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Characterization of the compounds involved in the problems of taste and odour in the water of Sidi Mohamed Ben Abdellah dam (Morocco)

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Abstract
This work deals with the characterization of the organic compounds involved in the alteration of the taste and odour of the water of Sidi Mohamed Ben Abdellah (SMBA) dam, which is considered as the main source of the production of drinking water in Morocco. In late summer 2005, consumers receiving treated water from the SMBA dam complained about the deterioration of organoleptic properties of their drinking water. Examination of physico-chemical parameters of water showed that this dam is mesotrophic with a tendency to be eutrophic. Afterwards analysis of the volatile organic compounds of water has been undertaken; for this purpose, water samples were collected at different depths of the SMBA dam and were extracted by closed-loop stripping analysis. The volatile compounds obtained were analyzed by gas chromatography/mass spectrometry. A total of sixty-three compounds from different chemical classes were separated and identified. Geosmin and 2-methylisoborneol were not found among the identified substances. However, other compounds with odorous properties have been detected. These are terpenes such as borneol, limonene and α-pinene or benzenic compounds such as benzaldehyde, toluene and mesitylene. These substances have biological or chemical origin. These results suggest that the deterioration of the organoleptic properties of the SMBA dam water is not due to a single compound but rather a mixture of odorants.

Keywords: Alkanes, Benzenic compounds, Dam, Odour, Taste, Terpenes.

Introduction
Taste and odour problems have occasionally occurred at Sidi Mohamed Ben Abdellah (SMBA) dam in late summer and were more importantly accompanied by a strong growth of algae. This dam, located 20 km from the city of Rabat (Morocco), is used by a population of more than 5 million people as the major source of drinking and industrial water in the coastal area between Rabat and Casablanca.
Off-flavour problems in water are caused by the presence of volatile odour compounds (VOCs). Many of these compounds were identified by gas chromatography/mass spectrometry; they include straight chain aliphatic hydrocarbons, fatty acids, esters, alcohols, aldehydes, ketones, terpenoid hydrocarbons and sulfides [1, 2]. The most commonly implicated compounds in imparting the taste and odour to drinking water are 2-methylisoborneol (2-MIB) and geosmin. They are of a particular concern to water managers as they are perceived by the public at very low levels [3-5]. These compounds are produced by the members of certain groups of benthic and pelagic aquatic microorganisms found in source-waters such as lakes, reservoirs and running waters. In addition, there are several other sources, which originate from terrestrial systems, industrial waste treatment facilities and drinking water treatment plants [6, 7].
The origin and type of water sources would influence taste and odour, particularly when water is taken from various sources including that of surface water provisioning. On dam's level during the stratification period, the

hypolimnion can become anoxic due to the eutrophic state of the water supply, which results in nutrient release from sediments. However, this condition can also support formation and proliferation of algae and other compounds responsible for taste and odour in surface waters [8, 9].
The main purpose of this study was to present the first results concerning the extraction, characterisation and estimation of the concentrations of VOCs involved in off-flavour problems in the water of the main dam producing drinking water in Morocco.

2. Materials and methods

2.1. Water samples

The location of the SMBA dam is indicated in Figure 1. The dam capacity is 446 millions m^3. It is fed by three rivers (Bouregreg, Grou and Korifla). Water samples were collected from July to October 2005 at five different dam depths (surface, 5, 10, 14 metres and bottom) and several water quality parameters were measured. Odorous compounds were analyzed by gas chromatography/mass spectrometry in water samples collected from eleven depths (3, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 metres) during the same period. Water samples were collected using a Ruttner bottle from a point approximately 500 m from the dam body. Collection, transport and storage of water samples refer to the protocol defined by the French Association for Standardization AFNOR (NF-T90-10). The analytical methods used are those given in the Moroccan standard (NM). Table 1 summarizes analyses carried out on water, as well as the reference methods used.

