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CLUSTER AND PRINCIPAL COMPONENT ANALYSIS IN THE ASSESSMENT OF FOUNTAIN SOLUTION QUALITY

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Abstract: This study includes the analysis of 23 physico-chemical parameters of spent fountain solutions from 8 printing facilities (PFs) of Novi Sad, Serbia. Spent fountain solution samples were collected once per one hour during 8-hr working shift from sheet-fed and web-fed offset printing presses and analyzed using the standard procedures. Multivariate statistical methods, such as cluster analysis (CA) and principal component analysis (PCA), were applied for the interpretation of the physico-chemical dataset of the fountain solution samples. Based on the dataset, CA showed three groups of similarity between the fountain solution samples and the physico-chemical parameters. Cluster 1 (PF 1, 3, 5 and 8) and cluster 2 (PF 6 and 7) correspond to less polluted printing facilities in comparison to cluster 3 (PF 2 and 4). Three principal components (PCs) were identified as responsible for the data structure explaining 86.82% of the total variance of the dataset. The results obtained from this study could be very useful for the offset printing companies since they provide a complete quality overview of spent fountain solutions through the analysis of physico-chemical parameters and indicate the main sources of quality variation during the printing.

Keywords: wastewater, fountain solution, offset printing, environmental impact, cluster analysis, principal component analysis

1. INTRODUCTION

The printing industry is a very diversified industry, due to the multiplicity of utilized printing processes (offset, flexography, gravure and screen), the size of the printing plants and the quantity of printed products. The choice of printing process is usually based upon technical and commercial considerations, such as length of run, required print quality, used substrate, speed of printing and drying, and the end-use product (The European Commission, 2003; INTERGRAF, 2010). But at the same time consideration of environmental impacts has to be taken into account along with all other factors on an individual basis, when selecting the most appropriate printing process. An accumulation of waste in the printing industry is inevitable given the large scale of production and the continuous nature associated with modern day operations. Waste is predominantly comprised of unused paper and off cuts, however the printing industry also produces a large amount of hazardous waste in the form of inks, cleaning solvents and fountain solutions which can be extremely damaging to the environment if not stored or collected in an appropriate manner (BCF, 2010; Moger, 2006).

Industrial printing ink is relatively thick and viscous in comparison to other inks (BCF, 2010), for the reason to ensure that cylinders and press plates remain coated for longer periods of time. If thinner inks were used, they would simply filter through the presses without suitably covering vital parts of the machinery. The use of thicker ink also promotes the ability of presses to print on different surfaces. The thick texture is achieved through the use of plasticizers called phthalate esters. In 2002, an investigation led by the British Coating Federation classified phthalates as toxic and thus a potential threat to the environment if used carelessly. Although phthalate free plasticizers are available, they do not match the performance and commercial benefits provided by phthalate alternatives (Moger, 2006). Toxicity of printing ink is further highlighted by the fact that a majority of the colourings originate from heavy metals. If left open to the elements, quantities of waste inks can find their way into local water systems and pose a particular threat to local communities (BCF, 2010; Moger, 2006).

Before a new contract can be printed, printing presses are cleaned to remove the remnants of ink left over from prior operations. Chemical solvents break down the oil based composition of the inks making them easier to wipe away. Although many recent printing presses are accompanied by automated cleaning systems, manual application of the solvents is still required in order to clean inaccessible parts of the machinery. Waste solvents must undergo the same level of care as waste ink when handled in order to prevent damage to local environments (Moger, 2006).

Beside the printing ink and cleaning solvents the printing process also requires the application of fountain solution. It supports the ink distribution to the image areas and cleans printing plates and rubber blankets. During the printing, the fountain solution circulates from the fountain solution tank to the aggregates of printing press and the surplus of fountain solution flows back to the tank through an overflow pipe. Ink residue, oil, paper dust and spray powder, which are usually deposited in pans, circulator tanks or on blankets and/or rollers, contaminate fountain solution. These pollutants can load fountain solution in terms of the high levels of copper, zinc, cadmium, phosphates, pH, chemical oxygen demand, biological oxygen demand and total suspended solids. Also, they greatly shorten the fountain solution life, influence to its aging process and make it useless for further printing process (Froberg et al., 2000; Radin Oros et al., 2009; Kiurski et al., 2010). Environmentally, it is necessary to ensure that spent fountain solution, which is fully used in printing process, does not adversely affect the overall quality of the printing wastewaters. Because, discharging of printing wastewaters without any treatment into the water recipients undermines the water quality which is reflected in the occurrence of eutrophication or the pollution by heavy metals and must be regulates by the appropriate Legislation and Regulation relating to wastewater quality. In this way, the necessity of monitoring the specified physico-chemical parameters in printing wastewaters which are taken at different sampling times from different monitoring sites (printing facilities) and selection of the most suitable statistical method for the data analysis is of crucial importance for the better evaluation of the printing wastewater contamination.

