CLASSIFICATION OF STORM WATER AND SEA WATER SAMPLES BY ZERO-, FIRST- AND SECOND-ORDER DERIVATIVE UV SPECTRA AND PATTERN RECOGNITION METHODS

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ABSTRACT

This paper deals with the quality of storm water and its recipient sea water. For this purpose, UV spectroscopy and pattern recognition methods were used. The treatment of the zero-order spectral data showed that almost all storm water samples were classified into two groups. The treatment of the first-order derivatization spectral data showed that each of these groups can be divided into two subgroups, with few samples common, while the second-order derivatization has highlighted the final group of the common samples. Sea water samples were classified into two groups by all methods of treatment of spectral data. The great majority of the samples was classified to one group and only few of them to the other.

KEYWORDS: Storm water; sea water; UV spectroscopy; first-order derivative spectra; second-order derivative spectra

1. INTRODUCTION

Storm water is the water that comes from sources such as runoff from streets, land and roofs. It enters a sewer system and finally flows to rivers, lakes, sea, etc. Storm water can be considered either as dirty water or as clean wastewater.

Wastewater comes from different sources, such as the consumer - houses, businesses, and industries. Storm water is usually not mixed with wastewater as their co-treatment is expensive and difficult. Storm water dilutes the wastewater extremely, so there is an increase in volume. Also, the diluted wastewater will contain different concentrations of compounds, so the microorganisms have to be adjusted. For these reasons, the storm water is usually kept separate from other types of wastewater. Of course, the separate way has some disadvantages because if the quality of the storm water is not good, there are negative consequences to the receiving water bodies.

The quality is strongly dependent on the conditions of the city like the lifestyle of the citizens. It changes during storm events. The parameters that are most often measured are Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), total phosphorus (TP), total nitrogen (TN) (Ghafouri and Swain 2005) as well as the microorganisms (Aryal et al. 2012b). The analytical techniques that have been used include UV and fluorescence spectroscopy (Aryal et al. 2012a; Hur et al. 2010) and bioassays (Chong et al. 2011).

The seawater quality is most difficult to be determined because of the extremely high concentration in chloride. UV spectroscopy has been approved to be a powerful tool for the quality monitoring of water and wastewater by measuring parameters like phosphate, nitrite, nitrate, COD. The last years has been applied to storm water samples (Vaillant et al. 2002). It has been applied to sea water samples in a less extent (Ogura and Hanya 1966; Noto and Mecozzi 1997; Johnson and Coletti 2001).

In this work we study the quality of storm water and sea water samples by using the zero-order, the first and the second derivative UV spectra. These spectra can give much information about the composition. The processing of the spectral data was done by statistical methods.

2. MATERIALS AND METHODS

2.1 Site description

The study area is a highly density residential area with many commercial shops located in the center of Chania. Chania is a city of Crete, island of Greece. The climate is typical Mediterranean, with very hot, dry summers and mild, wet winters. For a 40-year period the value of the average rainfall of January is 122.6 mm and of July is 0.2 mm. The mean annual rainfall is 642.5 mm (for a 50-year period). Storm water samples were collected from the outlets of two pipes, I and II, as shown in Figure 1. Pipe I is a very old one as it had been constructed from the enetic years. Pipe II is a new one and it drains a much smaller area. Both of them run directly near the old port of the city. Also, four samples were collected once from accessible points of pipe I (Ia, Ib, Ic, Id).

The sea water samples were collected from eight points nearby the outlet of pipe I and specifically from the old port (St1-St8). The sampling depth was mainly zero but some samples were collected and from six meters. The sea sampling points are also shown in Figure 1.

FIGURE 1. Map of the area with the sampling points

2.2 Samples

Totally, 26 storm water and 34 sea water samples were collected during two years sampling period, from 2012 to 2014. The collected samples were transported to the laboratory and analyzed within 24 hours.

