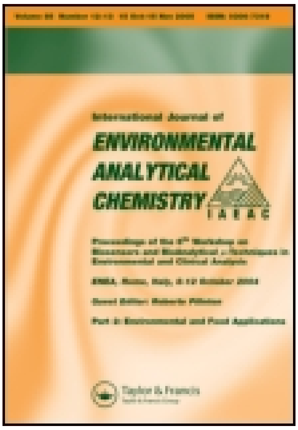

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Removal of selected organic pollutants and coliforms in pilot constructed wetlands in southeastern Mexico

Amado E. Navarro [a], María E. Hernández [b], Josep M. Bayona [c], Lorenzo Morales [a] & Paola Ruiz [b]

[a] Technological University of Izúcar de Matamoros, Izúcar de Matamoros, C.P. 74420, Mexico

[b] Biotechnological Management of Resources Network, Institute of Ecology A.C., Km 2.5 Ant. Carretera a Coatepec # 351 Congregación El Haya Xalapa, Veracruz 91070, Mexico

[c] IDAEA-CSIC, Jordi Girona 18, Barcelona E-08034, Spain

To cite this article: Amado E. Navarro, María E. Hernández, Josep M. Bayona, Lorenzo Morales & Paola Ruiz (2011): Removal of selected organic pollutants and coliforms in pilot constructed wetlands in southeastern Mexico, International Journal of Environmental Analytical Chemistry, 91:7-8, 680-692

To link to this article: http://dx.doi.org/10.1080/03067319.2010.547578

Intern. J. Environ. Anal. Chem.
Vol. 91, Nos. 7–8, 15 June–15 July 2011, 680–692

Removal of selected organic pollutants and coliforms in pilot constructed wetlands in southeastern Mexico

Amado E. Navarro[a]*, María E. Hernández[b], Josep M. Bayona[c],
Lorenzo Morales[a] and Paola Ruiz[b]

[a]*Technological University of Izúcar de Matamoros, Izúcar de Matamoros, C.P. 74420, Mexico;* [b]*Biotechnological Management of Resources Network, Institute of Ecology A.C., Km 2.5 Ant. Carretera a Coatepec # 351 Congregación El Haya Xalapa, Veracruz 91070, Mexico;* [c]*IDAEA-CSIC, Jordi Girona 18, Barcelona E-08034, Spain*

(*Received 18 February 2010; final version received 2 December 2010*)

The removal efficiency of selected emerging pollutants, total (TotCol) and faecal (FecCol) coliforms in surface (SF) and subsurface (SSF) flow constructed wetlands (CWs) was compared. The pilot plant (located in southeastern Mexico) consisted of eight CWs: four with SF and four with SSF. Two cells of each type were planted with *Typha* sp. and two were left without plant as controls. CWs were fed with water from Sordo river, which receives untreated urban sewage and industrial wastewaters. Water samples from river and outflow from each CW were collected in four sampling campaigns, they were filtered, extracted and analysed by GC/MS. Redox potential (Eh) was measured in all cells. The following pollutants were identified and quantified: Caffeine, CAF; Galaxolide, GAL; Methyl dihydrojasmonate, MDHJ; Linear alkylbenzenes, LAB; Butylated hydroxytoluene, BHT; Surfynol 104, SSURF; Alkylphenols, AP; 4-alkylphenol monoetoxylates, APE; Parsol, PAR. Typical removals of studied compounds were attained with slightly better results in SSFCW. A multiple linear regression analysis considering Eh, time, influent pollutant concentration (C_0) and the presence of plants and filtering media (Fmedia) as independent variables showed that Eh has a significant influence in the removal for almost all the studied compounds with the exception of BHT and AP. C_0 influences removal processes with the exception of coliforms. A significant influence of Fmedia in the BHT and PAR removal is observed, also positive for AP, APE, CAF, LAB and GAL in decreasing order. The effect of plants is positive for PAR (significant), GAL, CAF, BHT and MDHJ. SURF has a distinct behaviour with a negative coefficient for its C_0. For TotCol and FecCol the most significant effects are Eh and time. This may be related to the fact that predation by aerobic microbial communities may be the predominant factor in their removal and the development of these microbial communities with time.

Keywords: emerging pollutants; coliforms; removal; constructed wetlands

1. Introduction

After more than 40 years of research and constructed wetland (CW) development, they are a key feature in the arsenal of wastewater treatment technologies (WWTT). They have been successfully used around the world especially in US and Europe, providing a reliable

---

*Corresponding author. Email: navarro48_99@yahoo.com

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067319.2010.547578
http://www.informaworld.com

decentralised treatment technology for a variety of polluted waters, including industrial and agricultural wastewater, stormwater runoff, municipal sewage and landfill leachate. Compared with conventional systems, CWs show less construction, operation and energy costs, more flexibility in pollutant loading and by-product reduction, combined with the enhancement of environmental and aesthetic values. CWs are used as secondary or tertiary treatment, as a stand alone technology or combined with other WWTT and are well suited for individual household or small rural communities. In developing countries, facing limitations for the construction, operation and maintenance of conventional systems and water shortages for agricultural reuse, this sustainable WWTT is less implemented than in developed countries [1–8].

Numerous pollutant removal mechanisms occur in constructed wetlands, including both abiotic and biotic processes, such as settling of suspended particulate matter; filtration and chemical precipitation; chemical oxidation/reduction; sorption and ion-exchange on the rizosphere, breakdown, transformation and uptake of pollutants and nutrients by microorganisms (through aerobic/anaerobic processes) and plants, volatilisation, photodegradation (obviously in SFCW where water is exposed to sunlight) and predation and natural die-off of pathogens. They operate simultaneously and influence each other making difficult to understand the system as a whole. Moreover the removal mechanisms principally depend on hydraulic conditions (influenced by the porosity of the solid media in SSFCW); types, number of microorganisms and oxygen supply for them; wastewater properties and the chemical conditions of the substrate and different environmental factors. Nevertheless, it is considered that pollutant removal is mainly biologically mediated. One aspect that has been controversial is the role of vegetation and the effects of different plant species in pollutant removal. A general positive role is already well established as plants influence the microbial communities present in CWs and participate in contaminants depletion through different phytoremediation mechanisms. Further research is needed in their effect in specific pollutants removal especially in CWs optimisation [8–16].

