Desalination and Water Treatment
www.deswater.com
1944-3994/1944-3986
doi: 10/5004/dwt.2012.2963

Taylor & Francis
Taylor & Francis Group

40 (2012) 209–214
February

Water quality monitoring by nanostructured films in a sensing unit system

Kássia Barbosa Cajuela[a], Paaron Guenka Dauer[b], Miriã Camargo Rosa[c], Francisco Javier Cuba Teran[d,*], José Alberto Giacometti[e]

[a]*Universidade Estadual Paulista, Naftale Pereira Dias, 30, Gastão Vidigal SP, Brazil*
[b]*Universidade Estadual Paulista, Av Afonso pena, Campo Grande MS, Brazil*
[c]*Universidade Estadual Paulista, Jusselino Kubischek de Oliveira, 4000, São Jose do Rio preto SP, Brazil*
[d]*Escola de Engenharia Civil da Universidade Federal de Goiás, Praça Universitária, 1488 Goiânia GO, Brazil*
Tel. +551839096979; email: fteran@fct.unesp.br
[e]*Universidade Estadual Paulista, José Alberto Giacometti, Roberto Simonsen, 305, Presidente Prudente SP, Brazil*

Received 13 May 2011; Accepted 5 February 2012

ABSTRACT

Presented here is a study about the capability of a sensing unit to detect changes in river water quality. In order to determine its accuracy, water quality was monitored at 11 points along the Veado River in Presidente Prudente, Brazil. To have a basis for comparison, a water quality index (WQI) was developed following methods previously applied in different watersheds. Results showed an accurate relationship between WQI and electric impedance readings detected by the sensing unit. Principal components analysis (PCA) was used to derive results in a form that can be correlated with WQI calculated for each sample point, which showed the potential application of this device.

Keywords: Nanotechnology; Water quality; Thin films; Water quality index

1. Introduction

Because of population growth, changes in the quality of river water take place so fast that there is little time for water treatment plant operators to take appropriate measures in order to adapt systems and produce water of adequate quality. Nowadays, there is a trend to use automated sensing units that will avoid tedious and time-consuming operations of sampling and analysis. In this context, research in non-selective sensor arrays combined with pattern recognition techniques has been proven to be effective in several analytical situations [1–3].

Sometimes, there are problems along stream courses related to disturbing odors, accumulation of garbage, disease and poor water quality. One of the reasons why these problems occur is that domestic and industrial wastewaters are dumped into the rivers without adequate treatment. During the dry period there is low inflow of fresh water to dilute the discharges, and water quality gets even worse.

In order to monitor river water quality, several researchers [4,5] have developed indices involving some laboratory-determined physical-chemical parameters. These WQI are meant to present results in a descriptive way and to avoid intensive monitoring.

A WQI coupled with an electronic monitoring system composes an excellent tool for studying spatial and temporal water quality in real time.

*Corresponding author.

Presented here is a field study examining the quality of the water of the Veado River running through Presidente Prudente, a city in São Paulo State, Brazil, by means of a sensing unit system provided with six sensors covered by different nanostructured polymeric films. Results from the electronic devices were compared with WQI determined for each sample point along the river course by means of PCA. The results of a WQI are also presented.

2. Methods

2.1. Sampling points

The study area stretches along the stream from its source in the center of Presidente Prudente, to about 7 km northwest of the urbanized area. Sampling points are identified in Table 1 and Fig. 1.

Discharges from the industrial zone of the city were very irregular both in terms of quality and quantity and besides that, the river is covered throughout most of the city's center. This made sampling and analysis difficult, so it was decided to start the sampling at an opening in the covered section, at P1 (Fig. 1). Six additional sample points (P2–P7) were selected in channel openings, after main tributaries and large wastewater discharges, down to the confluence with the Limoeiro River. Points P8–P10 were located after a slaughterhouse's discharge in an open channel, and the last sample point (P11) was selected 4.3 km downstream under the Sabesp Bridge.

Fig. 1. Location of sample points in Veado River (Google Earth 2011).

