Characterization of odourous compounds in air, leachate, stream and well in and around Taju-Bello Dumpsite, Lagos, Nigeria

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Abstract. This study investigated the concentrations of odourous compounds in air, leachate, stream and well in and around Taju-Bello dumpsite. Meteorological parameters (temperature, relative humidity, wind velocity) and six odour families comprising sulphur (H_2S), ammonia (NH_3), aromatic (benzene, toluene, ethylbenzene, styrene, p-xylene, m-xylene), aliphatic (hexane), oxygenated (formaldehyde, acetaldehyde) and halogenated (tetrachloroethene, trichloroethene, carbontetrachloride) compounds were measured. Meteorological parameters suggested low dispersal of pollutants at L1 with possible perspiration and suffocation from exposure to high temperature, relative humidity and low wind velocity. The trend of abundance of odourous compounds at studied locations is of the order dumpsite (L1) > leachate (L4) > 100 m away from dumpsite (L2) > 200 m away from dumpsite (L3) > stream (L5) > well (L6). H_2S, Oxygenated and aromatic compounds were the major contributors to odour strength in these locations. Correlation, factor and cluster analyses of the data revealed similarities of sources as biogenics and xenobiotics inherent in the wastes as the main sources of these odourous compounds.

Keywords: odourous compounds; dumpsite; GC-FID; meteorological parameters; cluster analysis

1. Introduction

The most popular method of waste disposal in Nigeria especially in semi-urban communities is non-regulated open dumping which is prone to pollute nearby air and water through release of gases and leachates (Odukoya and Abimbola 2010, Karthikeyan *et al.* 2010, Amadi 2012). Leachates have been reported to contain hazardous contaminants such as heavy metals and toxins of which volatile organic compounds (VOCs) are part (Abdus-Salam *et al.* 2011). Many well and stream water resources have been rendered wholesomely hazardous through contamination by leachates and incidentally, many people in Nigeria depend on wells and streams for water (Abdus-Salam *et al.* 2011). Since most dumpsites have been brought closer to people through unplanned urbanization, when it rains, it leaches toxins from dumpsites into the ground water and

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streams thereby contaminating and rendering them unfit for drinking (Adelekan and Alawode, 2011). Emissions of methane and carbon dioxide which are the major gases in a dumpsite and trace amounts of ammonia (NH_3), hydrogen sulphide (H_2S), carbon monoxide (CO), and VOCs have serious implications for both health and environment because of their toxicological relevance and global warming effects (Chiriac *et al*. 2007, Saral *et al*. 2009, Kabir and Kim 2010). Exposure to chemical combinations in densely populated area near dumpsites has been shown to cause chromosomal and mutageic disorders (Karthikeyan *et al*. 2010).

The presence of VOCs is considered risky even at low concentrations because of their involvement in photochemical smog, depletion of stratospheric ozone and formation of tropospheric ozone which are harmful to humans, animals and vegetation (Nikolaou *et al*. 2002, Komilis *et al*. 2004). They affect olfactory functions of the body because of their malodorous properties and offensive odours (Zou *et al*. 2003). Studies have shown that VOCs are capable of causing odour problems accompanied by adverse health effects, environmental nuisance and unpleasantness (Sarkara *et al*. 2003, Pandey and Kim 2009, Fang *et al*. 2012). VOCs such as formaldehyde and benzene are carcinogenic and a prolong exposure to them could have negative consequences on human health.

Population growth and unplanned urbanization have brought dumpsites close to the people. Little or no attention is paid to waste disposal in most semi-urban communities like Taju-Bello by individuals and government agencies due to lack of information on the possibilities of life-threatening emissions and contaminations from dumpsites. The pollution and odourous assessments of VOCs from dumpsites on air and water quality have not been well reported in Nigeria except for effects of heavy metals from dumpsite on water quality. Therefore, this study was designed to determine levels of hazardous and odourous compounds in air and leachates in and around Taju-Bello dumpsite.

Fig. 1 Map of Taju-Bello showing the sampling location

2. Material and methods

2.1 Site characteristics

Taju-Bello is a town at the border between Lagos and Ogun states. It is a semi-urban community. The dumpsite is located within Taju-Bello (Fig. 1), is a non-regulated open dumpsite. It is located on a hilly terrain, big and covers almost one and half acres of land. It has been in existence for close to thirty years but the volume of refuse dumped on it has increased due to population increase and likewise the odours emanating from it. This dumpsite is characterized by wastes ranging from left-over foods, scrap metals, plastics, used electronic gadgets, sachet water nylon, and containers of paints, body cream, grease e.t.c. Scavengers are usually on the dumpsite to sort out metals and burn off the refuse.

