



Atmosphere Distribution Assessment of Volatile Organic Compounds Concentration Using Factor Analysis in a Refinery Plant

Ching-Lin Ho¹ and Shu-Lung Kuo^{2*}

1. Department of Technology Management, Open University of Kaohsiung, No.436, Taiwan

2. Kelee Environmental Consultant Corporation, Taiwan *Corresponding author E-mail: singsuey@ms28.hinet.net

Common volatile organic compounds (VOCs) in daily life include benzene, toluene, formaldehyde, alkanes, and other substances. Once exposed to the air, these substances will quickly volatilize from liquid or solid to gas; they are widely used in paints, solvents, oil-based pens, nail polish, correction fluid, aromatics, joss paper, insecticides, electric mosquito-repellent fluid and other consumer goods because of this characteristic. In order to reduce the impact of VOCs on the environment, Taiwan's Environmental Protection Administration (EPA) has formulated standards for the use of VOCs and relevant punitive provisions to reduce environmental pollution. In this study, a refinery plant in Kaohsiung, Taiwan, was selected as a sampling site. The VOCs in the atmosphere around the refinery plant were sampled by activated carbon adsorption at a specific flow rate of 200 ml/min. The concentrations of 12 kinds of VOCs were analyzed by gas chromatography and the correlations among the 12 kinds of VOCs were explored by factor analysis with multivariate statistical methods to identify the major factors causing air pollution around the refinery plant. The results show that acetone has a higher concentration in both the gasoline hydrodesulphurization factory and the heavy oil cracking factory, followed by *n*-butanol, while the other 10 kinds of VOCs have a lower concentration among the 12 specified kinds of VOCs in these factories. It is concluded that these two kinds of organic compounds are emitted from the waste solvent storage areas of both the gasoline hydrodesulphurization factory and the heavy oil cracking factory; of the two, acetone has a more frequent higher concentration of emission. The present results of factor analysis using multivariate statistical methods also showed that one of the three major factors comprised two organic compounds: acetone and *n*-butanol; it is called the "recurrent high concentration emission factor." It is reasonable to conclude that there is high concentration dependence between acetone and *n*-butanol among various VOCs emitted from the refinery plant. The analysis results of this study will be useful for assessing the pollution emission potential of currently operating refinery plants and the possible concentration risks to local households in Taiwan.

Keywords: Volatile Organic Compound, Refinery Plant, Factor Analysis, Acetone.

RESEARCH ARTICLE

1. INTRODUCTION

In recent years, with the development of the economy and improvement of national income, people in Taiwan increasingly demand the improved quality of living environment. They are paying more and more attention to the harmfulness of the substances contained in the exhaust gas discharged from factories, or in the oil gas emitted from gasoline service stations, to their health. Particularly in recent years, the proportion of respiratory diseases, especially children's asthma and upper respiratory tract allergy, has increased significantly. People have protested against

the air pollution in their surrounding living environment; they do not hesitate to resort to taking forceful actions against the factories involved. VOCs emissions are not only the culprit in the increased surface ozone concentration, but also the root cause of many respiratory tract and circulatory system diseases and tumors.

VOCs (Volatile Organic Compounds) encompass a very wide range of chemicals, and many may cause acute or chronic health effects. These chemicals arise from both indoor and outdoor sources; thus, indoor and outdoor VOC concentrations are often correlated and sometimes vary seasonally [6, 12, 14]. The VOCs most commonly measured include benzene, toluene, xylene, ethylbenzene, α -pinene, and *d*-limonene [3, 5-7, 12, 13]. Several studies

*Author to whom correspondence should be addressed.

have focused on characterizing selected IAQ (indoor air quality) parameters and evaluating the impacts of pollutant exposure on children's health [1, 16], but relatively few have provided comprehensive measurements of VOCs, the emphasis of the present paper. VOCs come from a wide ranges of sources such as household air fresheners, aerosol sprays cans, cleaners and disinfectants. Paints and glues are also able to release VOCs in the air. For the most part, VOCs are present if you can smell a very strong chemical scent coming from one of these products. While a strong smell is a sure sign of be careful, these chemicals can still be present and cause damage even at concentrations that you cannot smell or perceive.