Table 1
Sampling points along river course

Points	Altitude (m)	East	West
P1 (grate)	483	459,065	7,552,414
P2 (culvert in front Crave and canella)	421	458,923	7,552,656
P3 (red enclosure Unoeste Health)	417	458,799	7,552,757
P4 (near the affluent Foundation Mirim)	403	458,410	7,553,734
P5 (enclosure near the Foundation Mirim)	406	458,446	7,553,489
P6 (square in construction)	397	458,379	7,554,201
P7 (affluent after colony miner)	395	457,898	7,554,459
P8 (Bon Mart – Previous)	390	457,232	7,554,196
P9 (Bon Mart – Later)	387	457,223	7,554,166
P10 (Adelino Rodrigues Gato Street)	394	456,278	7,554,143
P11 (Sabesp bridge)	380	451,838	7,554,061

2.2. Water quality index

The parameters analyzed were selected based on the assumption that, at the time of sampling, the pollution in the river would consist mainly of domestic and industrial wastewater from the three top manufacturing companies in terms of production, for example, slaughterhouse, tanning and dairy products.

The parameters analyzed were ammonia nitrogen (NH_3-N), chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved oxygen (DO), pH, total phosphate, total solids (TS), turbidity and temperature. All tests were performed according to methods described in the twentieth edition of Standard Methods for the Examination of Water and Wastewater [6].

WQI in this report was used for the investigation of temporal and spatial quality variations along the river's course. Normalization of all parameters was carried out according to specific assumptions and remained unchanged during the development of WQI. Weighting factors were determined according to mean values obtained from values suggested by experienced environmental researchers. In order to simplify this procedure a scale of 1–4 was used.

WQI was mainly based on the article by Pesce and Wunderlin [4], with normalization adapted from Pesce and Wunderlin [4] and from Prakash et al. [5]. For further details, the reader is urged to refer to these papers.

Table 2
Weighting factors for parameters W_i

Temperature (°C)	DO (mg. l^{-1})	pH	NH_3-N (mg · l^{-1})	TS (mg · l^{-1})	BOD (mg · l^{-1})	Turbidity NTU	COD (mg · l^{-1})	Total phosphate (mg · l^{-1})
3.8	4	2.4	2.8	2.92	3.72	3.48	2.92	3

The WQI was calculated using Eq. (1).

$$WQI = \frac{\sum_{i=1}^{n} C_i \cdot W_i}{\sum_{i=1}^{n} W_i} \quad \begin{cases} C_i = \text{normalisation factor for parameter } i \\ W_i = \text{weighting factor for parameter } i \\ n = \text{number of parameters included in the } WQI \end{cases}$$

The parameters used in this study and their weights are presented in Table 2.

2.3. Electronic tongue description

An electronic tongue is a sensor array with limited individual selectivity that can be used as an appropriate pattern recognition tool. The sensor array in these systems produces signals which are not necessarily specific for any particular chemical species in water, but a signal pattern is generated which can be related to certain features or qualities of the sample.

Since a single material is unlikely to be sensitive to different substances present in an analyte, a combination of sensors has to be used. The electronic device applied in this study was made of six interdigitated gold electrodes with 50 pairs of digits, 10 µm wide and 10 µm high, each covered by a different ultrathin polymeric film. Only one was coupled without a film and readings from all sensors were based on measures of electric impedance. Fig. 2 shows the interdigitated sensors.

Two different techniques of film assembly were used, namely, Langmuir-Blodgett (LB) and self-assembled layer-by-layer (LBL). Details on LBL and LB film depositing techniques can be found in the literature [1–3,7–9,11].

Materials deposited on interdigitated electrodes by LBL were ultrathin films of polypyrrole/poly(allylamine hydrochloric) (PAH), copper phthalocyanine tetrasulfonate /PAH, chitosan/PSS and poly(3,4-ethylenedioxythiophene) (PEDOT)/PAH. They were chosen according to a previous study [10] that proved the capability of their interaction in order to produce high sensitivity responses in liquid systems. The LB technique was used for the sixth electrode, also with polypyrrole polymer.

