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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 derivative 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. Finally, sea water samples were classified into two groups after processing of the spectral data. The majority of the samples was classified to the first group and the rest of them to the second group.

Keywords - first order derivative spectra, sea water, second order derivative spectra, storm water, UV spectroscopy

I. INTRODUCTION

Storm water is the water generated by rain precipitation and snow melting, that flows on land or impermeable surfaces (streets, roofs and others) accumulating various dangerous or less dangerous substances. The hydro graphic net (rivers, streams and lakes) and the oceans constitute the recipient of the sediments, chemicals, debris and rest of the pollutants, transported by storm water. 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. Stormwater is usually not mixed with wastewater as their co-treatment is expensive and difficult. Stormwater dilutes the wastewater, increasing its volume. Also, the diluted wastewater contains different concentrations of compounds, so the microorganisms have to be adjusted. Because of the pre-mentioned 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) [1] as well as the microorganisms [2]. The analytical techniques that have been used include UV and fluorescence spectroscopy [3, 4] and bioassays [5].
The seawater quality is most difficult to be determined because of the extremely high concentration in chloride. UV spectroscopy is proved to be a powerful tool for the quality monitoring of water and wastewater by measuring parameters like phosphate, nitrite, nitrate, COD. The last years is extensively applied to storm water samples [6] and less [7- 9] to seawater samples The processing of the UV spectral data with proper pattern recognition computer software has provided information about the classification of wastewater samples and surface water into categories according to their origin [10].

In this work we study the quality of stormwater and seawater samples by using the zero-order, the first and the second derivative UV spectra [11]. These spectra provide precious information concerning the composition of the stormwater. Spectral data have been further statistically processed.

II. EXPERIMENTAL

2.1 Site description

The study area is a highly populated area with many shops located in the center of Chania, Crete, Greece. The climate is typical Mediterranean, with very hot, dry summers and mild, wet winters. For a long period of about 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 Fig. 1. Pipe I is a very old one constructed in 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. Four samples were collected once from accessible points of pipe I (Ia, Ib, Ic, Id) and 8 samples from accessible points of pipe II (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 Fig. 1.

Figure 1: Google map of the study area showing sampling points

2.2 Samples

Totally, 26 stormwater 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

Chemical methods

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.

Statistical data processing

Pearson’s Correlation Coefficient (r_{xy}, implemented in Matlab), was used in order to estimate the correlation among the parameters estimated in the context of this study. This technique has been successfully used in previous studies in order to process large datasets [12]. Initially, a scatter plot of all data pairs has been done to establish if the data indicates a linear relationship, because r_{xy} indicates the strength of a linear relationship between two variables x and y for N samples. rxy is defined as:

$$r_{xy} = \frac{Cov\ (x, y)}{\sqrt{Var\ (x)}\sqrt{Var\ (y)}} \tag{1}$$

where Cov the covariance and Var the variance

defined as: $$Var\ (x) = \frac{\sum (x_i - \bar{x})^2}{N - 1} = \frac{SS_{xx}}{N - 1} \tag{2}$$

and

$$Cov\ (x, y) = \frac{\sum (x_i - \bar{x}) \sum (y_i - \bar{y})}{N - 1} = \frac{SS_{xy}}{N - 1} \tag{3}$$

Values of r, ranging from -1 to -0.75 and 0.75 to 1, correspond to perfect-strong relation of the two variables. In case the r value lies in the ranges (-0.75 to -0.5) and (0.5 to 0.75) it indicates a moderate relation of the two variables. Finally, r values lying in the ranges (-0.5 to -0.25) and (0.25 to 0.5) or (-0.25 to 0.25) are suggestive of a weak or no linear relation between the two variables.

III. RESULTS AND DISCUSSION

3.1 Stormwater samples

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

3.1.1 Number of groups

The criterion for the classification of samples between groups was the r_{xy} 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_{xy} values were decreased. Three of the seawater samples showed low r_{xy} values and so did not present any similarity with any of the stormwater samples. For this reason they were excuded in the final evaluation of the data. The classified stormwater groups are shown in Fig. 2.

As is shown in Fig. 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.