Multivariate statistical techniques include two unsupervised pattern recognition methods are cluster analysis (CA) and principal component analysis (PCA). The application of these methods helps in the reduction of the original dataset and offers better interpretation and understanding of the wastewater quality changes. Many studies related with these methods have been carried out (Mihailov et al., 2002; Simeonov et al., 2003; Barraud et al., 2005; Praus, 2005; Shrestha & Kazama, 2007), but no studies have applied the CA and PCA in the analysis of the printing wastewaters.

The assessment of the spent fountain solution quality has been conducted for the first time in offset printing facilities from Novi Sad, Serbia. The target physico-chemical dataset was analyzed using CA and PCA in order to determine the aging of spent fountain solution and its timely replacement in printing process.

2. MATERIALS AND METHODS

2.1. Site description

In order to characterize the levels of pollutants concentrations as well as the quality of spent fountain solutions during printing process five sheet-fed and three web-fed offset printing facilities (PFs) from Novi Sad, Serbia were selected. These printing facilities belong to the medium or large-sized printing companies which differ in area (300 - 7000 m2), number of employees (20 - 200) and production volume (500 - 25,000 impressions per hour).

2.2. Samples of fountain solution

The samples of spent fountain solution from sheet-fed and web-fed offset printing presses were collected once per one hour during 8-hr working shift (eight samples for each printing facility). The fresh fountain solution for sheet-fed printing is a mixture of 3% buffer (ACEDIN DH 2010), 10% IPA and 87% tap water. The fresh fountain solution for web-fed printing contains 0.5% hardening component (AQUADOT 250010), 5% buffer (ROLLSIL CT60), 6% IPA and 88.5% tap water.

2.3. Determination of physico-chemical parameters

The study included the analysis of 23 physico-chemical parameters of spent fountain solutions from 8 printing facilities (PF 1-8) in Novi Sad, Serbia. Spent fountain solution samples were analyzed using the standard procedures for wastewaters listed in table 1. Measurements of pH and electrical conductivity (EC) were performed in situ during the sampling process.

Table 1. Analyzed physico-chemical parameters of spent fountain solution

Parameter	Abbreviations	Methods	Apparatus
pH	pH	SRPS H.Z1.111:1987 (potentiometric)	Multi pH/Cond/Temp 340i handheld meter
Electrical conductivity	EC	Standard methods for hygienic acceptability, 1990 (conductometric)	Multi pH/Cond/Temp 340i handheld meter
Biochemical oxygen demand	BOD_5	SRPS ISO 5815:1994 (dilution)	-
Chemical oxygen demand	COD	SRPS ISO 6060:1994 (volumetric)	-
Dissolved oxygen	DO	SRPS ISO 5813:1994 (iodometric)	-
Total suspended solids	TSS	Offical Gazette SFRY No. 42/66, method III/22 (gravimetric)	-
Nitrate	NO_3^-	Standard methods for drinking water, SZZZ:1990 (UV spectrophotometric)	PerkinElmer EZ 301
Nitrite	NO_2^-	SRPS EN 26777: 2009(E) (UV spectrophotometric)	PerkinElmer EZ 301
Sulphate	SO_4^{2-}	EPA 375.4:1978 (turbidimetric)	Turbidimeter 2100N IS HACH
Chloride	Cl^-	SRPS ISO 9297:1997 (volumetric)	-
Total nitrogen	TN	EPA 351.3 (Total Kjeldahl)	-
Total sulfur	TS	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Total phosphorus	TP	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Chromium (total)	Cr (total)	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Copper	Cu	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Iron	Fe	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Nickel	Ni	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Lead	Pb	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Zinc	Zn	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Mercury	Hg	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Cadmium	Cd	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Aluminium	Al	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo
Silver	Ag	EPA 200.7 (ICP-OES)	Thermo ICAP 6500 Duo

2.4. Data analysis

Multivariate analysis of the physico-chemical dataset was performed using the two most common methods: cluster analysis and principal component analysis. These methods were applied on the standardized data through z-transformation in order to avoid misclassification due to the wide difference in the data dimensionality.

All mathematical and statistical calculations were made using Microsoft Office Excel 2003 and XLSTAT (version 2011.4.04) software for Windows.