In order to characterize the films present on the sensors, polymeric material was first mounted on quartz plates with very low absorbance, which were read with a UV-Vis spectrophotometer.

Fig. 3 shows absorption spectrum curves for each layer of LBL copper phthalocyanine tetrasulfonate self-assembled film.

The curves in Fig. 3 show the absorbance of layers deposited on quartz plate, varying with the wavelength. The increment of absorbance shown in each curve indicated the presence of five different polymeric layers deposited by LBL technique. Similar methodology was applied when polymeric layers were mounted on sensors.

Once sensors preparation was performed as described above, they were attached to the electronic device and taken to 250-ml beakers where the water samples were poured and analyzed. Impedance readings by sensors immersed in water samples was compiled and evaluated by PCA, a multivariate statistical method permitting the recognition of patterns, characterized by simplicity and speed of calculation. The method is based on reducing the total number of variables and rewriting the coordinates of an initial set of data into a second system of axes, which permits

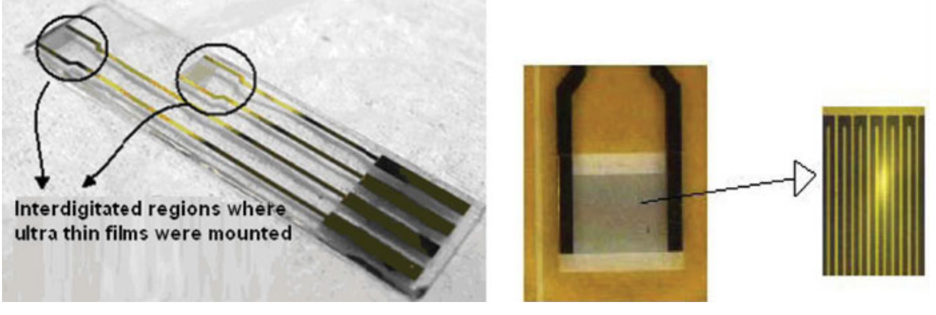

Fig. 2. Photograph of electrodes showing gold-covered digits.

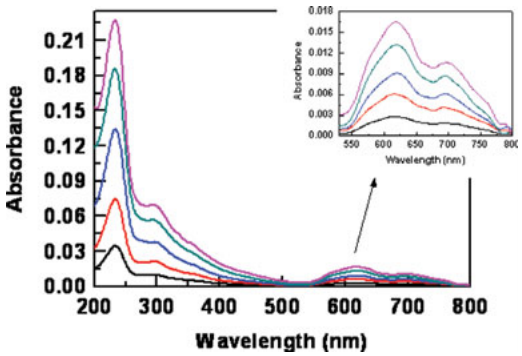

Fig. 3. UV-vis absorption spectra for cuprum tetrasulfonate phtalocianine/PAH LBL films containing five polymeric layers.

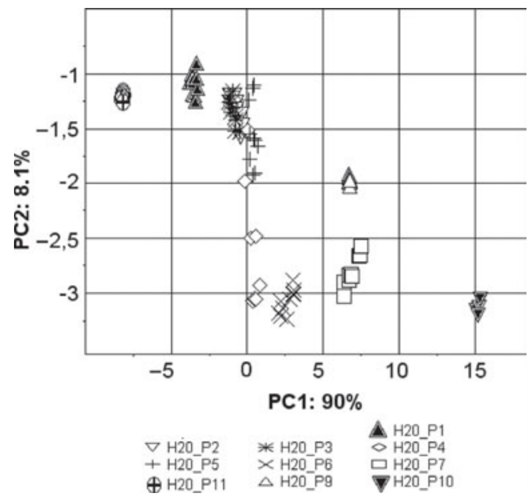

Fig. 5. PCA plot for samples 1–11. Expanded.

a more convenient correlation of the results. The new coordinates are obtained by linear combination of original variables and represented on orthogonal axes, avoiding unnecessary information. This information is displayed in order of decreasing variance, which means that the data can be represented by a smaller number of descriptive factors, reducing the size of all examined. For that, it sequentially creates a set of principal components from the original data. The first principal component (PC1) provides most of the information to discriminate the input data and presents the highest variance. In the results presented here, using the first principal component more than 90% of the relevant information is covered in all cases. The PCA results in Figs. 4 and 5 show the capability of the electronic device tested in this study in distinguishing water quality of different samples based on the substances dissolved in them.