Three locations (L) each for air and water samples were selected for analysis. For air; the dumpsite, 100 m away and 200 m away from the dumpsite were designated as L1, L2 and L3 respectively while for water; leachate, stream and well were designated as L4, L5 and L6 respectively. This was to assess the effects of odourous compounds on both air and water qualities in the vicinity of dumpsite. L1 is on lat $6^o38'$ N and long $3°19'$ E. L5 and L6 are 35 m and 160 m away respectively from L4.

2.2 Sampling and analysis

2.2.1 Characterization of pollutants and meteorological parameters

Concentrations of NH_3 and H_2S were measured with Multi Gas Detector MultiRAE IR, (Model No: PGM-54) and BW Gas Alert micro 5 PID (USA) respectively. Temperature and relative humidity were measured using Kestrel 4500 NV Weather Meter (USA). Wind velocity was measured using flexible anemometer (India). The procedure described by Olajire *et al*. (2011) was used for calibration of these instruments to ascertain their quality performance. Samplings were done every 30 min. in 1hr. for 6hrs. at every sampling time between 10th March and 9th June, 2012 at L1, L2 and L3.

2.2.2 Measurement of VOCs in air

Method of Kim *et al*. (2008) was used for the sampling of air at L1, L2 and L3. Before sampling, tubes were conditioned at 90°C by passing pure helium through them and checked to ensure no target VOCs were present. Air was sampled into tube containing 100 mg activated charcoal with P4LC sampler at rate of 0.5 L/min for 30 min. After each sampling, the tubes were tightly sealed and wrapped in aluminum foil. Duplicate samples were collected at each sampling point. The content in each tube was transferred into 10 ml vial borosilicate glass. The vial and its content were stoppered by silicone material. Vial was transferred to the cell of headspace sampler coupled with gas chromatography equipped with flame ionization detector (GC-FID) for analysis of VOCs.

2.2.3 Measurement of VOCs in leachate, stream and well

VOCs in leachates (L4), stream (L5) and well (L6) were determined using the method of Nikolaou *et al*. (2002) with modification. To each sample in 40 ml vial, four drops of 6 N HCl were added to prevent biodegradation, dehydrohalogenation and sealed with silicone material. This was transferred into a vial for analysis. Triplicate samples were collected at each sampling time.

2.2.4 Gas chromatography-flame Ionization detector working conditions

GC-FID (Hewlett-Packard Model, 501 (USA) was used for the analysis of volatile organic compounds in air, leachate, stream and well. Samples in the vials were pressurized to transfer the volatile compounds through the connecting tubing to capillary columns in the oven of the GC. An HP-VOC capillary column (25 m × 0.32 μm i.d × 0.12 μm film thickness) was used and carrier gas was ultra-pure nitrogen. The GC oven temperature was set initially to 35°C for 2 min., increasing at a rate of 5°C/min. to 80°C and then holding for 10 min. Detector and injector temperatures were maintained at 300°C. The target VOC species were identified by their individual retention time. Blank and laboratory samples were analyzed just as the samples to ensure that there was no contamination during transportation. Standards of VOC mixtures containing all investigated constituents were prepared and calibration curves gave significant correlation coefficients (r^2) between 0.9969 and 0.9998. Detection limits were 0.02 ppb and 0.01 ppb for air and water samples respectively.

2.3 Theoretical odour concentration

It is the concentration of odour compound divided by corresponding odour threshold calculated by the formula

$$C_{od} = \frac{c_i}{OT_i}$$

Where C_i is the concentration of the odour compound i, OT_i is the odour threshold concentration of the compound i and C_{od} is the threshold odour concentration. This can be used for estimating contribution from odourous compounds to odour strength in the absence of olfactory sensory measuring instrument (Capelli *et al.* 2008).