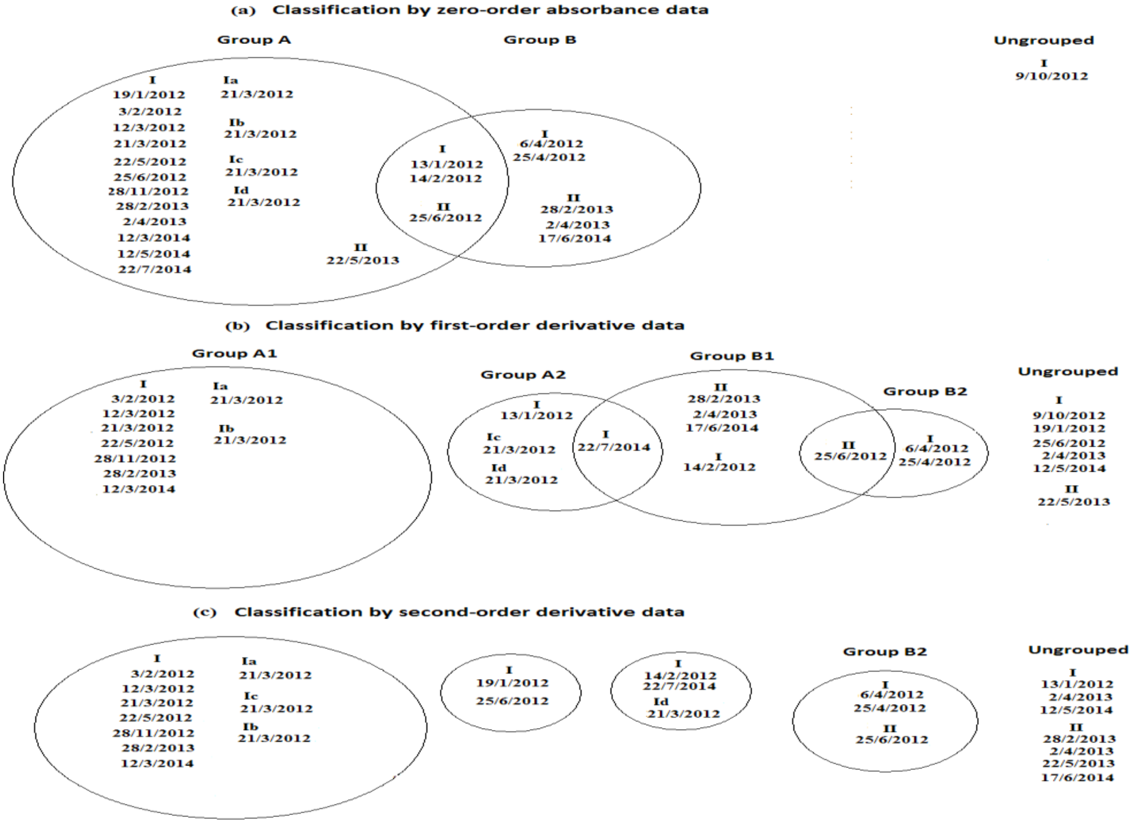

Figure 2: Classification of storm water samples according to: (a) zero-order absorbance, (b) first-order derivative and (c) second-order derivative data

Additionally, the first-derivative analysis indicated the presence of four groups, dividing the A group into two subgroups, A1 and A2 and the B group into two subgroups B1 and B2. Subgroup A1 contains 10 samples and subgroup A2 contains of 4 samples, with one common with B1. Subgroup B1 contains 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 finally belong to 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

Fig. 3 shows the zero-order UV spectra, the first-order derivative and the second-order derivative spectra of the stormwater 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 presents low concentrations while group B2 has high concentrations of nitrate.

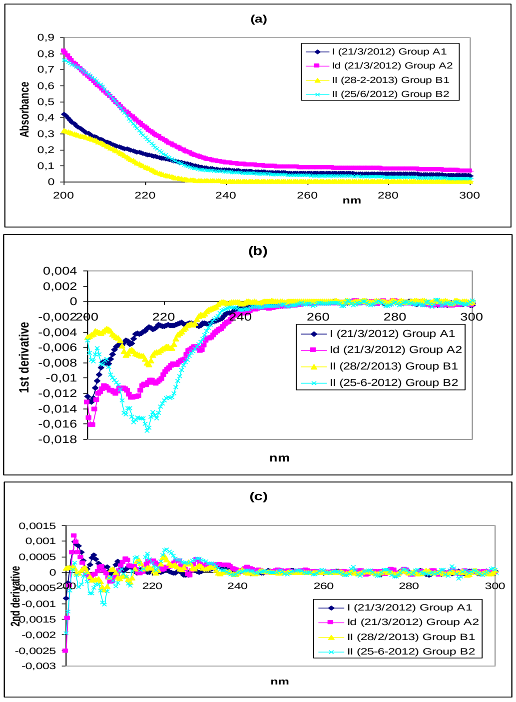

Figure 3: (a) Zero-order, (b) First-order derivative and (c) Second-order derivative UV spectra of specific stormwater samples that belong to each of the four groups

High nitrate concentrations are mostly due to leaking or poorly functioning septic systems. Also, the shape of their first derivative spectra is similar to that of nitrate. A very narrow peak appears below ranging between 200 to 240 nm.