Emerging pollutants (EP) are of a great environmental concern in the present days due to their not well known environmental consequences. They include an array of antibiotics, human and veterinary pharmaceuticals, personal-care products, household and industrial compounds that are continuously released in the environment owing to anthropogenic activities. Public awareness of their presence in waters has become through the advances in analytical techniques to detect them, their association with a newly reported effect, or through their recent introduction in the environment. Although they are present usually only at trace concentrations, their chemical persistence, biological effects, resistance to biodegradation and synergistic effects are not well understood. Many of the EPs are not completely removed by conventional WWTT, leading to their presence in effluents, rivers, lakes, and ground water. In fact, contradictory removals of the studied small number of these substances are reported. Some evidence indicates that different design and operation factors of wastewater treatment systems as solid residence time, hydraulic residence time, concentration levels in input waters, temperature, interaction of microbial communities, etc., influence EP removal. Special attention should be taken addressing the concept of "removal", as the depletion of the parent EP could lead to the formation of even more toxic intermediates. Therefore, the behaviour of EP in CWs is receiving greater attention. Evidence shows that CWs are successful technologies for removing EP from wastewater and the most significant removal process in these systems is biologically mediated. Nevertheless, it has been proposed that other competing removal mechanisms as sorption processes, volatilisation and plant uptake could play a significant role in their removal [17–29].

In Mexico, environmental laws were enacted in 1988 and water pollution control regulations were published in 1996. However, because of the lack of law enforcement, many rivers in the country are heavily polluted with a significant contribution from the direct discharge of sewer waters in surface waters and agricultural runoff. In this regard, CWs have proved to be an economic and ecologically mean to treat point and non point pollution sources and can be used to treat water from polluted rivers [30–41]. In Mexico, the use of riparian constructed wetlands to improve water quality in polluted rivers is an adequate strategy that should be included in river restoration projects. The aim of this work was to compare the removal efficiency of selected emerging pollutants, total and faecal coliforms in surface water flow (SF) and subsurface water flow (SSF) constructed wetlands, treating water from a polluted river.

2. Experimental

2.1 *Experimental mesocosms*

This study was conducted in the central part of Veracruz State in southeastern Mexico. The CW pilot plant is located in a greenhouse of the Botanical Garden Francisco Javier Clavijero in Xalapa (97° 01″ W 19° 33.5″ N), the capital of Veracruz State. CWs were fed with water from Sordo River which receives untreated urban sewage and industrial wastewaters. This river is a third-order stream that originates in the tropical mountain rainforest upstream from the botanical garden, downstream it joins the Pixquiac river and finally it merges to La Antigua River which flows into the Gulf of Mexico. The area of La Antigua river watershed is 2827 km^2 [42].

The experimental array of CW cells (1.5 m length, 0.25 m wide and 0.6 m depth) was as follows: four glass fibre cells were set up for SFCW (substrate upland soils, 0.4 m deep, free water surface flow column of 10 cm) and four for horizontal SSFCW (volcanic gravel $D_{60} = 0.04$ m, 0.4 m depth, water flow 10 cm below surface). Two cells of each type were planted with *Typha* sp. and two were left without plant as controls. CWs were planted on 15 April 2009 and flooded with river water, they were without flow for 45 days for vegetation adaption until 1 June, then were continuously feed with river water until the end of the experiment. Water was pumped to a 500 L homogenisation tank and its flowrate was adjusted for each cell to have an HRT of 5 days.

Redox potential (Eh) was measured using platinum rods, one calomel reference electrode (Corning 476340®) and a digital multimeter (Master MAS830B®). Platinum electrodes were calibrated before measurements with 0.005% hydroquinone (Sigma Q-1001) in pH 4.0 buffer solution [43]. To calculate Eh, 244 mV were added to each mV reading as a correction factor due to the potential of calomel reference electrode. Eh was monitored once a week, at 15 and 30 cm depths, near the influent and effluent in each wetland cell. For SSFCW, PVC piezometers (1.25 cm i.d.) were installed at the two depths to introduce the rods and the electrode, in the SFCW they were introduced directly into the soil and the reference electrode into the water.

2.2 *Sampling*

Four sample sets of influent (river) and effluent water of each CW unit were taken at 12, 22, 64 and 166 days of CWs operation. Grab samples were collected in 1 L pre-cleaned glass bottles, mixed with 10 mL of dichloromethane to retard microbial activities, stored in ice boxes and transported to the laboratory (Technological University of Izúcar de Matamoros) where they were filtered with Whatman® #40 paper (8 μm pore diameter) within 6 h after collection and stored in the darkness at 4°C until extraction. For microbiological analysis, all samples (150 mL) were collected in commercial sterile bags, immediately put in the cooling boxes, transported, stored at 4°C and analysed within 8 h after collection.