2.4.1. Cluster analysis

Cluster analysis is a multivariate method whose primary purpose is to assemble objects based on the characteristics they possess. Cluster analysis classifies objects, so that each object is similar to the others in the cluster with respect to a predetermined selection criterion. The resulting clusters of objects should exhibit high internal (within-cluster) homogenity and high external (between clusters) heterogenity. Hierarchical agglomerative clustering is the most common approach, which provides intuitive similarity relation between any sample and the entire dataset, and it is typically illustrated by dendrogram (tree diagram) (Shrestha & Kazama, 2007; Romesburg, 2004; McGarial, 2000; McKenna, 2003; Mihailov et al., 2005; Iscen et al., 2008). The dendrogram provides a visual summary of the clustering process, with a significant reduction in dimensionality of original data. The Euclidean distance gives the dissimilarity between two samples, and a distance can be represented by differences between analytical values from the samples. The Ward’s method uses an analysis of variance approach to evaluate the distance between clusters, minimizing the sum of squares (SS) of distances between any two clusters (Shrestha & Kazama, 2007; Romesburg, 2004; Iscen et al., 2008; Massart, 1983).

In this study, the clustering process was performed using Euclidean distance together with Ward's method because it produces the most distinctive groups where each member within the group is more similar to its fellow members than to any member outside the group.

2.4.2. Principal component analysis

Principal component analysis is a powerful pattern recognition tool that attempts to explain the variance of the dataset of intercorrelated variables, transforming them into a smaller set of independent (uncorrelated) variables (principal components). PCA extracts the eigenvalues and eigenvectors from the covariance matrix of original variables. The principal components (PCs) are the uncorrelated (orthogonal) variables obtained by multiplying the original correlated variables with the eigenvector, which is a list of coefficients (loadings). Thus, the PCs are weighted linear combinations of the original variables. Principal component provides information on the most meaningful parameters, which describe the whole dataset while affording data reduction with a minimum loss of original information (Simeonov et al., 2003; Shrestha & Kazama, 2007; Mihailov et al., 2005; Iscen et al., 2008; Jolliffe, 2002).

In this study, PCA was applied to the physico-chemical dataset in order to extract significant PCs and to reduce the influence of variables with minor significance. The obtained PCs were subjected to Varimax rotation in order to maximize the variation among the variables inside each principal component and to ease the interpretation of the obtained PCs.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical analysis of spent fountain solutions

The analyzed values (median, min, max and standard deviation) of physico-chemical parameters, which indicate the spent fountain solution quality, are presented in table 2. The concentrations of elements Hg, Cd and Ag were excluded from the analysis, because their values are lower than the instrument detection limit.

Evaluation of spent fountain solution quality was performed by comparing the obtained results (Table 2) with the maximum allowed concentrations (MACs) prescribed by the Regulation of water classification (Official Gazette of SRS, 1968), the Regulation of hazardous substances in waters (Official Gazette of SRS, 1982) and the Regulation of dangerous substances which can not be brought into the water (Official Gazette of SFRJ, 1966), (Table 3).

The analysis showed that all fountain solution samples are organic and inorganic loaded. The median COD values were almost 10 to 17 times higher than the median BOD values. The ratio BOD/COD in all samples was less than 0.3. Because of that, the spent fountain solutions can be classified as non-degradable or biologically incompatible waste liquids, or waste liquids that can not be mixed with household wastewaters without chemical pre-treatment. The median values of TSS were much above the MAC, especially in sheet-fed offset.

The median NO_3^- concentrations were almost 1.4 to 7.0 times higher than the prescribed MAC values. The NO_3^- concentrations vary significantly among the fountain solution samples (the higher values in sheet-fed offset). The median NO_2^- concentrations were in limit of 0.5 mg/L, except in PF 2 where the median value exceeds the MAC. The MACs for TN, TP and TS have not been adopted yet. Based on the organic contamination and suspended solids the best quality of spent fountain solution was observed in PF 8 (web-fed offset) in comparison to the other PFs.

Inorganic pollution as reflected by heavy metals concentrations caused considerable concern for the quality of spent fountain solutions. The presence of metal ions in spent fountain solution comes from the usage of printing inks and their main ingredients (pigments and driers). The analysis showed that in both offset printing processes the amount of Cu, Fe, Ni, Pb, Zn and Al ions is significantly higher in comparison with the MAC values. Only the median values of Cr(total) ions are below the prescribed MAC (0.6 mg/L).

3.2. Cluster analysis

In this study, hierarchical clustering was performed to investigate the similarities or dissimilarities between the fountain solution samples and the physico-chemical parameters. The dendrograms of the analyzed samples and the parameters, providing a visual summary of the clustering process, are presented in figures 1 and 2, respectively. Three clusters are observed from dendrogram in figure 1. Clusters 1 and 2 correspond to less polluted printing facilities, whereas cluster 3

Table 2. Descriptive statistics of physico-chemical parameters for studied printing facilities