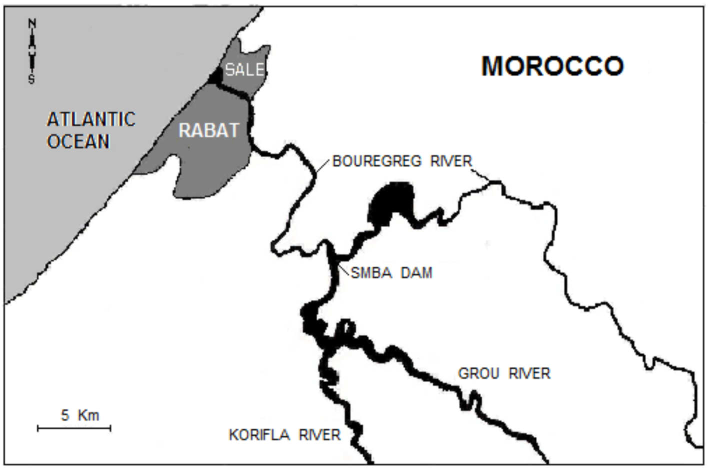

Figure 1: Geographical location of rivers feeding the SMBA dam.

Table 1: Physicochemical parameters measured on water of the SMBA dam.

Variable	*Unit*	*Principle and reference method*
Temperature (T)	°C	NM 03.7.008-1989
Potential hydrogen (pH)		Potentiometric method. NM ISO 10523-2001
Dissolved oxygen (DO)	mg O_2/L	NM 03.7.029-1991
Total phosphorus (Pt)	mg/L	Colorimetric method. NM ISO 15681-2-2007
Total nitrogen	mg/L	Continuous flow colorimetric method. NM ISO 5663-2000
Chlorophyll (a)	µg/l	Spectrometric determination. NM ISO 10260-2008

2.2 Extraction and analysis

Samples for gas chromatography/mass spectrometry (GC/MS) analysis were collected using the closed-loop stripping analysis (CLSA) method [10]. CLSA is a technique allowing the extraction of the VOCs from water. Its principle consists of stripping compounds from one litre of water by a recirculating stream of air, and trapping them on a carbon filter cartridge (1.5 mg). The carbon filter was extracted with carbon disulfide (3 x 10 µL). Extracted VOCs were separated by the injection of the extract in GC/MS system. 1-chlorooctane was used as internal standard and was added to the samples prior to CLSA.
Compounds were separated in a gas chromatograph (Hewlett-Packard 6890 Series) equipped with a HP-5MS 5% phenyl methyl siloxane column (30 m × 0.25 mm x 0.25 µm: film thickness). Column flow rate was 1.2 mL/min

He. A 1-2 µL sample was injected in the column using split mode. The GC conditions were: temperature held at 40°C for 2 min after injection, followed by an increase to 180°C by 10°C/min, and then to 250°C by 5°C/min, which was held for 5 min. Spectra were acquired with a HP 5973 Series mass spectrometer, using an ionization potential of 70 eV and a mass range to 800 amu in full scan mode. Identification of VOCs was done by comparison of retention times and mass spectra with those of available authentic standards. Additional identifications were made by comparison of mass spectra with those existing in the data system library (NIST 98).

3. Results and discussion

3.1. Water quality overview

Figure 2 summarizes some physico-chemical characteristics of the SMBA dam water during the period of study. The average temperature of dam water was 26°C but decreases as dam depth increases. In August, temperature gradient was wider (20°C) than in October (6°C). Vertical temperature variability indicates a temperature difference between surface and bottom individualizing a thermocline depth that changes with seasons. Permanence of thermal stratification in the dam may be interpreted by a low capacity of wind and stir to oxygenate water layers. Besides, pH ranges from 9.2 (August) to 7.5 (October); the largest variations in pH affect surface water. Water becomes basic in spring due to a high photosynthetic activity; in winter, water is acidic due to a bacterial activity that degrades abundant organic material at the bottom [11].

Analysis of dissolved oxygen shows that shallow waters are well oxygenated (6 to 9 mg O_2/L) while the deep ones are poor or lacking oxygen. Oxygen fall in summer can be explained by the importance of oxygen-consuming organisms. Monitoring of chlorophyll pigment shows a temporal variation in the content of chlorophyll (a); levels are high in spring and fall in summer.

On the other hand, total phosphorus was always less than 60 µg/L and the maximum quantity of chlorophyll (a) was 11 µg/L. These data and that of total nitrogen (< 0.07-1.89 mg/L) compared to the three trophic-state classes [12] indicate that the SMBA dam is mesotrophic and tends to become eutrophic.

3.2. Qualitative analysis

The main objective of this study was to identify the compounds that cause off-flavour problems in water of the SMBA dam and also to estimate quantitatively these compounds by GC/MS.