2.3 *Analytical procedures*

Liquid-liquid extraction of filtered water samples was performed according to the EPA SW-846 3510C. Prior to extraction samples were spiked with 25 mL of d_{10}-phenantrene ($4\,\mathrm{ng}\,\mu\mathrm{L}^{-1}$), as surrogate to evaluate target compounds recoveries. Briefly, the recovered extracts were concentrated and evaporated to dryness under a gentle nitrogen stream, weighed, spiked with 25 μl of an internal standard solution of d_{12}-chrysene ($4\,\mathrm{ng}\,\mu\mathrm{L}^{-1}$), reconstituted with dichloromethane (DCM) to a final volume of 50 mL and stored at −20°C until chromatographic analysis. As the main goal of the study was the identification of a broad spectrum of semivolatile organic compounds (EPA method 8270), no derivatisation procedures were used. Several samples were fractionated by column chromatography in Pasteur pipettes to allow a more precise identification of selected compounds (stationary phase – Al_2O_3 top layer 0.5 g, SiO_2 bottom layer 0.6 g; hexane (HEX); HEX : DCM 8 : 2, hexane : DCM 2 : 8; DCM and methanol as eluents in this order, 4 mL of each solvent).

Sample extracts and column chromatography fractions were analysed on a Turbomass® quadrupole mass spectrometer fitted with an Autosystem XL® gas chromatograph (Perkin Elmer). A PE-5® (Perkin Elmer), 18 m fused silica capillary column, 0.18 mm i.d. and 0.1 μm film thickness, was used with helium as the carrier gas ($1\,\mathrm{mL\,min}^{-1}$). The GC-MS operating conditions were set at 70 eV ionisation potential with the ion source and the GC interface set at 280°C. The injection port was maintained at 290°C and 2 μl of the sample was injected in the splitless mode followed by a 1 min purge after the injection. The column temperature was held at 100°C for 1 min, then temperature programmed at $4^{\circ}\mathrm{C\,min}^{-1}$ to 280°C and held enough time to complete a run time of 90 min. Full scan mode (35–450 amu) was employed after an initial solvent delay of 2.5 min.

The following compounds or families of compounds were unambiguously identified and quantified (name, abbreviation, quantification ions, uses or sources): Caffeine, CAF, 109 + 194, stimulant present in some drugs and foods widely used as tracer of anthropogenic inputs; Galaxolide, GAL, 213 + 243 + 258, used as synthetic fragrance in personal care products and household cleaners; Methyl dihydrojasmonate, MDHJ, 83 + 153 + 156, manufacture of fragrances and flavors; Linear alkylbenzenes, LAB, 91 + 105 + 119 + 133 + 147, present in detergents as a residue of their production; Butylated hydroxytoluene, BHT, 205 + 220, a common antioxidant in foods and other products; Surfynol 104 (2,4,7,9-tetramethyl-5-decyne-4,7-diol) SURF, 43 + 109 + 151, nonionic surfactant; Alkylphenols, AP, 107 + 121 + 135, biodegradation metabolite of alkyl phenolic nonionic surfactants; 4-alkylphenol monoetoxylates, APE, 179, biodegradation metabolite of alkyl phenolic nonionic surfactants; Parsol, PAR, 161 + 178, a widely used UVB filter in cosmetics.

Quantification was performed measuring peak areas from reconstructed ion chromatograms, multiplying them by the factor (total ion intensity of mass spectrum)/(quantitation ions intensity) obtained from fractions where the selected compound isolately elutes and comparing the obtained total area with that of the internal standard. According to the accepted procedures of the SW-846 8000C, 8270D and the common practices for calibration methods [44], the limit of detection (LOD) and limit of quantification (LOQ) were determined in the linear range of a six points calibration curve using dimethyl-, diethyl- and butyl benzylphthalate obtained by successive dilutions. Calculations were done using the standard error of the intercept (SE_{b0}) and the slope (b_1) of the calibration curve of each external standard:

$$LOD = 3 \times SE_{b0}/b_1;\ LOQ = 10 \times SE_{b0}/b_1$$

The used standards covered the retention windows of target compounds (relative retention times of the analytes in the range 0.70–1.04 of the standards) and have structural similarities with some of them. A blank run showed no presence of these phthalates in the solvent. LOD and LOQ ($\mu g\,L^{-1}$) ranged from 0.0003–0.0042 and 0.0052–0.0253 respectively with at least two points of the calibration curve below the LOQ.

All glass material was thoroughly cleaned with chromic mixture, tap, distilled water and dichloromethane in that order prior to use. Quality assurance samples included laboratory and field blanks consisting of produced deionised water certified as free of organic compounds. These blank water samples received the same treatment and processing as environmental samples and target compounds were not detected in them. Recoveries of d_{10}-phenantrene, which elutes in the same range as the studied compounds, were between 94–103% (mean 98), then no correction of recoveries was used.

Determination of total and faecal coliforms (TotCol and FecCol) was performed by a standard membrane filtration procedure with Chromocult filters (Sartorius®).

3. Results and discussion

3.1 *Occurrence of organic contaminants in river waters*

Table 1 shows retention time windows and some physicochemical properties of the studied compounds obtained from EPIsuite v4.00 [45]. The mean and the coefficient of variation, of the concentrations of target compounds in the river (influent) waters, in $\mu g\,L^{-1}$, and their percentages of removal in the CWs are shown in Table 2.

The concentrations of CAF, GAL, BHT, LAB, AP and APE are consistent with those reported for effluents of WWTP and some surface and riverine waters [46–52]. The presence of SURF may be related with the paper plant upstream of the mesocosms which processes recycled paper. This non-ionic surfactant is used in industrial maintenance, wood coatings, wood finishes, paper coatings, printing inks and overprint varnishes and it has been recently identified in Rhine river waters at lower concentrations (0.2–0.3 $\mu g\,L^{-1}$) [53].

3.2 *Removal of detected contaminants*

Figure 1 shows the variation of the redox potential (Eh) with time. A general trend observed for all the systems studied is a decrease in the Eh with time but in the time span of this study, its value was always positive. Up to about 90 days, there are no significant

Table 1. Retention windows and some physicochemical properties of target compounds.