The UV spectra of samples, corresponding to group A1, reflect the domination of humic substances [5, 6]. The samples, corresponding to group A2, present 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 in the past [13, 14]. For this reason, the spectra of representative compounds such as nitrate, caffeine, phenacetin, sodium benzene sufonate and nonylphenol were recorded and the results are presented in Fig. 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.

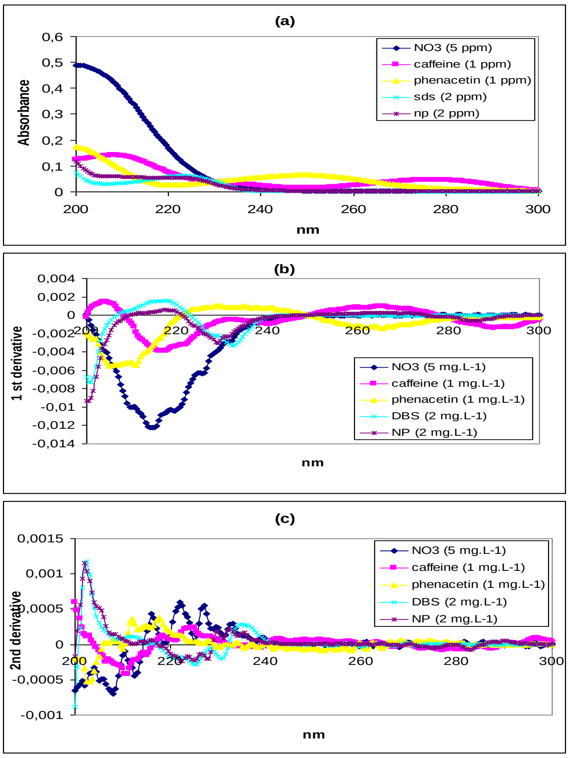

Figure 4: (a) Zero-order UV spectra, (b) First-order derivative and (c) Second-order derivative spectra of the specific compounds nitrate, caffeine, phenacetin, DBS and NP

3.2 Seawater samples

3.2.1 Number of groups

Two groups were formed by all data processing methods as is shown in Fig. 5. The criterion for the classification was the r_{xy} 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 stormwater samples, the criterion became more flexible as the degree of derivatization increased, because the r_{xy} 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 correspond to different dates of sampling. There was only a slight seasonal variation. No spatial or depth variation was observed between samples of the same group.

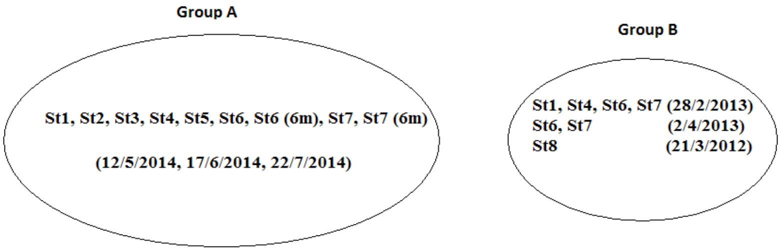

Figure 5: Classification of sea water samples derived at the final processing stage of the collected data

3.2.2 Description of spectra

Fig. 6 shows the zero-order, first-order and second-order derivative spectra of the samples corresponding to groups A and B. The UV spectrum of the sample corresponding to 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 corresponding 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, it has been found that for samples of same salinity they depend mainly in order to KBr>$MgCl_2$>NaCl [8] and to a much lesser extent to organic matter [7].

IV. CONCLUSION

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. Concerning the application of the above techniques in the study area:

- The stormwater samples were classified mainly according to the sampling points revealing spatial variations.
- The seawater samples were classified mainly according to the sampling dates revealing slight seasonal variations.