2.3 Reagents

Solutions of sodium nitrate (5 mg/L as nitrate), caffeine (1 mg/L) phenacetin (1 mg/L), sodium dodecylbenzene sulfonate (DBS) (2 mg/L) and nonylphenol (NP) (2 mg/L) were prepared by dissolving the required amounts in deionized water. All the reagents were purchased from Aldrich and were of analytical grade except from the detergents, DBS and NP that were of technical grade.

2.4 Methods of analysis

UV analysis was performed with a UV spectrophotometer. The Hitachi U-2001 dual beam spectrophotometer was operated at 0.5 nm bandwidth, with a quartz cell of 10 mm, wavelength of 200 to 400 nm and a scanning speed of 800 nm/min.

Deionized water was used as blank. The samples were not subject to any treatment. When the absorbance was above 2, the samples were properly diluted. The zero-order absorption spectra and the first and second derivative spectra were recorded between 200-400 nm and stored in the memory of the spectrophotometer. The dilution factor was calculated for the final results. The data obtained was analyzed using the Pearson's correlation coefficient (r_{xy}). Values of r, ranging from 1 to 0.75 correspond to strong correlation (or high similarity) between the samples (Sarris et al. 2009).

3. RESULTS AND DISCUSSION

3.1 Storm water samples

In order to certify if there are or not any similarities between storm and sea water samples, the data of three sea water samples were co-processed with the data of the storm water samples.

<u>3.1.1 Number of groups</u>

The criterion for the classification of samples between groups was the r value of 0.98, 0.98 and 0.75 for the zero-order, the first-order and the second-order data treatment respectively. The criterion became more flexible as the degree of derivatization increased, because the r values were decreased. The three sea water samples showed low r values and so did not present any similarity with any of the storm water samples, except between them. They were not discussed furthermore. The groups that the storm water samples were classified are shown in Figure 2.

As is shown in Figure 2, the processing of zero-order data categorized 25 from 26 samples into two groups A and B. Three samples were found to belong in both groups.

The first-derivative classification showed that two of them belong in B group and the third one remains to group A. Also, the first-derivative results has indicated the presence of four groups, dividing the A group into two groups, A1 and A2 and the B group into two groups B1 and B2. A1 contains of 10 samples and A2 contains of 4 samples, with one common with B1. B1 contains of 6 samples with one common with A2 and one common with B2.

The second-order derivative results have shown that the common sample of B1 and B2 goes to B2. The other groups are slightly changed, while there are many samples that remain uncategorized. The second-derivative results did not offer any other significant information about the classification of the samples.

Samples from group A1 are from the same pipe and we can conclude that there is no temporal variation. Samples from group A2 were from different sampling points.

3.1.2 Description of spectra

Figure 3 shows the zero-order UV spectra, the first-order derivative and the second-order derivative spectra of storm water samples that belong to each of the four groups, A1, A2, B1 and B2.

The samples of group B1 and B2 are typical of natural water without organic matter as the absorbance below 240 nm is close to zero. The Gaussian shape around 210 nm indicates the presence of nitrate. Group B1 has low concentrations while group B2 has high concentrations of nitrate. Also, the shape of their first derivative spectra is similar to that of nitrate a very narrow peak is appeared down from 200 to 240 nm.

High nitrate concentrations are mostly due to leaking or poorly functioning septic systems.