Substance	CAS RN	RtW	$\log K_{ow}$	$\log K_{oc}$	WS	Biowin 1	Biowin 7	PSA[d]
SURF	126-86-3	11.07 ± 0.02	3.61	1.634	26.35	0.2719	−0.5895	18.5
BHT	128-37-0	13.73 ± 0.01	5.1	4.169	0.6	0.4453	−0.7917	20.2
MDHJ	24851-98-7	17.92 ± 0.03	2.98	2.18	91.72	0.9292	0.108	43.4
AP[a]	104-40-5	19–24	5.76	4.583	1.57	0.9215	0.1979	9.23
LAB[b]	123-01-3	19–27.6	8.65	5.256	0.01	0.9214	0.3179	0
GAL	1222-05-5	23.17 ± 0.04	5.9	4.294	1.75	−0.036	−0.9272	9.23
CAF	58-08-2	23.29 ± 0.11	−0.07	1	21600	0.6551	0.5019	58.4
APE[c]	027986-36-3	26–27.5	5.58	3.48	1.1	1.0754	0.48	18.5
PAR	70356-09-1	34.51 ± 0.04	5.8	3.935	0.155	1.0238	0.0648	35.5

RtW – Retention time window, min; WS – Water solubility at 25°C, $\mathrm{mg\,L^{-1}}$; Biowin 1 – Fast biodegradation probability, linear model; Biowin 7 – Anaerobic Fast biodegradation probability; PSA – Polar surface area, Å^2.

[a] nonylphenol; [b] dodecylbenzene; [c] nonylphenol monoetoxylate; [d] obtained from ChemSpider Data Collection (http://www.chemspider.com/).

Table 2. Mean values of the studied contaminant concentrations in influent (River) in $\mu\mathrm{g\,L^{-1}}$ and their removal (%) from the CW units.

		CAF	GAL	MDHJ	LAB	BHT	SURF	PAR	AP	APE	TotCol	FecCol
Influent (River)	MV	1.43	0.97	0.75	2.30	0.19	1.72	1.95	0.86	0.44	$2.3*10^6$	$6.5*10^5$
	CV	57.2	60.9	55.6	58.5	37.5	72.3	97.8	68.4	54.2	68.9	66.0
SF-C	MV	80.8	70.5	79.3	*	27.8	72.8	46.3	*	*	99.0	99.8
	CV	28.3	34.3	16.2	*	20.3	24.6	15.1	*	*	1.2	0.2
SF	MV	89.6	73.2	76.6	75.4	22.5	59.7	73.3	51.8	75.6	99.9	99.9
	CV	11.8	36.9	17.7	12.2	16.2	47.8	13.6	56.3	20.9	0.1	0.1
SSF-C	MV	89.8	66.5	71.5	*	33.7	62.6	58.7	*	*	98.5	99.6
	CV	11.9	39.3	23.7	*	39.4	38.1	17.8	*	*	1.4	0.5
SSF	MV	97.5	81.8	76.6	80.2	42.7	57.5	83.2	61.3	85.3	98.6	99.6
	CV	2.3	17.0	17.8	8.5	23.7	21.2	10.1	35.2	10.7	2.0	0.6

SF – Surface flow unit; SSF – Subsurface flow unit; C – control; * – not quantified because of interference of other unidentified compounds. MV: mean value; CV coefficient of variation in %.

differences between planted and unplanted mesocosms showing the SSF units slightly higher values. Further the SSF planted CW maintains this difference (about 20 mV). This is related to the development of the system. From 0–90 days, the plants showed an increase in height in both types of wetlands (from 0.1 to 0.16 m), then from 90 to 150 days the plants remain the same height. It is well documented that macrophytes influence Eh in the substrate because they ventilate oxygen through their aerenchyma [54,55]. However in our study, we did not observed higher Eh in planted units. We did observed a rapid decrease in Eh during the first 40 days of the operation, due to the initial flooding that caused the oxygen trapped in the substrate or present in the water was consumed quickly by microbes, as long as molecular oxygen acts as the preferred electron acceptor [56]. The following 100 days, Eh decreased slowly and during this period, a gap between Eh values

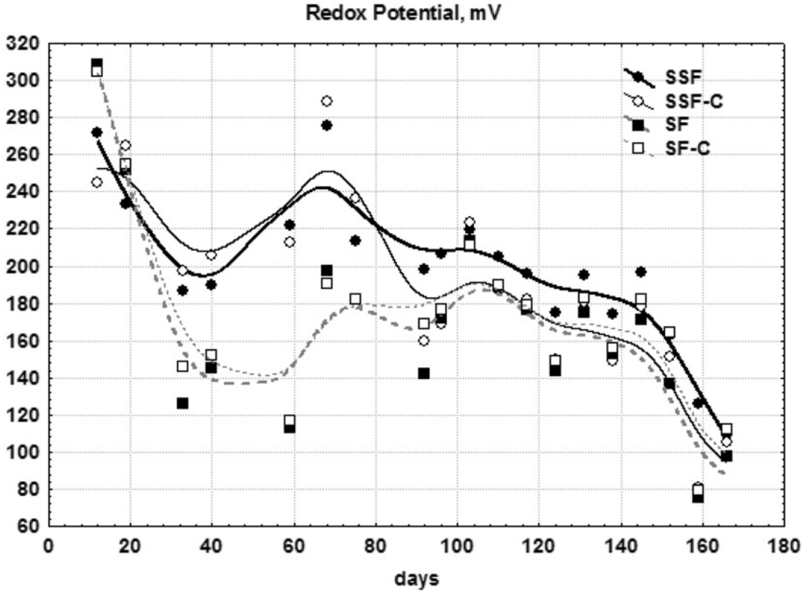

Figure 1. Mean Eh vs time. SSF, subsurface flow and SF, surface flow both planted with Typha. SSF-C, subsurface flow and SF-C surface flow both unplanted.

Table 3. Total suspended solids (mg L^{-1}).