Multivariate monitoring methods that consider all available data simultaneously can extract key information about the relationships and combined effects of air pollutants. When failures occur in air quality management systems, univariate monitoring methods are often inadequate to identify causes because the signal-to-noise ratio is very low in each air pollutant measurement. But multivariate monitoring can improve the signal-to-noise ratio through averaging, resulting in a more realistic evaluation of the environmental context. In chemometrics area, multivariate statistical techniques have become one of the most active research areas in modeling and analysis over the last decade [2, 18]. However, to the authors' knowledge, only limited research on the effectiveness of multivariate models for the assessment and management of air pollution has been conducted thus far [10, 15, 19].

Accordingly, in this study, 12 kinds of VOCs emissions were sampled by activated carbon adsorption at a specific flow rate of 200 ml/min around a refinery plant in Southern Taiwan. The adsorption concentrations of the 12 kinds of VOCs were analyzed by gas chromatography and their emission potential in the atmosphere is also discussed. In addition, factor analysis was carried out by using multivariate statistical methods to discover the major emission factors affecting the atmospheric environmental pollution around the refinery plant resulting from the emission of the 12 kinds of VOCs, while achieving the purpose of preventing air pollution in advance.

2. METHODOLOGY

2.1. Types and Selection Time of Gaseous Organic Pollutants

This study utilized 12 kinds of VOCs emissions from a refinery plant in Xiaogang District, Kaohsiung City, Taiwan: acetone (ACE), methyl ethyl ketone (MEK), *n*-Hexane (HEX), chloroform (CHL), benzene (BEN), carbon tetrachloride (CTC), cyclohexane (CYC), *n*-Butanol (BUT), 1,2-Dichloropropane (DIC), 1,4-Dioxane (DIO), methyl isobutyl ketone (MIK), and toluene (TOL). From January 2016 to July 2018, a total of 120 monitoring data were used to analyze the air quality around the refinery plant. In addition, they were further used to carry out a

factor analysis of multivariate statistics to understand the correlations among these 12 kinds of VOCs and the pollution trend of the surrounding environment. All statistical analyses were carried out with SPSS for Windows, version 18.0.

2.2. Study Area

Figure 1 shows the geographic location of this refinery plant in Kaohsiung, Taiwan. It is located at the southern tip of the second harbor at the Port of Kaohsiung with an area of 307 hectares. It is currently the oil transportation, storage and refining center in Taiwan. Its main products include unleaded gasoline, aviation fuel, diesel oil, low sulfur fuel oil, lubricating oil, light cracking feed oil, hydrogen, liquefied petroleum gas, etc.

2.3. VOCs Sampling Method

Three activated carbon adsorption tubes were taken to each sampling point in the refinery plant. The seals at both ends of each adsorption tube were opened, and air sampling was carried out with two tubes at the same time, while the other tube was taken as blank value (only the adsorption tube was opened, but gas was not pumped into it). The sampling pump flow was set at 100 ml/min; each sampling time was about 100 minutes. The sealing caps on both ends of the activated carbon adsorption tube should be immediately sealed after the sampling was done. Ambient and sunshine temperatures above 45 °C should be avoided when carrying out sampling. Samples should be immediately sent to the laboratory for a sample analysis.

2.4. Multivariate Statistical Analyses—Factor Analysis

For selecting the elements to be included in FA, a minimum of 70% of the samples needs to have measurable levels of the element. In principle, FA actually groups the elements whose concentrations fluctuate together from one sample to another and separates these elements into so-called "factors" [8, 11]. Factor analysis is used for source apportionment in environmental data, with the argument that those elements that fluctuate together have some common characteristics. Ideally, each extracted factor represents a source affecting the samples. Factor analysis has been performed using the Statgraphics Plus program package Statgraphics Manual 3.1, 1997. The initial components were rotated using the varimax method to obtain final eigenvectors with more representatives of individual sources of variation. Although there are no well-defined rules on the number of factors to be retained, usually either factors that are meaningful or factors with eigenvalues larger than 1 are retained. In theory, irrelevant factors have zero eigenvalues and eigenvalues less than 1 indicate that factor contributes less than a single variable. The physical meaning of the factors must be interpreted by observing which elements or variables display high (≥ 0.25) loading