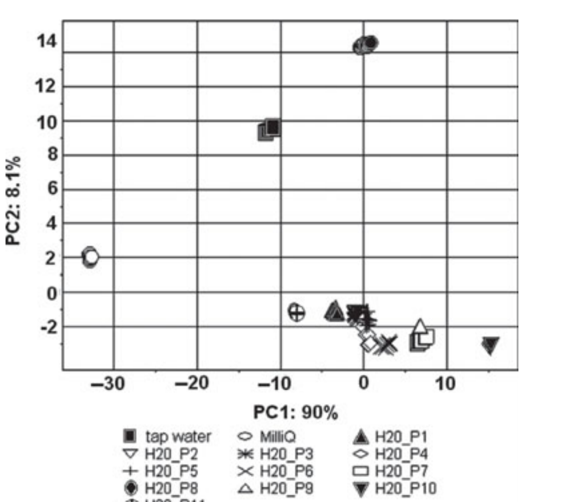

Fig. 4. PCA plot for MilliQ water, tap water and samples 1–11.

3. Results

3.1. Water quality index

In order to obtain results leading to WQI calculation, physical-chemical analyses were carried out on samples at every point described above. These results are shown in Table 3.

Data used by Prakash et al. [5] and Pesce and Wunderlin [4], after regression analysis, resulted in normalization equations which were applied to obtain the normalization factors Ci. Those equations are given in Table 4.

Results obtained from normalization equations along with WQI values are presented in Table 5.

As can be noted, the quality of river water is shown to decrease along its course through the city and recovers downstream. Also, some WQI values reflect impacts from industrial wastewater discharges, such as those obtained at points 9 and 10.

3.2. Electronic tongue

PCA results of impedance (represented as PC1 and PC2) of samples taken from points P1 to P11 as well as results of impedance from samples of MilliQ and tap water, are presented in Figs. 4 and 5. Analyzing the PC1 axis, it is interesting to note the successive deterioration in quality from MilliQ water through tap water, and water from P1 to P10 sampling points. An evident improvement is shown only in point 11.

Individually, sample point data became less stretched along PC1 axis than along PC2 axis, so PC1 was chosen as the representative axis associated to changes in sensor readings due to interaction with the analite. However, according to the PCA, the new coordinate's origin is in

Table 3
Results of the parameters analyzed sample

Point	Temperature (°C)	Dissolved oxygen ($mg \cdot l^{-1}$)	pH	Turbidity (NTU)	NH_3-N ($mg \cdot l^{-1}$)	Total solids ($mg \cdot l^{-1}$)	BOD ($mg \cdot l^{-1}$)	COD ($mg \cdot l^{-1}$)	Total Phosphate ($mg \cdot l^{-1}$)
1	27.80	5.0	7.33	77.00	30.8	271	1.2	21.70	0.91
2	27.30	5.0	7.42	95.00	22.4	220	4.2	12.27	1.58
3	26.35	4.2	6.64	105.00	28.0	876	3.3	244.72	0.71
4	25.20	4.0	6.70	67.29	16.8	454	2.1	27.98	0.26
5	24.50	4.2	6.81	74.69	22.4	435	3.1	43.68	0.37
6	24.30	2.2	7.47	72.30	11.2	369	1.3	98.66	0.20
7	25.30	2.3	7.40	31.19	11.2	532	0.9	26.41	0.58
8	27.60	7.5	7.97	36.10	16.8	352	10.2	37.40	0.39
9	31.40	7.5	8.33	25.60	39.2	313	8.5	26.41	0.35
10	20.50	6.4	7.47	331.00	44.8	406	5.1	56.25	0.64
11	21.60	6.3	7.41	37.30	33.6	295	2.7	0	0.11