Sample	Campaign 1	2	3	4
River	44.3	9	21.5	54.9
SF-C	2.5	6.9	2.7	3.7
SF	0.4	5.3	2.8	14.6
SSF-C	2.5	4	10.9	1.3
SSF	3.5	2.6	0.5	2.8

of SSF and SF CW was observed probably due to the fact that gravel has less organic matter than soils, therefore less microbial activity in SSF than SF. After 140 days a rapid decrease in the Eh values was again observed and the differences between the two types of CW also decreased, probably due to the biofilm building up. This indicates that during this study, the CWs were in a stabilisation period. The fact that Eh did not decreased to negative values might be attributed to fact that they were feed with water from polluted river with relative low carbon concentrations and they were in their first growing season therefore inputs of carbon from plants was limited.

The lowest inputs of the analytes were generally found in the second campaign (data not shown) which also accounts for suspended solids (Table 3). Most of the low removal percentages were found therein which also coincides with a local minimum of the Eh. Higher removal efficiencies were attained, in first place, in campaign one, concurrently with the higher Eh values and, in second place, in the fourth campaign, when more developed microbial communities should be expected in all the CW. So it may be concluded that Eh has a marked influence in the degradation of the studied pollutants, a fact that has already been discussed [16]. Also there is an influence of the initial pollutant concentration and in a lesser extent of time which should be related with the maturity and establishment of more developed biofilms in the CW. The existence of cases which not confirm these statements undoubtedly shows the complexity of the interactions of all processes occurring in these systems.

Regarding to the mean values of the removal percentages of individual compounds, CAF shows the highest ones, which is in fair agreement with the results reported in the literature [21,24,26], especially in SSF systems and in the planted ones with respect to the controls. GAL exhibits higher values than tonalide (not shown) and both coincide with some reported values [21] with slight better results in planted systems, especially in SSF. MDHJ exhibits more uniform percentages of removal, lower than the reported values [25]. AP show lower removal than APE. This may be related to the fact that AP may be metabolites of APE biodegradation. The removal of AP in SSF systems is close to reported values [24]. AP and APE exhibit higher removals in SSF systems which suggest influence of sorption mechanisms. For the other studied compounds, literature reports of their removal were not found. PAR is removed in a greater extent in SSF systems and plants have a positive influence in their removal. LAB show similar removals in SF and SSF systems. SURF has a particular behaviour showing slightly better removal in unplanted systems.

To determine the influence of the physicochemical properties (Table 1) of the studied compounds in their behaviour in the CW, a multiple linear regression (MLR, Statistica 7.0) of the mean percentage of removal considering $\log K_{\mathrm{ow}}$, the probability of aerobic biodegradation, Biowin1, anaerobic biodegradation, Biowin7 and PSA, was performed. $\mathrm{Log}\, K_{\mathrm{oc}}$ was not considered as it is strongly and positively correlated with $\log K_{\mathrm{ow}}$. The obtained regression equation ($R = 0.88$):

$$\%\mathrm{Removal} = 68.3 + 6.82 \times \log\ K_{\mathrm{ow}} - 69.0 \times \mathrm{Biowin1} + 55.0 \times \mathrm{Biowin7} + 0.8 \times \mathrm{PSA}$$

It indicates that the physicochemical properties of the pollutants have a significant influence in the removal of the target compounds. The negative coefficient of Biowin1 indicates the complexity of interactions between properties and maybe that at this stage of the CW stabilisation aerobic biodegradation processes compete with other processes in which the aerobic flora is involved. Nevertheless as a standalone variable, it has a positive influence in pollutants removal (coefficient = 11.3). It should be considered that in MLR, coefficients values (including sign) can change according to the other variables considered. A good correspondence between the observed and predicted values was found (Figure 2).

In order to obtain a deeper insight in the factors influencing to the pollutant removal, a multivariate exploratory technique, principal component analysis (Statistica® 7.0, unsupervised with variables autoscaling), was used taking as variables the removal percentages of CAF, GAL, MDHJ, BHT, SURF, PAR, TotCol and FecCol. The 3D plot of sample scores in the first three principal components (% of the total variance explained: factor 1 – 31.8; factor 2 – 26.4; factor 3 – 23.0) are shown in Figure 3 where some groupings according to: (i) system life-time (Figure 3a); (ii) the presence of plants (Figure 3b) and (iii) the presence of a porous media (Figure 3c) were observed. This suggests that these variables have a role in the performance of the studied CW.

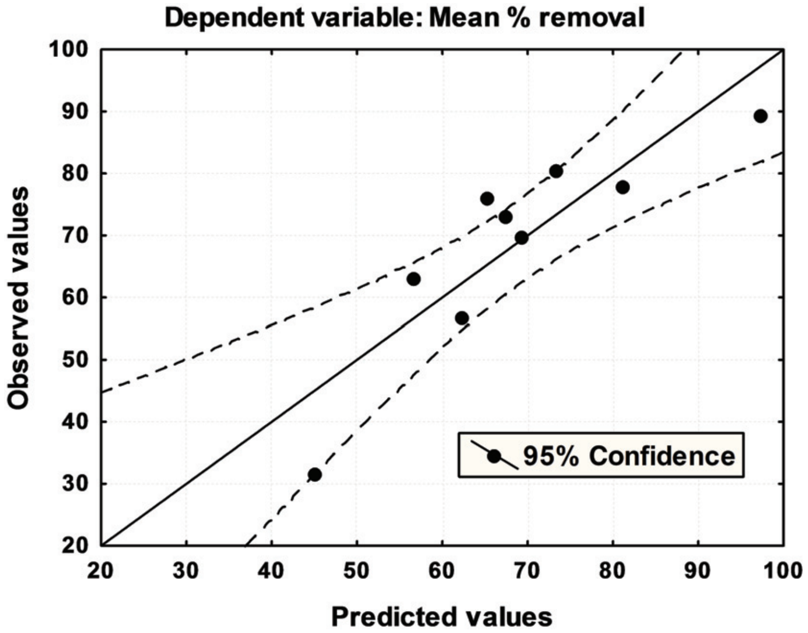

Figure 2. Observed vs. predicted values obtained by MLR considering the influence of physico-chemical properties of target compounds in their mean %removal.