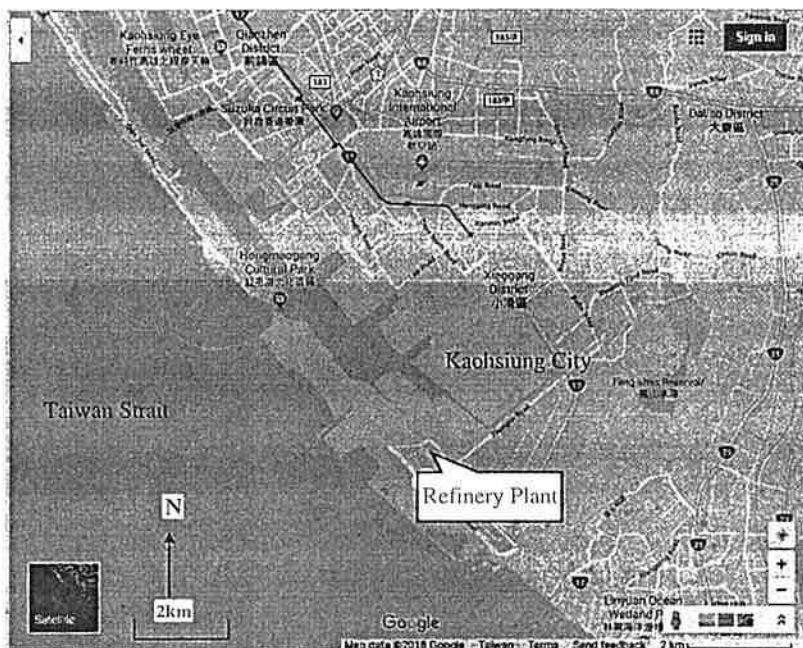


Fig. 1. Geological location of the refinery plant, Kaohsiung City, Taiwan.

within the factor. Loadings less than 0.25 in absolute value may be dominated by random errors.

3. RESULTS AND DISCUSSION

3.1. Selecting the Results of Factor Analyses

This study used the 12 kinds of VOCs collected from the refinery plant to perform the orthogonal rotation of the Varimax Rotation method, in order to explain the characteristics of various factors. According to the analysis results, there are three common factors whose eigenvalues are greater than 1, as shown in Table I and the scree plot of Figure 2. The cumulative explanatory variance of the three factors is 64.106%, and their eigenvalues are 1.988, 1.530 and 1.186, respectively.

Table I. Results factor analysis and the variances.

Components	Initial eigenvalues	% of total variance	Cumulative variance %
1	1.988	26.117	26.117
2	1.530	21.156	47.273
3	1.186	16.833	64.106
4	0.953	10.915	75.021
5	0.909	9.558	84.579
6	0.811	9.144	93.723
7	0.550	3.075	96.798
8	0.503	1.128	97.926
9	0.417	0.552	98.478
10	0.202	0.312	98.790
11	0.183	0.665	99.455
12	0.007	0.545	100.000

3.2. Determination of Factors

The aforementioned eigenvalue greater than 1 can be used to determine the number of major factors. Table II lists the component matrix after orthogonal rotation that can be used to explain the characteristics of various factors. These 3 factors can be used to describe the difference among the concentrations of various VOCs in the refinery plant.

3.3. Explanation of Factors

Table II shows that there are three major factors affecting the air quality and characteristics of the refinery plant.

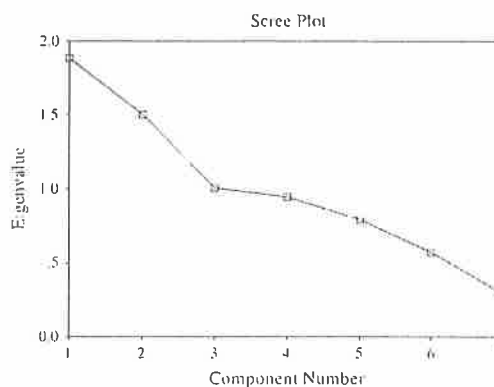


Fig. 2. Scree plot of 12 VOCs.

RESEARCH ARTICLE

Table II. Results factor analyses and the variance explained.

Pollutants	Factors		
	1	2	3
BUT	0.910	-0.138	-0.03
ACE	0.905	-0.257	0.07
BEN	0.262	0.758	0.009
HEX	0.032	0.751	0.289
TOL	-0.040	0.673	0.475
MIK	0.027	0.028	0.746
MEK	-0.001	-0.0003	0.854
CHL	0.083	0.044	0.733
CTC	0.091	0.003	0.628
DIC	0.001	0.116	-0.936
CYC	0.008	0.004	0.077
DIO	0.0003	0.008	0.729

A complete description of the characteristics of these three factors is given below.