Parameter		PF 1	PF 2	PF 3	PF 4	PF 5	PF 6	PF 7	PF 8
pH	Median	5.27	5.43	5.08	5.36	5.18	5.19	5.23	5.16
	Min	5.18	5.27	4.78	5.27	5.08	5.15	5.19	5.08
	Max	5.40	5.75	5.34	5.47	5.34	5.22	5.29	5.21
	SD	0.08	0.16	0.17	0.07	0.09	0.03	0.03	0.05
EC	Median	816.00	1042.00	627.00	990.00	897.00	867.00	911.00	789.00
	Min	736.00	816.00	518.00	908.00	747.00	787.00	864.00	684.00
	Max	951.00	1283.00	798.00	1121.00	1062.00	945.00	976.00	846.00
	SD	70.10	164.38	92.45	78.63	121.37	65.58	37.45	52.68
BOD_5	Median	10431.00	11980.00	9950.00	12342.00	8250.00	13950.00	11720.00	9982.00
	Min	9720.00	10438.00	7520.00	10838.00	7938.00	13288.00	10762.00	9355.00
	Max	11491.00	14204.00	12791.00	13884.00	8531.00	14731.00	12961.00	10874.00
	SD	625.27	1205.20	1775.95	1053.36	232.93	510.70	772.25	526.36
COD	Median	180445.00	194180.00	135164.00	171679.00	124184.00	134184.00	123118.00	111282.00
	Min	175327.00	176004.00	105770.00	163373.00	123057.00	131057.00	121259.00	108259.00
	Max	185643.00	212220.00	187122.00	178612.00	125633.00	138633.00	124983.00	114983.00
	SD	4258.08	13381.73	29714.96	6202.16	933.64	2874.90	1294.71	2410.21
DO	Median	2.74	2.67	2.61	2.65	2.63	2.96	2.91	2.44
	Min	2.54	2.54	2.40	2.57	2.49	2.82	2.84	2.30
	Max	2.96	2.90	2.92	2.73	2.88	3.18	2.98	2.62
	SD	0.15	0.11	0.18	0.06	0.14	0.13	0.05	0.12
TSS	Median	359.70	409.00	330.30	382.00	440.30	340.30	360.40	250.00
	Min	302.00	358.60	276.00	353.20	398.20	305.30	334.70	234.70
	Max	419.00	470.30	409.00	407.30	487.10	367.10	397.10	264.10
	SD	40.30	38.04	44.77	17.91	29.80	22.24	23.96	12.23
NO_3^-	Median	49.30	83.70	57.80	80.60	55.50	27.80	26.50	20.70
	Min	35.90	49.10	35.90	62.30	48.00	24.30	24.30	19.00
	Max	66.90	120.80	89.50	98.60	64.60	32.60	29.40	22.60
	SD	10.77	26.47	20.30	12.42	5.66	2.98	1.96	1.34
NO_2^-	Median	0.10	0.60	0.50	0.40	0.50	0.50	0.40	0.20
	Min	0.02	0.17	0.11	0.18	0.40	0.43	0.33	0.13
	Max	0.21	1.07	0.81	0.56	0.63	0.59	0.50	0.31
	SD	0.06	0.32	0.26	0.14	0.08	0.06	0.06	0.06
SO_4^{2-}	Median	4.80	5.50	4.30	5.45	4.63	36.50	24.83	22.45
	Min	3.20	4.80	2.10	4.80	3.80	33.50	22.40	21.10
	Max	6.70	7.20	7.60	6.30	5.50	40.90	27.80	24.70
	SD	1.35	0.74	1.75	0.52	0.62	2.73	1.91	1.16
Cl^-	Median	650.00	900.00	500.00	800.00	600.00	500.00	400.00	450.00
	Min	570.00	650.00	350.00	650.00	550.00	425.00	300.00	350.00
	Max	800.00	1300.00	800.00	975.00	650.00	550.00	500.00	550.00
	SD	77.09	243.06	139.51	128.17	30.71	47.58	65.47	66.87
TN	Median	251.00	725.00	81.00	517.00	178.00	78.00	62.00	47.00
	Min	237.00	351.00	63.00	356.00	120.00	68.00	55.00	41.00
	Max	269.00	1150.00	114.00	664.00	256.00	89.00	70.00	54.00
	SD	11.05	289.52	17.95	106.88	48.17	7.45	5.76	4.54
TS	Median	18.20	31.00	13.20	41.00	12.60	13.20	16.20	12.00
	Min	16.80	16.70	10.90	34.20	11.50	11.50	15.50	10.90
	Max	19.80	52.80	16.50	47.00	14.00	15.70	16.90	12.70
	SD	1.11	11.79	2.19	4.15	0.88	1.49	0.57	0.62
TP	Median	40.30	64.50	18.00	51.50	29.00	180.00	150.00	133.50
	Min	35.00	38.80	13.00	42.50	26.20	172.00	132.00	122.00
	Max	43.00	92.20	23.00	58.00	33.80	190.50	169.60	145.60
	SD	2.75	19.20	3.70	5.32	2.47	6.06	13.98	7.87
Cr (total)	Median	0.01	0.01	0.04	0.03	0.02	0.44	0.04	0.01
	Min	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
	Max	0.40	0.06	0.13	0.12	0.12	1.21	0.10	0.02
	SD	0.14	0.02	0.05	0.06	0.04	0.46	0.04	0.01
Cu	Median	0.01	4.01	0.33	3.09	2.71	0.32	0.12	0.02