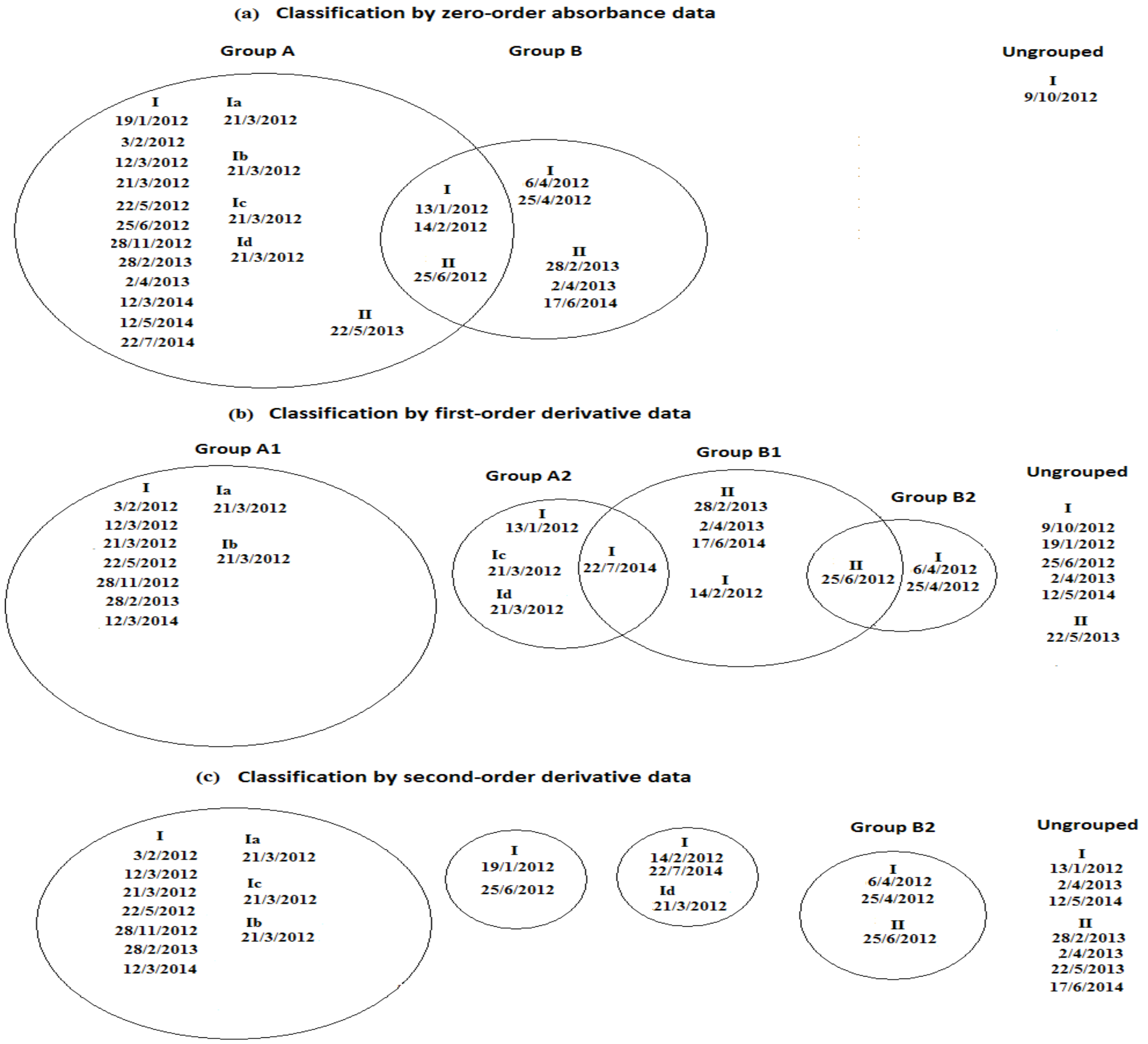

FIGURE 2. Classification of storm water samples by: (a) zero-order absorbance, (b) first-order derivative and (c) second-order derivative data

The UV spectra of samples from group A1 reflect the domination of humic substances (Chong et al. 2011; Vaillant et al. 2002). The samples from group A2 have dissimilarity in organic matter as they showed a shoulder around 220 nm.