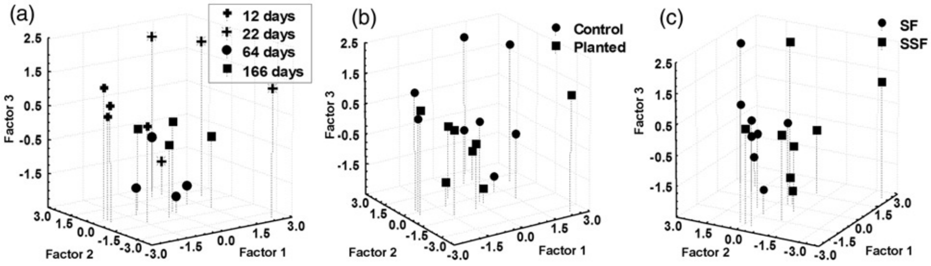

Figure 3. Score plots of samples in the first three principal components.

Not bearing in mind the modelling of the behaviour of the analytes in the CW, which is a more complicated task [11], a MLR was performed considering time, Eh, initial concentration of the pollutant (C_0), the presence of plants (0 – control CW; 1 – planted systems) and the presence of a filtering porous media, Fmedia (0 – SF; 1 – SSF). Table 4 shows the statistical parameters of the regression analysis for the general equation:

$$\%\text{removal} = a_1 \times \text{Plants} + a_2 \times \text{Fmedia} + a_3 \times \text{Time} + a_4 \times \text{Log Eh} + a_5 \times C_0$$

Log Eh was used instead of Eh in order to minimise the standard error of estimation. In Figure 4, the observed vs. predicted values for the considered contaminants are shown. It may be observed that a good prediction is achieved considering the studied factors. Of course the inclusion of other factors, as microbial biomass, may improve prediction but they were not measured in this study.

Table 4. Regression coefficients and statistical parameters for the removal of studied pollutants.

	a_1	a_2	a_3	a_4	a_5	R	SEE
CAF	8.5162	7.4270	0.0187	**28.1082**	11.1532	0.9943	11.6495
GAL	9.1377	1.8527	0.0511	**12.9007**	**35.7990**	0.9935	10.4320
MDHJ	1.5179	−4.6859	0.0261	**24.7586**	**25.6997**	0.9954	8.9486
LAB		3.2612	0.0436	**32.5048**	−0.3777	0.9968	8.8381
BHT	1.8243	**12.9141**	−0.0080	2.1069	**103.3597**	0.9829	7.4418
SUR	−8.6234	−7.5612	−0.0043	**40.4114**	**−12.1470**	0.9773	16.8774
PAR	**25.8614**	**10.4584**	−0.0410	**18.9572**	3.3649	0.9939	8.9757
AP		9.2944	0.2490	0.5915	**39.7486**	0.9821	16.2339
APE		8.3543	0.1226	**27.7266**	11.1031	0.9925	14.0711
TotCol	0.8795	−2.3718	**0.1011**	**40.7905**	0.0000	0.9997	2.8912
FecCol	0.4488	−1.7490	**0.1114**	**40.9534**	0.0000	0.9998	2.6865

R – multiple regression coefficient; SEE – Standard error of the estimate; statistically significant coefficients at $p = 0.05$ are indicated in bold.

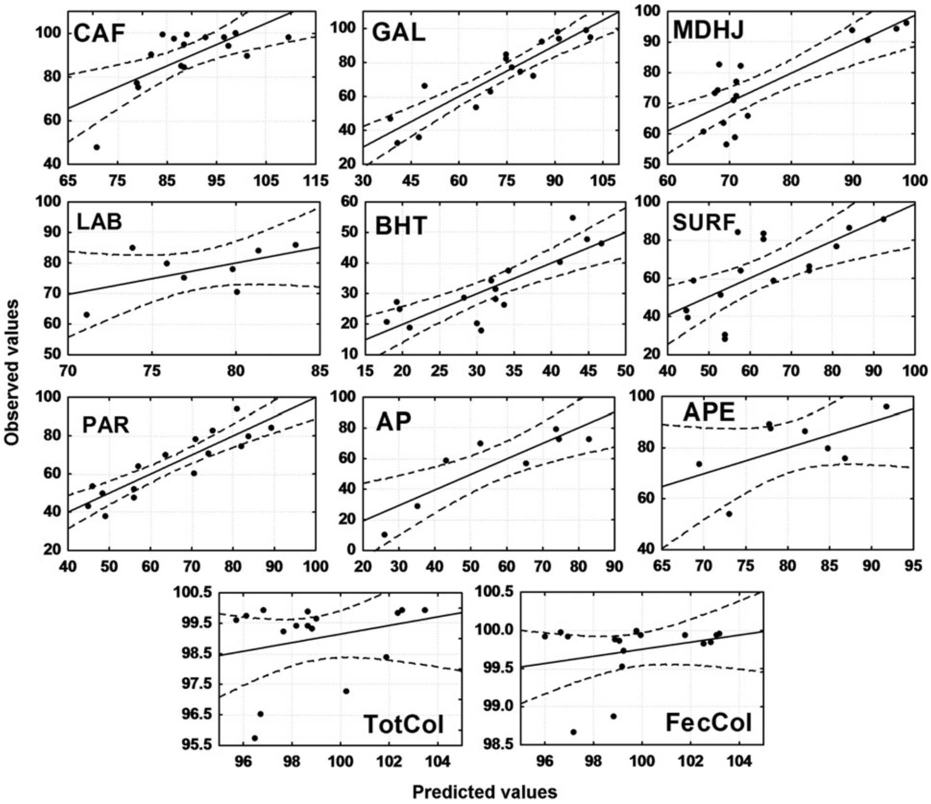

Figure 4. Observed vs. predicted values with the regression equation for considered pollutants.