2.4 Statistical analysis

Data were subjected to multivariate statistics using correlation, factor and cluster analyses. Correlation analysis was done using Pearson correlation to establish the relationship between different odourous pollutants. R^2 was obtained at 95 % and 99 % confidence levels. Factor analysis was done using principal component analysis (PCA) technique. It was employed to reveal the likely sources and the contributions of odourous compounds. Cluster analysis using hierarchical clustering based on Ward linkage and Euclidian distance was applied to identify and classify pollutants of similar origins into respective categories so that degree of association between pollutants is maximal, if they are in the same group and minimal if otherwise. SPSS 17 software was used for the analyses.

3. Results and discussion

3.1 Meteorological parameters

Table 1 presents values of meteorological parameters in air at L1, L2 and L3. Temperature and relative humidity decrease as the distance is farther away from the L1 while wind velocity (WV) increases though not steadily with distance away from L1. Meteorological parameters are used for analyzing and predicting atmospheric dispersion of pollutants. Their most important roles are in

Table 1 Concentrations of odourous compounds in air in and around Taju-Bello dumpsite

Meteorological parameters	L1	L2	L3
Temperature (°C)	30.76 ± 1.99	24.38 ± 0.59	24.27 ± 1.36
Wind Velocity (ftmin^{-1})	177.45 ± 5.74	202.08 ± 18.69	197.4 ± 15.16
Relative Humidity (%)	78.70 ± 1.54	63.61 ± 1.78	60.07 ± 1.67

dispersion, transformation and removal of air pollutants from atmosphere (Ocak and Turalioglu 2008, Kgabi *et al*. 2011). Therefore, there is need to measure meteorological parameters on their effects on pollutants dispersion and transformation. High temperature measured at L1 could have resulted from the heat accompanying the burning of wastes. Since there is no landfilling facility open air, burning is used to reduce the volume of the waste. Relative humidity (RH) is an important parameter in measuring comfort index (Godo and Abam 2002). High RH measured at L1 could expose the scavengers and people in the vicinity to excessive perspiration and suffocation (Ocak and Turalioglu 2008). Since WV determines the dispersion of pollutants in the atmosphere, L1 would have the least dispersion of pollutants and expectedly, higher concentrations of pollutants which could undergo both physical and chemical changes to form reactive pollutants.

3.2 Characterization of odourous compounds

Table 2 presents concentrations of odourous pollutants at L1, L2, L3, L4, L5 and L6. H$_2$S and NH$_3$ were not measured in L4, L5 and L6. The trend of abundance of odourous compounds at different locations follows L1 > L4 > L2 > L3 > L5 > L6. Concentration of NH$_3$ was highest at L1 while concentrations of aromatic and aliphatic compounds were highest at other locations. The concentrations of these compounds decrease as distance is farther from L1 and L4. NH$_3$, acetaldehyde, hexane and halogenated compounds were not detected at L3. At L6, acetaldehyde, styrene, hexane, trichloroethene and carbontetrachloride were not detected. NH$_3$, H$_2$S, acetaldehyde and formaldehyde are usually products of food degradation; NH$_3$ and H$_2$S from protein degradation while acetaldehyde and formaldehyde from carbohydrate degradation (Fang *et al*. 2012). As observed during sampling, left-over foods could be the sources of these odourous compounds. Aromatic and halogenated compounds are products of hydrocarbon, rubber and pharmaceutical combustions (Leusch and Bartkow 2010). In this study, burning of refuse which is used to reduce its volume might be the source of these pollutants. Dispersion, transportation in air and leaching in water of odourous compounds from L1 and L4 might have affected the qualities of air and water at L2, L3, L5 and L6 as they were found contaminated with odourous compounds. These compounds are hazardous and have been found to cause various problems such as dizziness, leukemia, lack of muscle coordination and headaches. Continuous inhalation in air and ingestion of water may lead to abnormities (Azeez *et al*. 2012).