The results of chemical analyses for eleven samples (from 3 to 14 m) using a GC/MS system are presented in table 2 (a, b and c). In all samples, several compounds were identified, but to better understand these results, we arranged them into several classes: alkanes, alkenes and their derivatives (table 2a), benzenic compounds (table 2b), terpenes and various ones (table 2c).

The constituents of these classes may have different origins. The possible origins of these compounds and their involvement in the alteration of the taste and odour of water are discussed in the following paragraphs.

Terpenes have been extensively studied in different science fields as botany [13], pharmacology and food chemistry [14]. Plant terpenes are used extensively for their aromatic qualities. In this study, several terpenic compounds were identified such as *α*-pinene, limonene and borneol; they are found in many oils distilled from plants [15]. Detergents supplemented with odorants are another source of terpenes in waters receiving domestic sewages: camphor, limonene, terpineol and bornyl/isobornyl acetate [16]. Camphor and limonene are also algal metabolites responsible for odours; they are produced respectively by *Synedra delicatissima* and *Scenedesmus subspicatus*. These two algal species have previously been associated with taste and odour episodes in drinking water supplies [17]. *Synedra ulna* and *Peridinium cinctum* were already isolated from the SMBA dam (unpublished results) and are important algal species associated with taste and odour in water [18].

Concerning terpenoid compounds, in our experimental conditions neither geosmin nor 2-MIB were detected in the water of SMBA dam during the investigation period; although tests carried out by Foutlane *et al.* [19] in September and October 1993 on the waters of the same dam have shown the presence of geosmin (13-50 ng/L) and 2-MIB (16-78 ng/L). These substances are the most powerful odorous compounds of biological origin that severely affect water quality in the world [20].