3.3.1. Factor 1

The first factor mainly comprised BUT and ACE, and the total variance is 26.117%, as shown in Table I. In addition, Table II shows that BUT has the highest loading degree in the first factor, which is 0.910, followed by 0.905 of ACE. Sampling results of this study show that BUT and ACE have higher concentrations in the waste solvent storage areas of both the gasoline hydrodesulphurization factory and the heavy oil cracking factory, and that their residence time in the atmosphere is longer; this means that the two kinds of organic compounds are often in a higher concentration than the other 10 kinds of organic compounds in the refinery plant. Currently, there are 11 distillation factories in the refinery plant, which can refine approximately 300,000 barrels of crude oil per day. After the crude oil is sent to a distillation factory for distillation, the results of field sampling and analysis show that the BUT concentration in the atmosphere is at the highest value for a long residence time around the gasoline hydrodesulphurization factory and the heavy oil cracking factory, while the ACE concentration in the atmosphere also has a relatively high value for a long residence time around the two factories. After being distilled in a distillation factory, crude oil will be sent to a low sulfur fuel oil factory for refining to produce diesel and heavy oil; the heavy oil will then be sent to the heavy oil cracking factory and the gasoline hydrodesulphurization factory. In the process of producing propylene and its derivatives from the heavy oil cracking process, a high concentration of BUT will be generated, which is most obvious in the atmospheric environment of the heavy oil cracking factory, followed by the gasoline hydrodesulphurization factory. With regard to ACE, the propylene produced by the refinery plant mentioned above will be combined with benzene to further generate a high concentration of ACE [17], which is most obvious in the atmospheric environment of the heavy oil

cracking factory, followed by the gasoline hydrodesulphurization factory. In the gasoline blending factory, the nearby atmosphere also has a high concentration of ACE because it mainly produces various unleaded gasoline; however, its concentration is much lower than that of the heavy oil cracking factory and the gasoline hydrodesulphurization factory. The atmospheric concentrations of other organic compounds in this factor are lower than that of BUT and ACE, so their loading degrees in Table II are also lower. The above analysis results show that ACE and BUT remain at higher concentrations for a longer time in the atmosphere of the gasoline hydrodesulphurization factory and the heavy oil cracking factory; the first factor can thus be called the "recurrent high concentration emission factor."

3.3.2. Factor 2

The second factor mainly comprised BEN, HEX and TOL, and the total variance is 21.156%, as shown in Table I. In addition, Table II shows that BEN has the highest loading degree in the second factor, which is 0.758, followed by 0.751 of HEX and 0.673 of TOL. The results of a sampling analysis show that BEN and TOL present higher concentrations in the atmosphere of the reforming factory during certain periods of time. The main reason is that the refinery plant first performs distillation in the distillation factory, and then sends the resulting product to the reforming factory to convert the low-octane light oil into high-octane gasoline. A portion of this gasoline is sent to the gasoline blending factory, where various unleaded gasoline are produced, and the other portion is used to produce BTX (benzene, toluene and xylene). Therefore, some concentrations of BEN and TOL will be discharged into the atmosphere [4] when BTX is produced, but the overall emission concentration of BEN and TOL and the number of days they reside in the atmosphere are slightly lower than those of BUT and ACE in the first factor. With regard to HEX, it is a chemical substance produced by fragmentation in the process of oil refining. In this study, higher concentrations are found in the waste solvent storage area of the heavy oil cracking factory, followed by those of the reforming factory. However, the overall HEX emission concentration and the number of days it resides in the atmosphere in these two sites are also slightly lower than those of BUT and ACE in the first factor. The above analysis results show that BEN and TOL in this factor are the main products of the refinery plant, and that a portion of these products will be discharged into the atmosphere [9], while HEX is mainly a by-product of the refining process. Although the concentrations of BEN, TOL and HEX are also high in the atmosphere, they are still slightly lower than those of BUT and ACE in the first factor, and their residence time in the atmosphere is also less than those of BUT and ACE. According to the above comprehensive analysis, the second factor can be called the "occasional high concentration emission factor."