There is lack of data in the literature in order to compare the shape of the first and second derivative spectra except some individual organic compounds that have been studied (Kokot and Burda, 1998 Abbaspour and Mirzajani 2005). For this reason, the spectra of representative compounds such as nitrate, caffeine, phenacetin, sodium benzenesufonate and nonylphenol were recorded and the results are presented in Figure 4. The similarity between the spectra of group B1 and B2 and nitrate is obvious as their spectra are superposed. The spectra of the other compounds do not resemble the spectra of groups A1 and A2 and therefore the samples should not contain any of these compounds at least at high detectable concentrations.

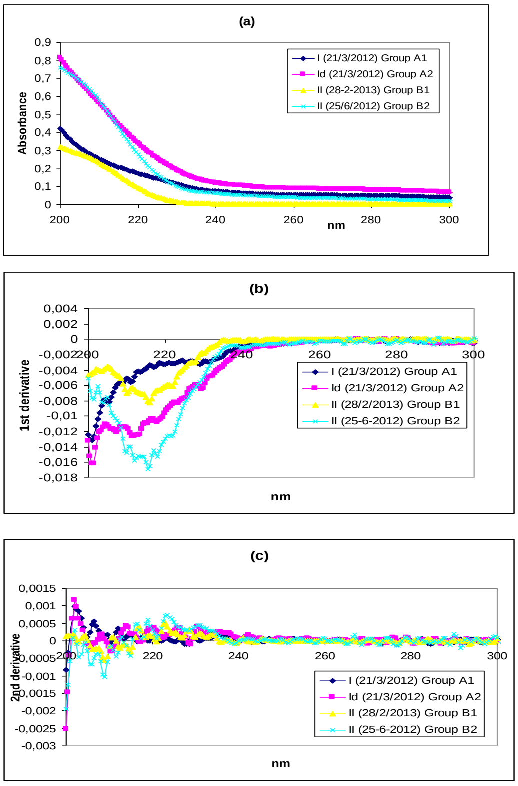

FIGURE 3. (a) Zero-order UV spectra, (b) First-order derivative and (c) Second-order derivative spectra of specific storm water samples that belong to each of the four groups

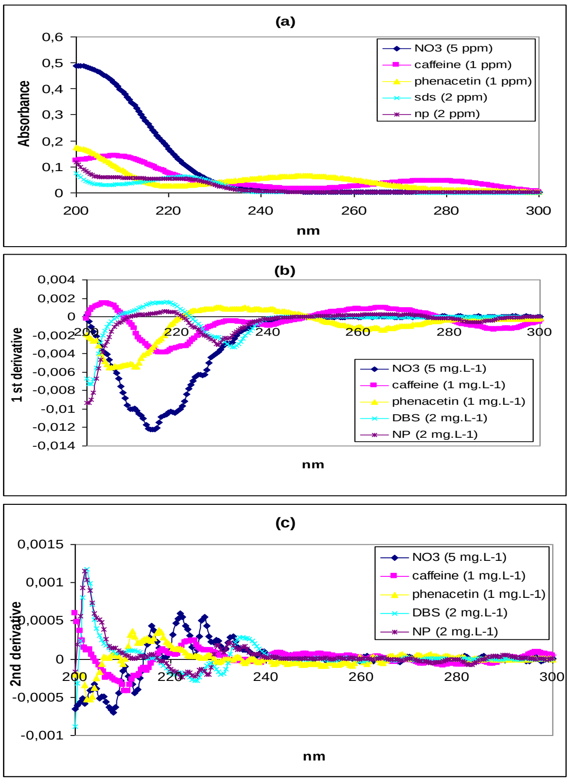

FIGURE 4. (a) Zero-order UV spectra, (b) First-order derivative and (c) Second-order derivative spectra of the specific compounds nitrate, caffeine, phenacetin, DBS and NP.

3.2 Sea water samples

3.2.1 Number of groups

Two groups were formed by all data processing methods as is shown in Figure 5. The criterion for the classification was the r value of 0.99, 0.99 and 0.90 by the zero-order, the first-order and the second-order data processing respectively. Like the storm water samples, the criterion became more flexible as the degree of derivatization increased, because the r values were decreased. Group A consists of the majority of the samples while group B consists only of seven samples. The samples from group B were from different dates. There was only a slight seasonal variation. No spatial or depth variation was observed between samples from same group.