Parameter		PF 1	PF 2	PF 3	PF 4	PF 5	PF 6	PF 7	PF 8
	Min	0.00	0.00	0.00	2.50	0.00	0.00	0.00	0.00
	Max	0.03	17.2	1.66	4.05	7.15	0.90	0.30	0.06
	SD	0.01	5.89	0.60	0.51	2.31	0.38	0.14	0.02
Fe	Median	0.03	0.54	0.25	0.20	0.41	0.25	0.20	0.12
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.10	1.80	0.77	0.58	1.00	0.79	0.56	0.40
	SD	0.03	0.63	0.30	0.22	0.42	0.28	0.24	0.18
Ni	Median	0.01	0.08	0.01	0.03	0.06	0.01	0.01	0.01
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.05	0.25	0.03	0.10	0.23	0.03	0.03	0.03
	SD	0.02	0.09	0.01	0.04	0.08	0.01	0.01	0.01
Pb	Median	0.01	0.15	0.02	0.15	0.02	0.02	0.02	0.25
	Min	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
	Max	0.05	0.60	0.13	0.37	0.07	0.09	0.09	1.00
	SD	0.02	0.20	0.04	0.14	0.03	0.03	0.03	0.38
Zn	Median	1.58	1.90	0.10	2.30	0.10	0.10	0.10	0.10
	Min	0.01	0.00	0.00	1.72	0.00	0.00	0.00	0.00
	Max	5.08	6.27	0.40	3.51	0.35	0.30	0.30	0.35
	SD	2.16	2.23	0.16	0.61	0.14	0.12	0.12	0.13
Hg	Median	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	Max	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	SD	-	-	-	-	-	-	-	-
Cd	Median	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	Max	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	SD	-	-	-	-	-	-	-	-
Al	Median	0.02	4.30	0.43	3.10	2.12	0.46	0.23	0.43
	Min	0.00	0.02	0.00	2.90	0.00	0.00	0.00	0.00
	Max	0.05	10.2	1.90	3.30	8.30	1.20	0.50	1.50
	SD	0.02	3.96	0.70	0.12	2.99	0.48	0.20	0.53
Ag	Median	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	Max	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	SD	-	-	-	-	-	-	-	-

Units: conductivity (EC) in µS/cm; other parameters in mg/L

corresponds to more polluted printing facilities. Such clustering is expected, because printing facilities 2 and 4 (cluster 3) have not installed the systems for the filtration of spent fountain solution and they still use the conventional liquid materials during the printing. Therefore in these facilities the contamination of fountain solution is multiply increased during the printing. The quality of fountain solution is slightly better in PF 1, 3, 5 - 8 (clusters 1 and 2), because they use eco-friendly liquid materials (printing inks and cleaning solvent) and they have installed an adequate, but outdated filtration systems. Thus, it is necessary to introduce the modern filtration systems in all investigated printing facilities to enable the reusage of the fountain solution in printing process. In this way, the discharge of the dangerous contaminants from spent fountain solution into the sewage system, and therefore the pollution of the environment can be prevented. Basically, the filtration systems separate the hazardous contaminants piled during the printing process (dust particles, paper fiber, emulgated printing ink, microorganisms, etc.) from spent fountain solution, maintaining the original composition by prescribed recipe (water, buffer, isopropyl alcohol, etc.) (Radin Oros et al., 2009).

Although the dengrograms show the dataset structure, they do not allow the interpretation of the observed patterns in terms of the original parameters. Therefore, the target physico-chemical dataset is subjected to PCA analysis in order to determine which parameters influence the variation in quality of fountain solution samples.

3.3. Principal component analysis

In this study, the Kaiser criterion (Kaiser, 1960) was applied to determine the total number of PCs for the dataset. Under this criterion, only PCs with eigenvalues greater than or equal to 1 will be accepted as possible sources of variance in the data, with the highest priority ascribed to the PC that has the highest eigenvalue sum.

Table 3. MACs for target parameters

Parameter	MAC	Parameter	MAC
pH	6.0[1]	TN	-
EC	1000.0[1]	TS	-
BOD_5	7.0[1]	TP	-
COD	-	Cr(total)	0.6[2]
DO	4.0[1]	Cu	0.1[2]
TSS	80.0[1]	Fe	1.0[2]
NO_3^-	12.0[3]-15.0[2]	Ni	0.1[2]
NO_2^-	0.5[2]	Pb	0.05[3]-0.1[2]
SO_4^{2-}	200.0[3]	Zn	1.0[2]
Cl^-	-	Al	-

Units: conductivity (EC) in μS/cm; other parameters in mg/L
- indicates that MAC value has not adopted
The superscript denotes the MACs according to the Regulations from 1968, 1982, and 1966.