3.3.3. Factor 3

The third factor mainly comprised MIK, MEK, CHL and CTC, and the total variance is 16.833%, as shown in Table I. In addition, Table II shows that MEK has the highest loading degree in the third factor, which is 0.854, followed by 0.746 of MIK, 0.733 of CHL and 0.628 of CTC. The sampling results of this study show that chloroform is mainly produced by heating the mixture of chlorine and methane (or monochloro methane) in the gasoline hydrodesulphurization factory and the low sulfur fuel oil factory of the refinery plant. These chloroforms further produce chloridization to obtain CTC, which is then discharged into the atmosphere, resulting in higher atmospheric concentrations in the gasoline hydrodesulphurization factory and the low sulfur fuel oil factory. However, the concentrations of CHL and CTC are generally lower than those of the organic compounds in the first factor and the second factor; the concentrations of CHL and CTC collected from the atmosphere during many periods of time are less than the MDL (method detection limit).

As for the organic compounds: MIK and MEK, both the MEK (also known as 2-Butanone) and MIK are products derived from acetone through a series of chemical reactions in the refinery plant. Therefore, the sampling results show that their concentrations in the waste solvent storage areas of both the gasoline hydrodesulphurization factory and the heavy oil cracking factory are slightly higher than those in other places. However, the concentrations of MIK and MEK in the atmosphere are generally lower than those of the organic compounds in the first factor and the second factor, and similar to the other two organic compounds: CHL and CTC in this factor; the concentrations of MIK and MEK collected in the atmosphere during many periods of time are less than the MDL. According to the above comprehensive analysis, the concentrations of CHL, CTC, MIK and MEK in the atmosphere of the refinery plant are generally not high; they are even the same as the MDL during many periods of time, which can be considered as sudden organic compounds; the third factor can thus be called the "sudden low concentration emission factor."

As for the other three volatile organic compounds: DIC, CYC and DIO, there is no corresponding correlation factor because their concentrations often show MDL phenomena in the atmospheric environment of the refinery plant.

4. CONCLUSION

In this study, 12 kinds of volatile organic compounds (VOCs) in the atmosphere around a refinery plant in Southern Taiwan were sampled to investigate their emission potential. In addition, factor analysis using multivariate statistical methods was also carried out. It is expected that major emission factors affecting the atmospheric environmental pollution around the refinery plant due to the emissions of these 12 kinds of VOCs can be identified, and

the prevention of air pollution can be achieved in advance. The results of the factor analysis show that volatile organic pollutants emitted from the refinery plant have three emission characteristics. The first factor, mainly comprising BUT and ACE, is called the "recurrent high concentration emission factor" because their atmospheric concentrations emitted from the refinery plant by measuring at the waste solvent storage areas of both the gasoline hydrodesulphurization factory and the heavy oil cracking factory are often at the highest degrees. The second factor, mainly comprising BEN, HEX and TOL, is called the "occasional high concentration emission factor" because their atmospheric concentrations emitted from the refinery plant, by measuring both at the reforming factory and the waste solvent storage area of the heavy oil cracking factory, are sometimes at the sub-high degrees. The third factor, mainly comprising MIK, MEK, CHL and CTC, is called the "sudden low concentration emission factor" because their atmospheric concentrations emitted from the refinery plant are generally at low degrees; they are even the same as the MDL during many periods of time. The results obtained in this research will be valuable references and effective tools for reviewing air quality control and management in a refinery plant, and developing appropriate air quality control strategies.