Table 4
Equations for the normalization of the parameters that were monitored

Parameter	Equation	Constraints	Correlation coefficient
Ammonia-N	$y = 89.868e^{-1.6376x}$	if $x > 1.25$ mg l^{-1} $y = 0$	$R^2 = 0.9797$
Total inorganic-P	$y = 90.871e^{-1.0839x}$	if $x > 2$ mg l^{-1} $y = 0$	$R^2 = 0.9906$
Total solids	$y = -22.167\text{Ln}(x) + 229.6$	if $x > 20{,}000$ mg l^{-1} $y = 0$	$R^2 = 0.9842$
Turbidity	$y = 109.7e^{-0.023x}$	if $x > 100$ NTU $y = 0$	$R^2 = 0.9885$
COD	$y = 122.92e^{-0.0601x}$	if $x > 40$ mg. l^{-1} $y = 0$	$R^2 = 0.9902$
DO	$y = 9.451x^{1.1466}$	if $x < 1$ mg. l^{-1} $y = 0$	$R^2 = 0.9943$
BOD	$y = 126.06e^{-0.1563x}$	if $x > 15$ mg. l^{-1} $y = 0$	$R^2 = 0.9811$
Temperature	$y = -129.3\text{Ln}(x) + 482.19$	if $x > 40$°C $y = 0$	$R^2 = 0.9896$
$2 < ph < 7$	$y = 0.0586x^{3.8135}$	if $x < 4$ $y = 0$	$R^2 = 0.9897$
$7 < pH < 12$	$y = -192.68\text{Ln}(x) + 475.81$	if $x > 11.5$ $y = 0$	$R^2 = 0.9931$

y : normalization factor x: measured parameter *R*: correlation coefficient.

Table 5
Normalized parameters and WQI calculated for sample points

Point	pH	BOD	COD	DO	Temp	Turbidity	Total phosphate	TS	Ammonia-N	WQI
1	92.00	104.50	33.36	59.83	52.26	18.67	33.86	[1]105.43	0	55
2	89.64	65.39	58.80	59.83	54.61	12.34	16.38	[1]110.05	0	51
3	79.21	75.26	0	48.99	59.19	0	41.84	79.42	0	43
4	81.97	90.79	22.87	46.32	64.96	23.34	68.26	93.99	0	55
5	87.22	77.65	0	48.99	68.60	19.69	61.03	94.94	0	52
6	88.35	102.88	0	23.34	69.66	20.80	72.98	98.59	0	52
7	90.16	109.52	25.14	24.56	64.45	53.54	48.51	90.48	0	56
8	75.87	25.60	12.98	95.24	53.20	47.82	59.72	99.63	0	52
9	67.35	33.39	25.14	95.24	36.52	60.88	61.91	[1]102.23	0	53
10	88.35	56.81	0	79.40	91.65	0	45.54	96.47	0	52
11	89.90	82.66	122.92	77.98	84.89	46.52	80.74	[1]103.55	0	78

[1]Values higher than 100 were obtained from equations in Table 4 due to regression analysis. For WQI calculations those values were adjusted to 100.

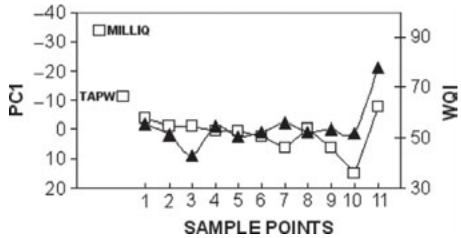

Fig. 6. Correlation of WQI (▲) with PCA(□) for sample points. PCA results from MilliQ and tap water (TAPW) are also included.

the cloud center, arising for the negative and positive values along PC1 and PC2 axes.