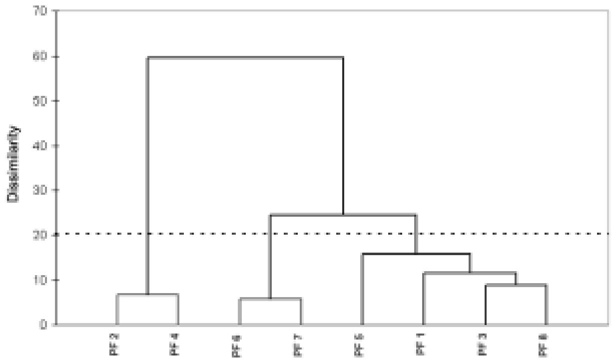

Figure 1. Clustering of the printing facilities according to the spent fountain solution parameters

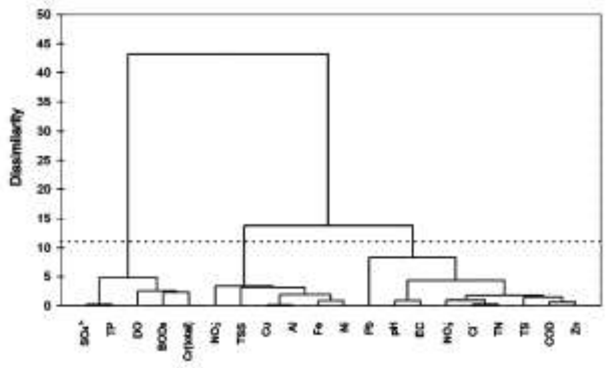

Figure 2. Clustering of the spent fountain solution parameters in studied printing facilities

An inital run using the Kaiser criterion (Kaiser, 1960) resulted in four principal components. However, it was observed that the fourth component would not constitute a unique source of variance since it had only one loading greater than 0.50 (loading for Pb). Thus, Pb parameter was excluded from further analysis, and three PCs were extracted and rotated using the Varimax method in order to maximize the variation among the physico-chemical parameters inside each principal component.

Table 4. PC loadings after Varimax rotation

Parameter	Component		
	PC 1	PC 2	PC 3
pH	0.924	0.249	0.102
EC	0.677	0.461	0.299
BOD_5	0.439	-0.049	0.849
COD	0.900	0.094	-0.127
DO	0.029	0.053	0.784
TSS	0.344	0.710	-0.134
NO_3^-	0.697	0.478	-0.430
NO_2^-	-0.037	0.892	0.213
SO_4^{2-}	-0.379	-0.197	0.869
Cl^-	0.859	0.399	-0.241
TN	0.879	0.421	-0.155
TS	0.916	0.161	-0.046
TP	-0.231	-0.190	0.871
Cr(total)	-0.204	0.051	0.830
Cu	0.586	0.750	-0.217
Fe	0.096	0.971	-0.017
Ni	0.379	0.838	-0.256
Zn	0.982	-0.009	-0.176
Al	0.644	0.701	-0.165
% of Variance	38.86	26.07	21.89
Cumulative %	38.86	64.93	86.82

The results show that the three PCs account for 86.82% of the total variance (Table 4), which is quite good and can be relied upon to identify the main sources of variation in fountain solution samples. Most of the variance is contained in the PC 1 (38.86%), which is associated with the parameters pH, EC, COD, NO_3^-, Cl^-, TN, TS and Zn. NO_3^- and EC have a moderate positive loading, whereas all other parameters have a strong positive loading with PC 1. The highest loading in PC 1 was carried by Zn (0.982), which is probably associated with the presence of zinc-based driers in printing inks. PC 2 represents 26.07% of total variance and has high positive loadings for Fe, NO_2^-, Ni and Cu and moderate positive loadings for TSS and Al, reflecting partly inorganic and organic pollution in the samples.