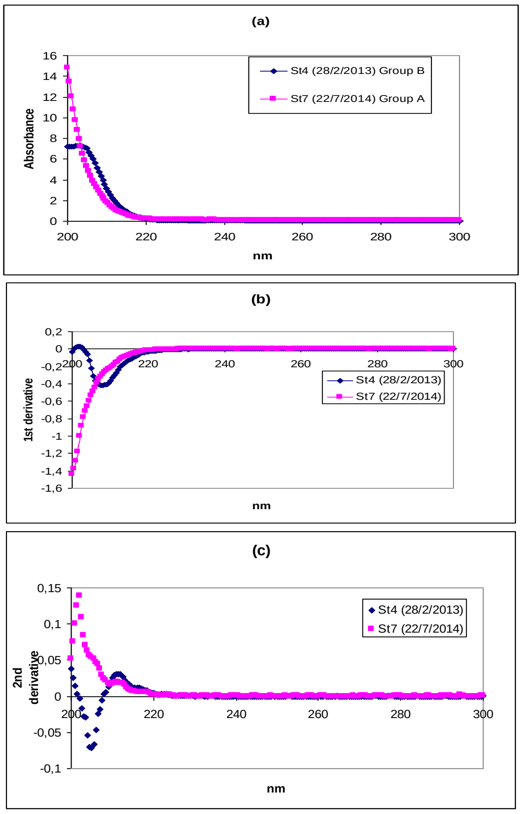

Figure 6: (a) Zero-order UV spectra, (b) First-order derivative and (c) Second-order derivative spectra of specific sea water samples that belong to each of the two groups

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REFERENCES

[1] M. Ghafouri and C.E. Swain, Spatial Analysis of Urban Stormwater Quality, *Journal of Spatial Hydrology, 5(1),* 2005, 33-46.

[2] R. Aryal, J. P. S. Sidhu, M. N. Chong, S. Toze, J. Keller and W. Gernjak, Inter-Storm Dissolved Organic Matter Variability and its Role in Microbial Transport during Urban Runoff Events, *7th Water Sensitive Urban Design Conference*, Melbourne 21-23 Feb, 2012

[3] R. Aryal, M. N. Chong and W. Gernjak Influence of pH on organic and inorganic colloids in stormwater, *Journal of Water and Environmental Technology, 10(3),* 2012, 267-276.

[4] J. Hur, B-M. Lee, T-H. Lee and D-H. Park, Estimation of Biological Oxygen Demand and Chemical Oxygen Demand for Combined Sewer Systems Using Synchronous Fluorescence Spectra, *Sensors, 10*, 2010, 2460-2471

[5] M. N. Chong, R. Aryal, J. Sidhu, J. Tang, S. Toze and T. Gardner, Urban stormwater quality monitoring: From sampling to water quality analysis, *7th International Conference on Intelligent Sensors, Sensor Networks and Information Processing*, 6-9 December, Adelaide, Australia**,** 2011, 174-179.

[6] S. Vaillant, M. F. Pouet and O. Thomas, Basic handling of UV spectra for urban water quality monitoring, *Urban Water, 4,* 2002, 273-281.

[7] N. Ogura and T. Hanya, Nature of ultra-violet absorption in sea water, *Nature, 212,* 1966, 758.

[8] D. V. Noto and M. Mecozzi Determination of Seawater Salinity by Ultraviolet Spectroscopic Measurements, *Applied Spectroscopy**,** 51(9),* 1997, 1294-1302.

[9] K. S. Johnson and L.J. Coletti, In situ ultraviolet spectrometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean, *Deep-Sea Research I, 49,* 2001, 1291-1305.

[10] M. E. Kotti, N. A. Parisis, A. G. Vlessidis and N. P. Evmiridis, Pattern recognition techniques for the classification of wastewater samples based on their UV-absorption spectra and their fractions after applying MW-fractionation techniques, *Desalination, 213*, 2007, 297-310.

[11] M. Kotti and G. Stavroulakis, Classification of storm water and sea water samples by zero-, first- and second-order derivative UV spectra and pattern recognition methods, *1st International Scientific Conf. Sustainable Solutions to Wastewater Management: Maximizing the Impact of Territorial Cooperation,* Kavala, Greece, 2015.

[12] Sarris, A, Kokkinou, E., Aidona, E., Kallithrakas- Kontos, N., Koulouridakis, P., Kakoulaki, G., Droulia, K. and O. Damianovits, Environmental study for pollution in the area of Megalopolis power plant (Peloponnesos, Greece), *Environmental Geology, 58*, 2009, 1769-1783.

[13] Z. Kokot and K. Burda, Simultaneous determination of salicylic acid and acetylsalicylic acid in aspirin delayed-release tablet formulations by second-derivative UV spectrophotometry, *Journal of Pharmaceutical and Biomedical Analysis, 18,* 1998, 871-875.

[14] A. Abbaspour and R. Mirzajani, Simultaneous determination of phenytoin, barbital and caffeine in pharmaceuticals by absorption (zero-order) UV spectra and first-order derivative spectra-multivariate calibration methods, *Journal of Pharmaceutical and Biomedical Analysis, 38,* 2005, 420-427.