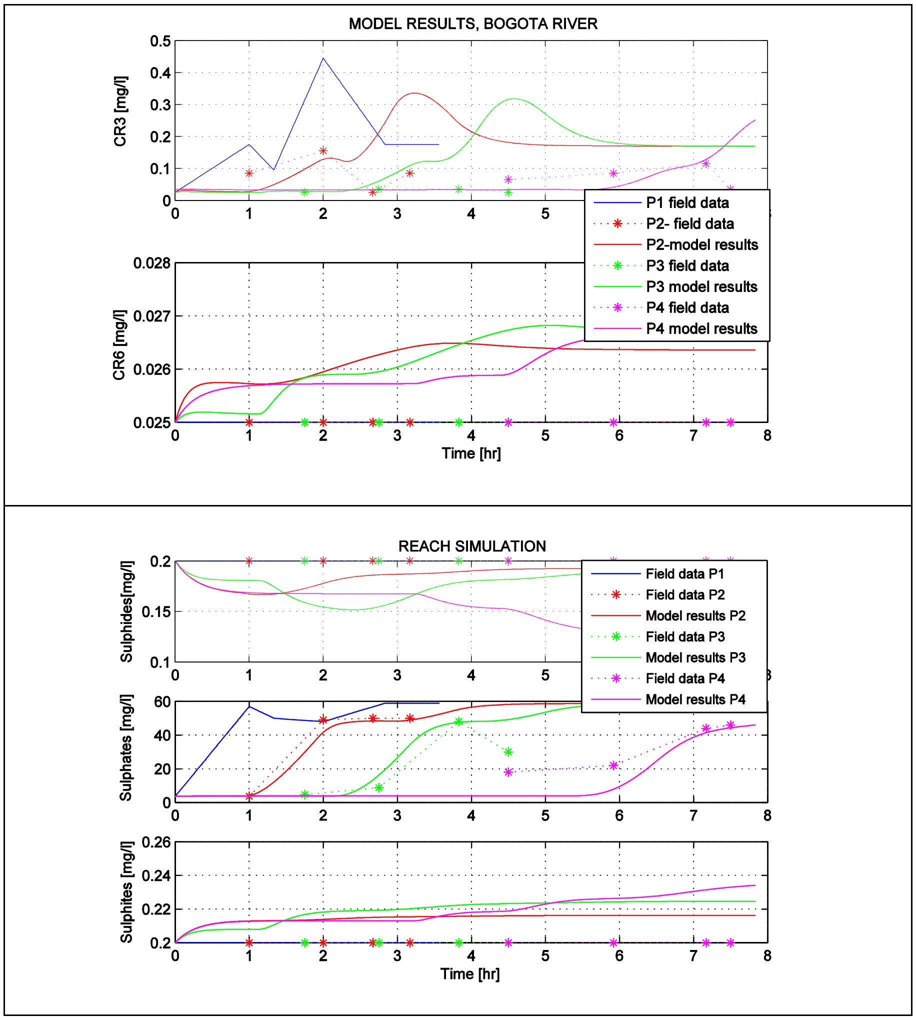

Figure 5**.Verification of pH, alkalinity, Chromium and Sulfur** R^2 0.97**. Sample station**: P1 RB Downstream Q Chingacio; P2 RB hacienda bridge; P3 RB Upstream Ag Chocontá; P4 RB Tarabita bridge.

MODELLING TO PLANNING.

The AMQQ model coupled with water quality determinands of tannery effluents, can be used as a planning tool for the entities that control water use in the basin. It is possible to determine the maximum pollutant load that the river has the capacity to assimilate to guarantee water quality goals and objectives. If the tanneries continue to discharge untreated effluents, the impacts on water quality will generate serious conflicts over the use of water in the basin. Almost all water quality determinands i.e. DO, BOD, TSS, Cr, sulphides and chlorides do not meet actual water quality goals. The model simulations show that if primary treatment is performed to the tannery effluents in compliance with the parameters defined in the regulation, the water quality goals of the river could be achieved except by BOD and chlorides. Finally, the Chlorides goal cannot achieved even if a secondary treatment of tannery effluents is implemented.

CONCLUSIONS

The AMQQ model has been extended to model the impact on a stream caused by the dumping of toxic substances such as chromium, sulfides and chlorides from industrial effluents of tanneries. The implementation of chemical equilibrium models for chromium sulfides allowed characterizing the behavior of these determinands according to the pH.

In the Bogotá River case study the proposed model could be calibrated and validated with good results following a rigorous calibration protocol. For this reason it is possible to use the extended model to analyze alternative treatment processes of tannery effluents and to determine their impact on the river water quality. The implemented generic model can be used in other rivers with similar discharges, but calibration and verification is necessary under local conditions.

The simulation scenarios show that if primary treatment is carried out to tannery effluents the water quality goals for the Bogotá River in the upper basin will be met except for BOD and chloride.

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