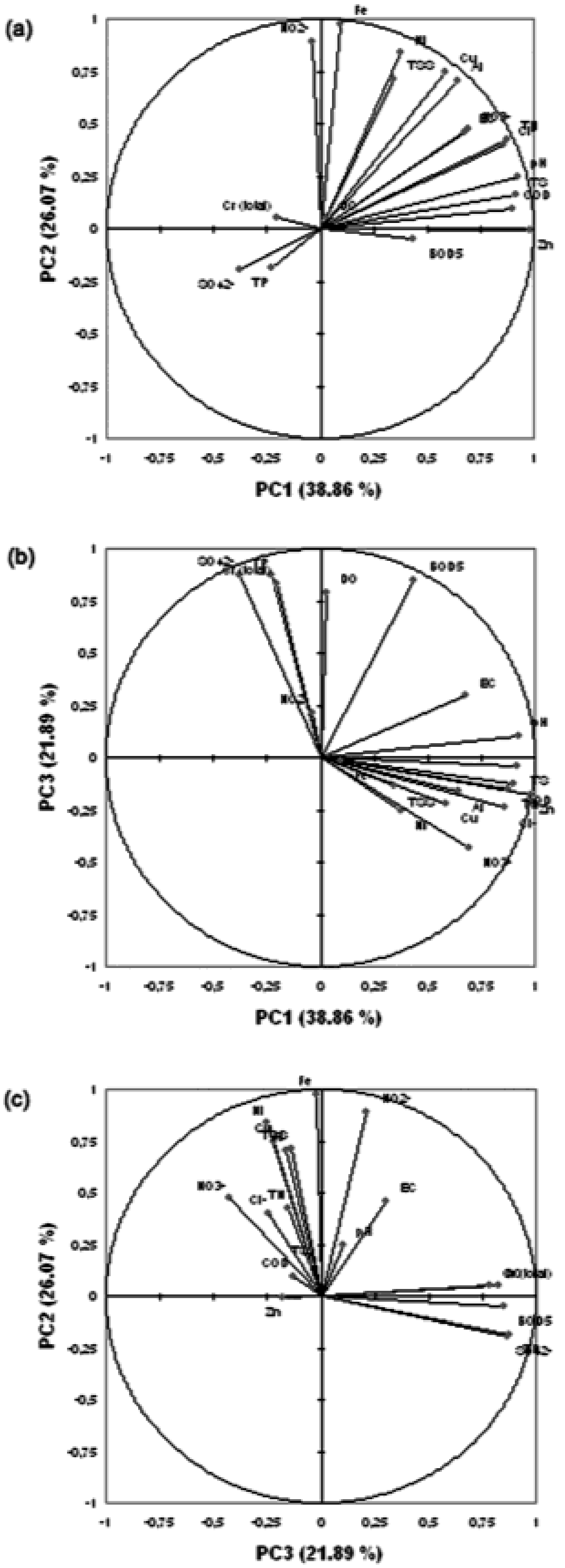

Figure 3. The loading plots of PC 1 vs. PC 2 (a), PC 1 vs. PC 3 (b) and PC 3 vs. PC 2 (c)