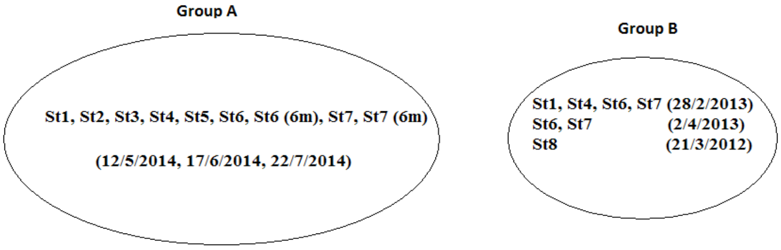

FIGURE 5. Classification of sea water samples by all processing methods of the collected data

3.2.2 Description of spectra

Figure 6 shows the zero-order, first-order and second-order derivative spectra of samples from group A and B.

The UV spectrum of the sample of group A is characteristic of high content in chloride. Chloride is responsible for an absorption wall below 220 nm. As no other constituent is present in so great concentration in seawater, the spectrum is close to zero for wavelengths that are greater than 225 nm. The UV spectrum of the sample that belongs to group B showed lower intensity from 200 to 225 nm and a peak around 205 nm.

The spectral pattern of the first-derivatives spectra from group A showed a peak down at 200 nm. The pattern from group B showed a concave down peak ranging from 203 to 220 nm.

The spectral pattern of the second-order derivatives of group A showed one high peak up at 202 nm and other two smaller peaks up at 210 and 215 nm. The pattern from group B showed a down peak at 205 nm and other two peaks up at 210 and 215 nm.

There are not any previous studies in literature about the first and second derivative spectra of sea water. As far as the zero-order UV absorption spectra of sea water concerned, it has been found that for samples of same salinity they depend mainly in order to KBr>$MgCl_2$>NaCl (Noto and Mecozzi 1997) and to a much lesser extent to organic matter (Ogura and Hanya 1966).

4. CONCLUSIONS

Based on the results of the present study it is obvious that the UV zero and the first-derivative spectroscopic techniques in combination with statistical methods can provide good knowledge for understanding the similarities in quality of the storm water and to sea water in a less extent.

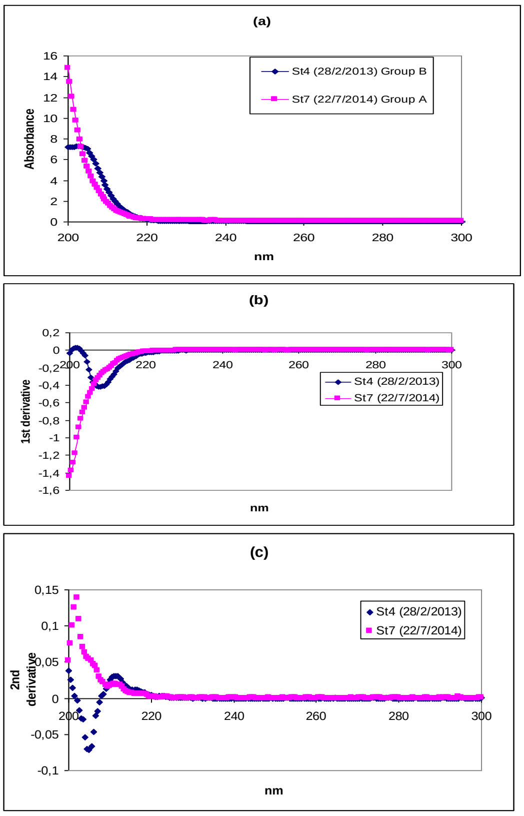

FIGURE 6. (a) Zero-order UV spectra, (b) First-order derivative and (c) Second-order derivative spectra of specific sea water samples that belong to each of the two groups

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