In order to determine the reliability of the sensor data, impedance results taken from PC1 axis, were plotted jointly with WQI results as shown in Fig. 6. From P1 to P8, correlation is reasonable, with deviation in data being higher at points 9 and 10. This was possibly due to a more accurate detection of pollutants by the sensors than by WQI developed in this study, which probably had limitations. Sensors cannot detect which substances are causing these alterations; they can just detect changes related to the presence of more substances in the analyte. MilliQ and Tap water PCA results are also plotted in order to show the response of the sensors to ultrapure and tap water and how they deviate from quality of river water samples.

4. Conclusions

The watershed of the Veado River is in the middle of an urbanized area, and therefore, the river's water quality is affected by intense anthropogenic changes.

Analysis of PCA results, though preliminary, clearly indicates that the device applied has the ability to distinguish between water samples with different physical-chemical characteristics, indicating whether water quality approaches or diverges from purity.

Monitoring river water quality by means of an instrument capable of producing results in real time will prevent the occurrence of unexpected events which can disturb the physical-chemical equilibrium in the water. The device tested in this study showed the capacity to do this, as confirmed by a WQI specially developed for this water course.

Despite deviations due to WQI limitations, the set of sensing units tested in this study showed their potential for application as an auxiliary tool for assessing river water quality.

Future research on this device will verify its accuracy in the analysis of flowing water as well as its capability of detecting the presence of certain types of microorganisms as reported by Ulman [11].

References

[1] B.A. da Silva, P.A. Antunes, D. Pasquini, A.S. Curvelo, R.F. Aroca, A. Riul Jr and C.J.L. Constantino, Nanostructured films employed as sensing units in an "Electronic Tongue" System, J. Nanosci. Nanotechnol., 7 (2007) 510–514.
[2] A. Riul Jr, H.C. Souza, R.R. Malmegrim, D.S. Santos, A.C. Carvalho, F.J. Fonseca, O.N. Oliveira Jr and L.H.C. Mattoso, Wine classification by taste sensors made from ultrathin films and using neural network, Sens. Actuators. B, (2004).
[3] C. Soderstrom, F. Winquist and C. Krantz-Rulker, Recognition of six microbial species with a biologycal tongue, Sens. Actuators. B, 89 (2003) 248–255.
[4] S.F. Pesce and D.A. Wunderlin, Use of water quality indices to verify the impact of Córdoba city (ARGENTINA) on Suquia River, Wat. Res. UK., 34(11) (2000) 2915–2926.
[5] R.K. Prakash, L. Seockheon, L. Young-Soo, R.K. Sushil and P.K. Siddhi, Application of Water Quality Indices and Dissolved Oxygen as Indicators for River Water Classification and Urban Impact Assessment, 2007.
[6] APHA, AWWA, WPCF Standard Methods for the Examination of Water and Wastewater, 20 ed. American Public Health Association, American Water Works Association and Water Environment Federation, New York, NY, 1998.
[7] N. Duran, L.H.C Mattoso and P.C. Morais, Nanotecnologia: Introdução, Preparação e Caracterização de Nanomateriais e Exemplos de Aplicação, ArtLiber, São Paulo, 2006.
[8] M. Ferreira, V. Zucolotto, M. Ferreira, K Wohnrath and O.N. Oliveira Jr, Layer-by-Layer and Langmuir- Blodgett Films from Nanoparticles and Complexes, In: Encyclopedia of Nanoscience and Nanotechnology. Edited by H. S. Nalwa.
[9] L.G. Paterno, L.H.C. Mattoso and O.N. Oliveira Jr, Filmes Poliméricos Ultrafinos Produzidos pela Técnica de Automontagem: Preparação, Propriedades e Aplicações, Química Nova, São Paulo, 2001.
[10] W. Stelutti, Utilização de uma "língua eletrônica" para classificação de amostras de açúcar em uma usina, MSc degree thesis, UNESP, Presidente Prudente SP, 2008.
[11] A. Ulman, An Introduction to Ultrathin Organic Films Langmuir—Blodgett to Self Assembly, Academic Press Boston, 1991.