Regression results confirm an already mentioned hypothesis. First, Eh has a significant influence in the removal for almost all the studied compounds with the exception of BHT and AP, indicating the occurrence of chemical oxidation processes. Another factor with more influence is the initial contaminant concentration with the significant exception of the microbial indexes. This is not surprising as in these systems behaves as a first-order kinetics [1,16]. SURF has a distinct behaviour, with significant positive coefficient for the Eh and negative for its initial concentration. Whether this is related with a toxic effect or insufficient adaptation of the microbial communities present in the CW merits further research. A significant influence of the porous media in the BHT and PAR removal is observed. Moreover, a positive influence is observed for AP, APE, CAF, LAB and GAL in decreasing order of the coefficient values. A negative coefficient value is observed for MDHJ and SURF, having the lowest values of Kow, with the exception of CAF which, in its turn, is efficiently removed in CW with porous media [57]. These facts agree with the observed influence of log K_{ow}, which points to the intervention of adsorption processes in the porous media surface in pollutants removal specially for the hydrophobic ones. The effect of plants is positive for PAR (significant), GAL, CAF, BHT and MDHJ. Obtained results confirm a general positive role of vegetation which may be explained considering that oxygen transport by plants create oxygenated zones in their roots and rhizomes enhancing oxidation processes and that contaminants uptake can not be discarded. This coincides with general findings about plants role in CW, which may be compound-dependant [13,57]. TotCol and FecCol also deserve a different discussion. The most significant variables in their removal are the Eh and time. This may be related to the fact that predation by aerobic microbial communities may be the predominant factor in their removal and the development of these microbial communities with time. There is a little influence of the filtering media and a slight negative effect of the plants related to a positive influence of temperature in their dye-off.

4. Conclusions

In the riverine waters a group of emerging pollutants and coliforms, denoting anthropogenic inputs, is present at characteristic concentrations of severe polluted waters. Surfynol 104 shows high concentrations related to the presence of a paper processing plant upstream. Typical removals of household products and surfactants in CWs were attained with slightly better results in planted SSFCW. The most significant factors influencing pollutants removal are the Eh and the initial concentration of each of them. The presence of plants and a porous media has a positive influence in the removal of almost all of the studied compounds. Finally, the obtained results show that CWs constitute a good alternative to improve water quality in polluted rivers.

Ackowledgements

Funding for this project was provided by the Mexican National Council for Science and Technology-CONACyT through the National Research System-SNI-Undergraduate project # 102122 and the basic science project # 81942. Additional support from the project 21-09-020351 of the Support Program for the State of Puebla (Secretary Rural Development) is gratefully acknowledged.

References

[1] J. Vymazal and L. Kröpfelová, Sci. Total. Environ. **407**, 3911 (2009).
[2] F. Masi and N. Martinuzzi, Desalination **215**, 44 (2007).
[3] J. Vymazal, Proceedings Book of the 10th International Conference on Wetland Systems for Water Pollution Control, Lisbon, Portugal, pp. 3–27 (2006); Ecol. Eng. 25, 478 (2005).
[4] M.E. Arias and M.T. Brown, Ecol. Eng. **35**, 1070 (2009).
[5] N. Moelants, G. Janssen, I. Smets, and J. Van Impe, Water Sci. Technol. **58**, 1 (2008).
[6] T.Y. Yeh and C.H. Wu, Water Sci. Tehnol. **59**, 233 (2009).
[7] G. Lofrano, S. Meric, and V. Belgiorno, Int. J. Environ. Pollut. **33**, 82 (2008).
[8] J. Vymazal, in *Encyclopedia of Ecology*, edited by Sven E. Jorgensen and Brian Fath (Academic Press, Oxford, 2008), pp. 748–64, *ibid*., pp. 765–76.
[9] R. Haberl, S. Grego, G. Langergraber, R.H. Kadlec, A. Cicalini, S. Martins, J.M. Novais, S. Aubert, A. Gerth, H. Thomas, and A. Hebner, J. Soils Sediments **3**, 109 (2003).
[10] E. Krasnits, E. Friedler, I. Sabbah, M. Beliavski, S. Tarre, and M. Green, Ecol. Eng. **35**, 1085 (2009).
[11] G. Langergraber, Vadose Zone J. **7**, 830 (2008).
[12] M. Truu, J. Juhanson, and J. Truu, Sci. Total Environ. **407**, 3958 (2009).
[13] J. Brisson and F. Chazarenc, Sci. Total. Environ. **407**, 3923 (2009).
[14] C. Calheiros, A.F. Duque, A. Moura, I.S. Henriques, A. Correia, A. Rangel, and P. Castro, Bioresource Technol. **100**, 3228 (2009).
[15] E. Kvesitadze, T. Sadunishvili, and G. Kvesitadze, WASET **55**, 458 (2009).
[16] J. García, D.P.L. Rousseau, J. Morató, E. Lesage, V. Matamoros, and J.M. Bayona, Critical Rev. Environ. Technol. **40**, 561 (2010).
[17] C.G. Daughton, Environ. Impact Asses. **24**, 711 (2004).
[18] D.A. Alvarez, W.L. Cranor, S.D. Perkins, V.L. Schroeder, S.L. Werner, E.T. Furlong, D. Kain and R. Brent, U. S. G. S. Open-File Report 2008–1231, (2008).
[19] M.J.M. Wells, A. Morse, K.Y. Bell, M. Pellegrin, and L.J. Fono, Water Environ. Res. **81**, 2211 (2009).
[20] H.C. Poynton and C.D. Vulpe, J. Am. Water Resour. Assoc. **45**, 83 (2009).
[21] K.M. Onesios, J.T. Yu, and E.J. Bouwer, Biodegradation **20**, 441 (2009).
[22] V. Matamoros and J.M. Bayona, Environ. Sci. Technol. **40**, 5811 (2006).
[23] V. Matamoros, C. Arias, H. Brix, and J.M. Bayona, Environ. Sci. Technol. **41**, 8171 (2007).
[24] V. Matamoros and J.M. Bayona, *The Handbook of Environmental Chemistry* (Springer, Berlin/Heidelberg, 2008), Vol. 5S/1, pp. 199–217.
[25] M. Hijosa-Valsero, V. Matamoros, J. Martín-Villacorta, E. Bécares, and J.M. Bayona, Water Res. **44**, 1429 (2010).
[26] M.A. Belmont and Ch. Metcalf, Ecol. Eng. **21**, 233 (2003).
[27] Y. Huang, A. Latorre, D. Barceló, J. García, P. Aguirre, R. Mujeriego, and J.M. Bayona, Environ. Sci. Technol. **38**, 2657 (2004).
[28] P. Bo, P. Ning, and B. Xing, Environ. Sci. Pollut. Res. **16**, 106 (2009).
[29] J. Xu, W. Chen, L. Wu, R. Green, and A.C. Chang, Environ. Toxicol. Chem. **28**, 1842 (2009).
[30] M.L. Martínez, R.H. Manson, P. Balvanera, R. Dirzo, J. Soberón, L. García, M. Martínez, P. Moreno, L. Rosenzweig, and J. Sarukhán, Front. Ecol. Environ. **4**, 259 (2006).
[31] J.P.A. Álvarez, J.E.R. Panta, C.R. Ayala, and E.H. Acosta, Rev. Inter Botan. **75**, 71 (2006).
[32] S.J. Kim, S.W. Hong, Y.S. Choi, W.K. Bae, and S.H. Lee, Wat. Pract. Technol. **1**, 1 (2006).
[33] E. Huertas, M. Folch, M. Salgot, I. Gonzalvo, and C. Passarell, Desalination **188**, 141 (2006).
[34] D.F. Juang and P.C. Chen, Int. J. Environ. Sci. Technol. **4**, 481 (2007).
[35] M. Scholz, R. Harrington, P. Carroll, and A. Mustafa, Wetlands **27**, 337 (2007).
[36] A.E. Navarro, presented at VI Congreso Internacional y XII Internacional de Ciencias Ambientales, Chihuahua, CH., 2007. http://www.uaemex.mx/Red_Ambientales/docs/congresos/CHIHUAHUA/docs/61-80.pdf, pp. 345–351 (Unpublished).