3.3 Major compounds causing odour

Odour thresholds of pollutant families at different locations are presented in table 2. It has been found that ratio of chemical concentrations to their respective odour threshold could be used to represent the contribution of compounds to odour strength (Scaglia *et al*. 2011). H$_2$S, aromatic with aliphatic and oxygenated compounds were the major contributors to odour strength at L1, L2

Table 2 Concentrations of odourous compounds at sampling locations

Odour families	Pollutants	OT[a,b]	C_{od}	L1	L2	L3	L4	L5	L6
					Concentrations (ppb)				
Sulphur compound	H_2S	0.41	7.1	47.14 ± 9.75	7.53 ± 2.04	2.34 ± 0.1	-	-	-
Ammonia compound	NH_3	1500	0.4	150.09 ± 28.71	20.77 ± 20.07	nd	-	-	-
Oxygenated compounds	Formaldehyde	500	2.7	12.65 ± 0.75	4.18 ± 0.21	0.16 ± 0.05	31.47 ± 7.26	5.87 ± 1.94	0.03 ± 0.01
	Acetadehyde	15		10.59 ± 1.26	2.12 ± 0.03	Nd	20.89 ± 4.10	0.92 ± 0.19	nd
Aromatic compounds	Benzene	2700	4.3	17.60 ± 2.21	7.94 ± 0.23	1.04 ± 0.08	17.90 ± 0.50	3.06 ± 0.22	0.33 ± 0.12
	Toluene	330		14.73 ± 0.81	10.07 ± 0.31	2.54 ± 0.36	27.10 ± 4.63	3.78 ± 2.03	0.88 ± 0.04
	Styrene	35		9.03 ± 0.19	9.33 ± 0.41	0.12 ± 0.08	3.52 ± 1.19	0.76 ± 0.07	nd
	Ethylbenzene	170		17.26 ± 0.87	6.66 ± 0.71	0.90 ± 0.13	20.23 ± 0.32	4.18 ± 0.15	0.82 ± 0.13
	p-Xylene	58		43.98 ± 11.61	23.57 ± 8.51	11.79 ± 2.31	6.60 ± 1.70	2.27 ± 0.49	0.64 ± 0.07
	m-Xylene	41		31.77 ± 5.04	23.79 ± 8.49	7.44 ± 1.31	8.55 ± 2.65	0.18 ± 0.04	0.21 ± 0.08
Aliphatic compound	Hexane	1500	0.001	2.62 ± 0.24	0.09 ± 0.01	nd	0.41 ± 0.28	nd	nd
Halogenated compounds	Tetrachloroethene	770	0.2	5.42 ± 0.23	3.85 ± 0.72	nd	5.81 ± 3.60	0.12 ± 0.04	0.08 ± 0.01
	Trichloroethene	3900		8.08 ± 0.73	0.69 ± 0.12	nd	8.91 ± 0.94	1.99 ± 0.56	nd
	Carbontetrachloride	4600		19.21 ± 4.57	5.71 ± 0.04	nd	8.79 ± 1.45	1.16 ± 0.22	nd

• OT – odourous threshold, [a]Fant et al. (2012), [b]Sarah et al. (2009), C_{od} – threshold odour concentration L1-Dumpsite, L2-100 m away, L3-200 m away, L4-Leachate, L5-Stream, L6-Well

Table 3 Correlation coefficients of odourous compounds at all sampling locations

	Tem	WV	RH	H$_2$S	NH$_3$	For	Ace	Ben	Sty	Eth	pXy	mXy	Hex	Tetra	Trich	Carb	Tol
Tem	1																
WV	**.964****	1															
RH	**.997****	**.964****	1														
H$_2$S	.574	.381	.595	1													
NH$_3$	.591	.381	.601	**.981****	1												
For	-.248	-.323	-.243	.137	.141	1											
Ace	-.125	-.223	-.119	.267	.275	**.946****	1										
Ben	-.049	-.113	-.043	.177	.185	**.908****	**.919****	1									
Sty	**.680***	.538	.593	**.861****	**.859****	.294	.320	.392	1								
Eth	.086	-.051	.094	.506	-.518	**.877****	**.925****	**.914****	.598	1							
p-Xy	**.792***	**.689***	**.812****	**.841****	**.814****	.076	.192	.231	**.927****	.440	1						
m-Xy	**.783***	**.686***	**.783***	**.698***	**.717***	.131	.248	.355	**.885****	.507	**.830****	1					
Hex	.469	.300	.495	**.935****	**.879****	.269	.376	.289	**.828****	.567	**.835****	.592	1				
Tetra	.252	.155	.259	.442	.452	.589	**.674***	**.812****	**.670***	**.829****	.487	.618	.426	1			
Trich	.058	-.110	.069	.604	.613	**.807****	**.869****	**.800***	.582	**.957****	.448	.429	.655	**.764***	1		
Carb	.469	.302	.483	**.842****	**.847****	.485	.585	.571	**.885****	**.794***	**.788***	**.721***	**.848****	**.744***	**.832****	1	
Tol	-.026	-.092	-.020	.241	.244	**.903****	**.917****	**.954****	.411	**.921****	.270	.357	.357	**.823****	**.828****	.613	1