References

1. Adgate, J.L., Eberly, L.E., Stroebel, C., Pellizzari, E.D. and Sexton, K., 2004. Personal, indoor, and outdoor VOC exposures in a probability sample of children. *Journal of Exposure Science and Environmental Epidemiology*, 14(S1), p.S4.
2. Charlton, A.J., Robb, P., Donarski, J.A. and Godward, J., 2008. Non-targeted detection of chemical contamination in carbonated soft drinks using NMR spectroscopy, variable selection and chemometrics. *Analytica Chimica Acta*, 618(2), pp.196–203.
3. Charzidiakou, L., Mumovic, D., Summerfield, A.J., Hong, S.M. and Altamirano-Medina, H., 2014. A victorian school and a low carbon designed school: Comparison of indoor air quality, energy performance, and student health. *Indoor and Built Environment*, 23(3), pp.417–432.
4. Cheng, J.H., Hsieh, M.J. and Chen, K.S., 2016. Characteristics and source apportionment of ambient volatile organic compounds in a science park in central Taiwan. *Aerosol and Air Qual. Res.*, 16, pp.221–229.
5. Shahriyar, Tavousi Tafreshi and Mohammad Reza, Nikoosmanesh, 2013. Study of the effect of the numbers of middle piers (bases) in the numbers of effective modes in seismic evaluation of bridge. *UCT Journal of Research in Science, Engineering and Technology*, (4), pp.1–5.
6. Geiss O., Giannopoulos, G., Tirendi, S., Barrero-Moreno, J., Larsen, B.R. and Kotzias, D., 2011. The airmex study-VOC measurements in public buildings and schools/kindergartens in eleven European cities: Statistical analysis of the data. *Atmos. Environ.*, 45, pp.3676–3684.
7. Godwin, C. and Batterman, S., 2007. Indoor air quality in Michigan schools. *Indoor Air*, 17, p.109.
8. Henry, R.C., Lewis, C.W., Hopke, P.K. and Williamson, H.J., 1984. Review of receptor model fundamentals. *Atmos. Environ.*, 18, p.1507.
9. Huang, C.H., Chen, K.S. and Wang, H.K., 2012. Measurements and PCA/APCS analyses of volatile organic compounds in Kaohsiung

- Municipal Sewer Systems, Southern Taiwan. *Aerosol and Air Qual. Res.*, 12, pp.1315–1326.
10. Liu, P.W.G., 2007. Establishment of a Box-Jenkins multivariate time-series model to simulate ground-level peak daily one-hour ozone concentrations at Ta-Liao in Taiwan. *Journal of the Air & Waste Management Association*, 57, pp.1064–1074.
 11. Martinez, M.A., Caballero, P., Carrillo, O., Mendoza, A. and Mejia, G.M., 2012. Chemical characterization and factor analysis of PM_{2.5} in two sites of Monterrey, Mexico. *Journal of the Air & Waste Management Association*, 62, pp.817–827.
 12. Pegas, P.N., Alves, C.A., Evtugina, M.G., Nunes, T., Cerqueira, M., Franchi, M., Pio, C.A., Almeida, S.M. and Freitas, M.C., 2011. Indoor air quality in elementary schools of Lisbon in spring. *Environ. Geochem. Health.*, 33, pp.455–468.
 13. Pegas, P.N., Alves, C.A., Evtugina, M.G., Nunes, T., Cerqueira, M., Franchi, M., Pio, C.A., Almeida, S.M., Verde, S.C. and Freitas, M.C., 2011. Seasonal evaluation of outdoor/indoor air quality in primary schools in Lisbon. *J. Environ. Monit.*, 13, pp.657–667.
 14. Pekey, H. and Arslanbaş, D., 2008. The relationship between indoor, outdoor and personal VOC concentrations in homes, offices and schools in the metropolitan region of Kocaeli, Turkey. *Water Air Soil Poll.*, 191, pp.113–129.
 15. Pires, J.C.M., Sousa, S.I.V., Pereira, M.C., Alvim-Ferraz, M.C.M. and Martins, F.G., 2008. Management of air quality monitoring using principal component and cluster analysis-part II: CO, NO₂ and O₃. *Atmos. Environ.*, 42, pp.1261–1274.
 16. Shendell, D.G., Winer, A.M., Stock, T.H., Zhang, L., Zhang, J.F., Mazeri, S. and Colome, S.D., 2004. Air concentrations of VOCs in portable and traditional classrooms: Results of a pilot study in Los Angeles county. *J. Expos. Anal. Environ. Epidemiol.*, 14, pp.44–59.
 17. Stepanova, E.E., Kasatkina, S.O., Dmitriev, M.V. and Mastivets, A.N., 2018. Diversity-oriented synthesis via catalyst-free addition of ketones to [*ε*]-fused 1*H*-pyrrole-2,3-diones. *Synthesis*, 50, pp.A–11.
 18. Tobiszewski, M., Tsakovski, S., Simeonov, V. and Namieśnik, J., 2010. Surface water quality assessment by the use of combination of multivariate statistical classification and expert information. *Chemosphere*, 80, pp.740–746.
 19. Yalcin, M.G., Tumuklu, A., Sonmez, M. and Erdag, D.S., 2010. Application of multivariate statistical approach to identify heavy metal sources in bottom soil of the Seyhan River (Adana), Turkey. *Environmental Monitoring and Assessment*, 164, pp.311–322.

Received: 1 January 2019. Accepted: 11 March 2019.