[37] S. Cid, A.E. Navarro, C. Rincón, V.A. Luna, presented at Congreso Internacional Gestión Sostenible del Agua: Reutilización, Tratamiento y Evaluación de la Calidad, Medellín, Colombia, 2008 (Unpublished).

[38] W.G. Crumpton, D.A. Kovacic, D.L. Hey and J.A. Kostel, presented at the Gulf Hypoxia and Local Water Quality Concerns Workshop. St. Joseph, MI, 2008 (Unpublished).

[39] SEMARNAT, Informe de la situación del medio ambiente en México. http://app1.semarnat.gob.mx/dgeia/informe_2008/index_informe_2008.html

[40] L. Li, Y. Li, D.K. Biswas, Y. Nian, and G. Jiang, Bioresource Tech. **99**, 1656, (2008).

[41] X. Tang, S. Huang, M. Scholz, and J. Li, Water, Air, Soil Poll. **197**, 61 (2009).

[42] D.G. Castro, Master thesis, Royal Institute of Technology, 2004.

[43] H. López, P. Moreno, and I. Mendelssohn, J. Plant Interact. **1**, 187 (2005).

[44] M.J. Rodríguez, Ph.D. thesis, Rovira I Virgili University, 2006.

[45] US EPA, 2010. Estimation Programs Interface Suite^{TM} for Microsoft® Windows, v 4.00. United States Environmental Protection Agency, Washington, DC, USA.

[46] L.J. Standley, L.A. Kaplan, and D. Smith, Environ. Sci. Technol. **34**, 3124 (2000).

[47] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, and H.T. Buxton, Environ. Sci. Technol. **36**, 1202 (2002).

[48] D. Mitjans and F. Ventura, Water Sci. Technol. **50**, 119 (2004).

[49] K.O. Isobe, M.P. Zakaria, N.H. Chiem, L.Y. Minh, M. Prudente, R. Boonyatumanond, M. Saha, S. Sarkar, and H. Takada, Water Res. **34**, 2449 (2004).

[50] L. Dsikowitzky, J. Schwarzbauer, and R. Littke, Chemosphere **57**, 1289 (2004).

[51] T. Sirivedhin and A.G. Kimberly, Water Res. **39**, 1154 (2005).

[52] J. Wu, J. Yue, R. Hu, Z. Yang, and L. Zhang, Proceedings WASET. **44**, 438 (2008).

[53] A.A. Guedez, S. Frömmel, P. Dile, and W. Püttmann, Environ. Sci. Pollut. Res. **17**, 321 (2010).

[54] A. Wieβner, U. Kappelmeyer, P. Kuschk, and M. Kastner, Water Res. **39**, 248 (2005).

[55] T. Matsui and T. Tsuchiya, Ecol. Res. **21**, 470 (2006).

[56] C.C. Tanner, Wat. Sci. Tech. **44**, 9 (2001).

[57] M. Hijosa-Valsero, V. Matamoros, R. Sidrach-Cardona, J. Martín-Villacorta, E. Bécares, and J.M. Bayona, Water Res. **44**, 3669 (2010).