- Bold values represent statistically significant correlations (2-tailed); **p < 0.01, *p < 0.05
- Tem-Temperature, WV-Wind velocity, RH- Relative humidity, H$_2$S-Hydrogen Sulphide, NH$_3$-Ammonia, For- Formaldehyde, Ace- Acetaldehyde, Ben- Benzene, Sty- Styrene, Eth- Ethylbenzene, pXy- p-Xylene, mXy- m-Xylene, Hex- Hexane, Tetra- Tetrachloroethene, Trich- Trichloroethene, Carb- Carbontetrachloride, Tol- Toluene

and L3 except for oxygenated compounds at L3. At L4, oxygenated and aromatic with aliphatic compounds are the major contributors to odour strength.

3.4 Statistical analysis results

3.4.1 Correlation analysis

Table 3 presents the correlation coefficients of odourous compounds using Pearson correlation analysis. Significant correlations were obtained for compounds in the same families such as H_2S and NH_3 from protein degradation; oxygenated compounds from carbohydrate degradation; aromatic and halogenated compounds from combustion. Significant correlations were also obtained between meteorological parameters, styrene, p-xylene and m-xylene. These correlation coefficients suggest that pollutants such H_2S, NH_3 were from biogenics and aromatic, oxygenated and halogenated compounds were from xenobiotics present in the waste (Fang *et al*. 2012). This also shows that meteorological parameters have minimal effects on the dispersal of odorous compounds.

3.4.2 Factor analysis using PCA

Table 4 presents the result of factor analysis using PCA of odourous compounds. This procedure reduces the overall dimensionality of the linearly correlated data by using a smaller number of new independent variables each of which is a linear combination of correlated variable

Table 4 Varimax rotated factor loadings and communality of odourous pollutants at all sampling location

Parameters	Component			Communality
	F1	F2	F3	
Temperature	-0.099	0.314	0.927	0.969
Wind velocity	-0.157	0.108	0.964	0.965
Relative humidity	-0.096	0.336	0.922	0.973
H_2S	0.136	0.932	0.311	0.983
NH_3	0.150	0.907	0.327	0.952
Formaldehyde	0.929	0.082	-0.224	0.920
Acetaldehyde	0.936	0.183	-0.129	0.926
Benzene	0.987	0.034	0.048	0.977
Toluene	0.974	0.100	0.044	0.960
Styrene	0.328	0.704	0.569	0.927
Ethylbenzene	0.914	0.389	0.052	0.988
p-Xylene	0.165	0.678	0.660	0.923
m-Xylene	0.307	0.443	0.762	0.871
Hexane	0.242	0.900	0.224	0.918
Tetrachloroethene	0.800	0.258	0.312	0.805
Trichloroethene	0.807	0.547	-0.058	0.954
Carbontetrachloride	0.545	0.736	0.317	0.939

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                              Similarity