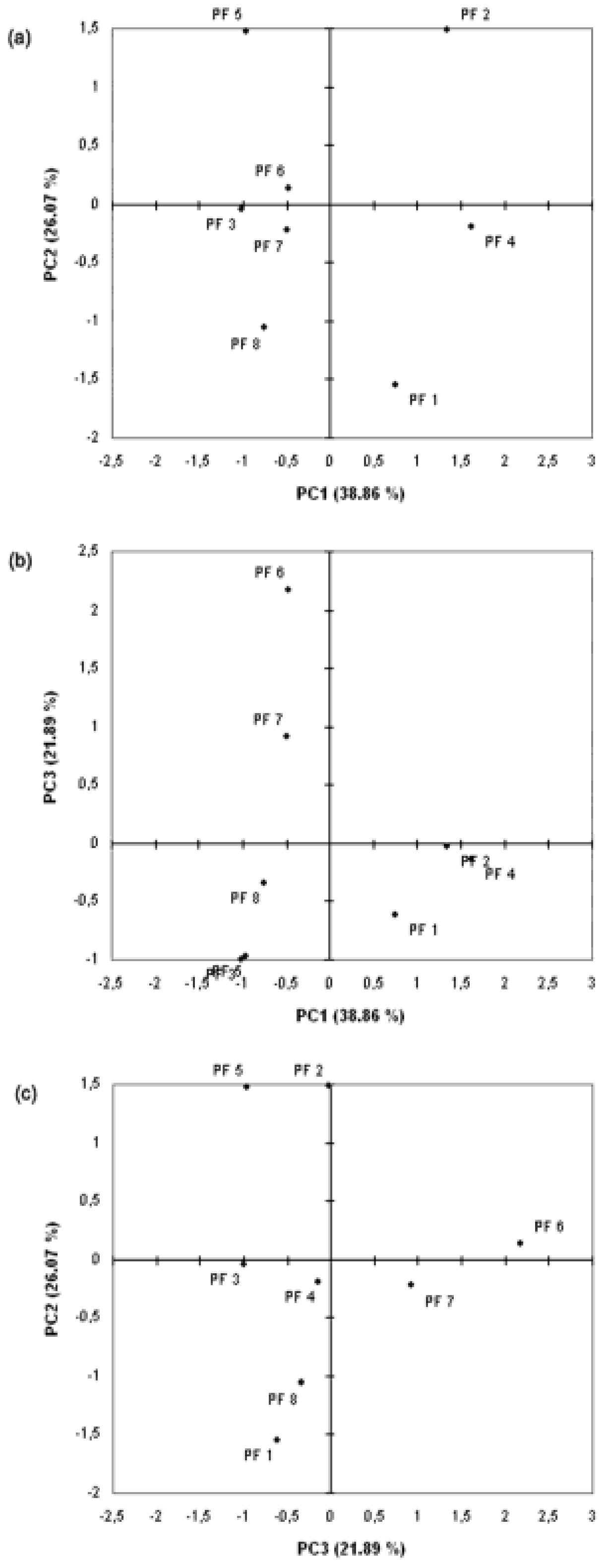

Figure 4. The score plots of PC 1 vs. PC 2 (a), PC 1 vs. PC 3 (b) and PC 3 vs. PC 2 (c)

Metal ions (Zn, Cu, Fe, Ni, Al) in fountain solution are related to the interaction between printing ink and fountain solution during printing process. TSS is associated with the interaction between fountain solution and printing material (paper, cardboard, etc.) and possibly with the usage of anti-offset powder in printing process. The PC 3 explains 21.89% of total variance and has high positive loadings for all remaining parameters (TP, SO_4^{2-}, BOD5, DO and Cr (total)).

The corresponding loading plots (Fig. 3 a-c) for the principal components (PC 1 versus PC 2, PC 1 versus PC 3 and PC 3 versus PC 2) indicate which physico-chemical parameters are responsible for the observed patterns in the score plots (Fig. 4 a-c). The first principal component (PC 1) score is strongly influenced by high values of pH, EC, COD, NO_3^-, Cl^-, TN, TS and Zn which are clustered together and have high positive loadings on the first axis. The loadings of Fe, NO_2-, Ni, Cu, TSS and Al on the second principal component (PC 2) suggest that the second component score could reflect the concentrations of these compounds in the samples. The third principal component (PC 3) score is influenced by the high values of TP, $SO4^{2-}$, BOD_5, DO and Cr(total).

It can be deduced from Figure 4 a-c that the contamination of spent fountain solutions in PF 6 and 7 could be explained by parameters TP, SO_4^{2-} and Cr(total), whereas all the remaining parameters are responsible for the contamination in PF 2 and 4. The contamination of spent fountain solutions in PF 1, 3, 5 and 8 is not directly related to the target physico-chemical parameters. Therefore, this contamination cannot be clearly explained due to the possible presence of undetected contaminants.

The results confirmed that there is a relation between cluster analysis and principal component analysis. Consequently, a parallelism between both multivariate techniques was exhibited, since the target physico-chemical parameters that are dominant in individual PCs are grouped in the identical cluster (Fig. 2 and Table 4).

Taking into account the results obtained by PCA and cluster analysis, it can be concluded that the fountain solution samples from PFs 2 and 4 require the immediate replacement with fresh fountain solution. Also, in PF 2 and 4 it is necessary to introduce the appropriate filtration system in order to reduce further contamination of fountain solution and extend the fountain solution life. Fountain solution samples from PFs 1, 3, 5 - 8 are shown to be suitable for further use in the printing process, because the existence of outdated filtration systems and application of eco-friendly chemicals greatly extended the fountain solution life.

4. CONCLUSION

The results of cluster analysis and principal component explained the differences in the quality of spent fountain solutions for sheet-fed and web-fed offset printing process.

Based on the similarity between the fountain solution samples and the physico-chemical parameters the three clusters were formed: cluster 1 (PF 1, 3, 5 and 8), cluster 2 (PF 6 and 7) and cluster 3 (PF 2 and 4). The PCA analysis through the three PCs explained 86.82% of the total variance. The physico-chemical parameters that are dominant for each PC were grouped in the same cluster suggesting that the results of PCA were in the good agreement with the CA results. The loadings and score plots indicated that TP, SO_4^{2-} and Cr(total) were responsible for the contamination of spent fountain solutions in PF 6 and 7, whereas all the remaining parameters explained the contamination in PF 2 and 4. The contamination in PF 1, 3, 5 and 8 was not directly related to the target physico-chemical parameters, but it could be explained by the presence of undetected contaminants. Samples from PFs 2 and 4 required the immediate replacement with fresh fountain solution, while samples from PFs 1, 3, 5 - 8 could be further used in the printing process. Regardless of the existence of the filtration system in some printing facilities, all the investigated printing facilities should approach the problem of spent fountain solution recycling more responsibly in order to completely eliminate the negative impacts of spent fountain solution on the water recipients and the environment.

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