              0         5        10        15        20        25
              +---------+---------+---------+---------+---------+
   Tetra      -+
   Toluene    -+-----+
   Forma      -+     +---+
   Aceta      -+     |   |
   Benzene    ---+---+   |
   Ethylben   ---+       +------------------------------------+
   Trichlo    -+         |                                    |
   Carbon     -+-+       |                                    |
   Styrene    -+ +-------+                                    |
   H₂S        ---+                                            |
   NH₃        -+                                              |
   Hexane     -+-+                                            |
   p-Xylene   -+ +-----------------------------------------+
   o-Xylene   -+ |
   Temp       ---+
   WV         -+
   RH         -+
```
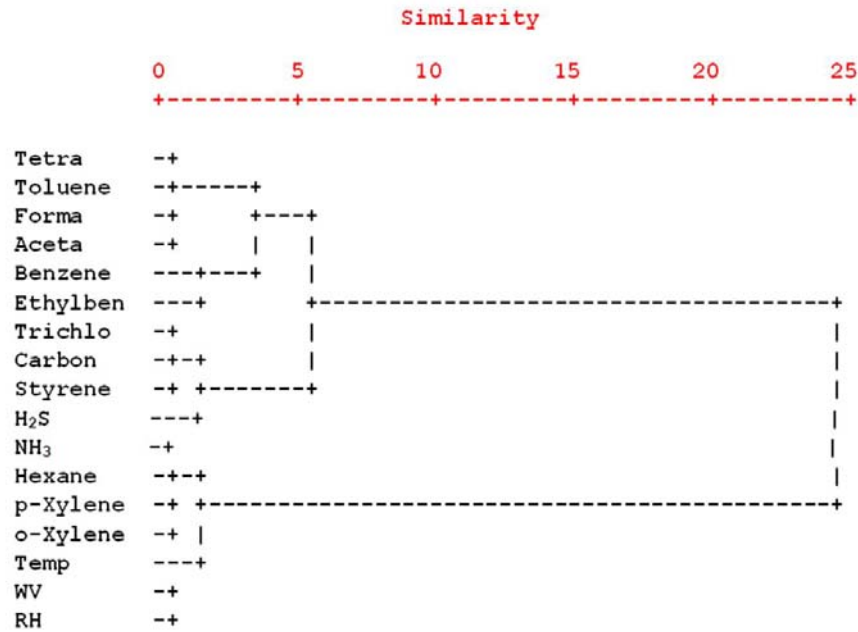
Fig. 2 Cluster analysis using hierarchical clustering of odourous compounds

* Tetra-Tetrachloroethene, Forma-Formaldehyde, Aceta- Acetaldehyde, Ethylben- Ethylbenzene,
  Trichlo-Trichloroethene, Carbon- Carbontetrachloride, H2S- Hydrogen sulphide, NH3- Ammoniia,
  Temp- Temperature, WV- Wind velocity, RH- Relative humidity

(Amadi 2012). Three factors with eigen value ≥ 1 extracted; F1, F2 and F3 explained 56.32%, 29.71% and 7.79% variances respectively and accounted for 93.83 % total variance. F1 had high loading of oxygenated, aromatic and halogenated compounds. This, obtained in correlation analysis suggests they are from xenobiotics in the waste (Fang *et al*. 2012). F2 had high loading of H_2S, NH_3, styrene, p-xylene, hexane and carbontetrachloride suggesting that the sources are likely to be from both biogenics and xenobiotics (Fang *et al*. 2012). F3 had high loading temperature, WV, RH, p-xylene and m-xylene. This suggests that transformation of pollutants would mostly take place at L1 and dispersal would be minimal (Godo and Abam 2002).

3.4.3 Cluster analysis

Fig. 2 shows the result of cluster analysis using hierarchical clustering based on Ward linkage and Euclidian distance. This method was to describe the similarities of sources using dendrogram which clarifies the influence and association of clusters (Sekabira *et al*. 2010). On this basis, three clusters were identified. First cluster illustrated halogenated, oxygenated and aromatic compounds comprising tetrachloroethene, toluene, formaldehyde, acetaldehyde and benzene suggesting a source from xenobiotics in the waste. Second cluster illustrated a combination of aromatic, halogenated, aliphatic, sulphur and ammonia compounds suggesting both biogenic and xenobiotic sources. Third cluster comprises meteorological parameters and aromatic compounds. Sources of pollutants as revealed by the statistical analyses show that both biogenic and xenobiotic compounds were present in the waste on the dumpsite (Fang *et al*. 2012).

4. Conclusions

This study measured meteorological parameters and concentrations of odourous compounds in dumpsite air at different distances and leachate, stream and well. Values of temperature and relative humidity were highest and wind velocity lowest in the dumpsite suggesting that scavengers and people within the vicinity of the dumpsite could be suffocated from the fumes of these gases. Dumpsite (L1) and well (L6) were found to have highest and lowest abundances of odourous compounds respectively. Ammonia dominated at L1 and aromatic with aliphatic compounds dominated the odourous compounds at both L2 and L4.

Theoretical odour concentrations provided the contributions of pollutant families to odour intensity at the sampling locations. H_2S, aromatic with aliphatic and oxygenated compounds were the major contributors at L1, L2, and L3 while oxygenated and aromatic with aliphatic compounds were the major contributors at L4.

Using correlation, factor and cluster analyses, similarity of sources was revealed to be from both biogenics and xenobiotics parts of the waste.

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