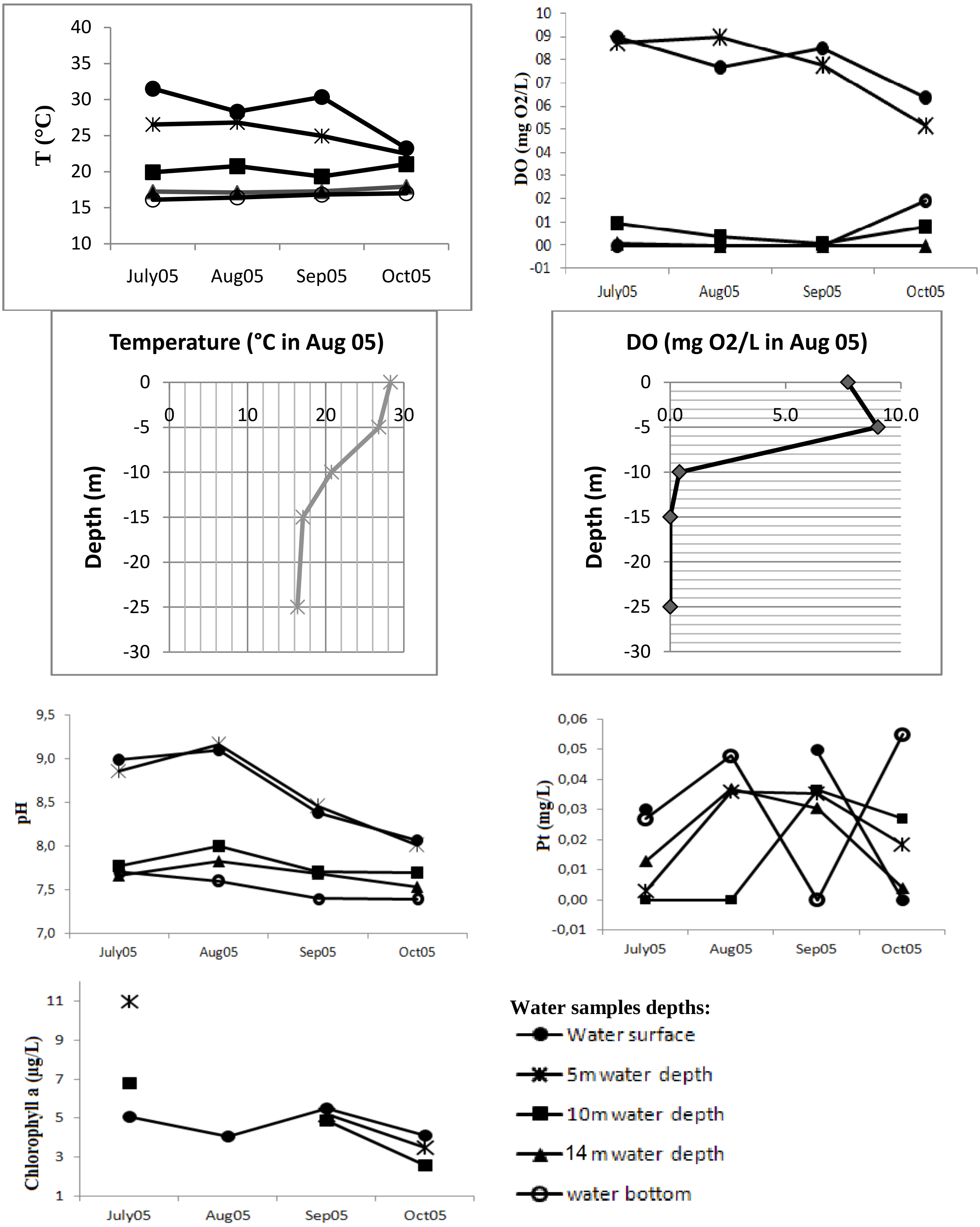

Figure 2: Some physico-chemical characteristics of the SMBA dam water.

The fraction of linear and cyclic alkanes and olefinic hydrocarbons and their derivatives was a mixture of biogenic and pollution products. In all samples, the complete homologous series of linear alkanes and cyclic alkenes was found. Many detected alkanes (decane, docosane, dodecane, eicosane, heptadecane, 2-methylpentane, nonane, octylcyclohexane, pentacosane, tetradecane, tridecane and undecane) are fuel oils components [21]. Heptadecane, a nonodorous metabolite [22], has also a biological origin and was found as a major alkane in blue-green algae [23]. It is well established that algae produce a diversity of potent odorous metabolites; about 200 have been identified by Watson *et al.* [24] and some of them include aldehydes, alkanes, alkenes, alcohols and esters [22, 25, 26].

Table 2a: Compounds identified by GC/MS at different depths in the SMBA dam.

Chemical compound			*Compound concentration (ng/L)*										
			Depth (m)										
Classe	Identity	Odour	3	5	6	7	8	9	10	11	12	13	14
Alkanes, alkenes and their derivatives	3-buten-2-one	*	235										
	cis-1-butyl-2-methylcyclopropane				x		25		x				
	cyclotetradecane	*	212		x								
	decane			x		x	29					x	127
	docosane		6				24						
	dodecane		97									x	40
	eicosane							x		x		x	
	heptadecane		87			x	196			x	x	x	48
	2-methylpentane				x								
	4-methyltetradecane									x			
	4-methylundecane		597					x					
	nonane		79					x				x	8
	1-nonene			x		x							
	octamethyl-1,4-cyclohexadiene					x							
	1-octene		181					x	x				
	octylcyclohexane									x			
	pentacosane						19			x			
	pentylcyclohexane									x			
	tetradecane		127	x		x	25	x		x	x	x	10
	4-tetradecene					x							
	tridecane		82	x		x				x	x	x	34
	4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	*				x				x			
	undecane		6	x		x		x					86

*: compound having taste and/or odour.
X: unquantified compound or quantity isolated at the indicated depth.

More than half of benzenic compounds identified were fuel oils products; they are: ethylbenzene, 1,2-dimethyl-3-ethylbenzene, isopropylbenzene, 1-methyl-2-propylbenzene, propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, toluene and *m* and *p*-xylenes [21].
Many benzenic compounds such as benzaldehyde, *o*-dichlorobenzene and toluene, or some terpenes (borneol, limonene, α-pinene, etc.) isolated from different depths of the SMBA dam have organoleptic properties and may confer taste and odour to the water [27].
Some odorous compounds isolated from the dam are of diverse nature and come from oil and coal tar (mesitylene, naphthalene and pseudocumene) or agriculture. The hydrocarbons may come from the leaching of roads within the watershed of the dam. Other pollutants isolated from water (cyclohexanol and cypermethrin) can find use as pesticides [27] in agricultural land upstream of dam.

3.3. Quantitative analysis
Several analytical methods have been developed in order to identify and quantify the compounds involved in taste and odour problem in water [2, 28]. While CLSA method was, so far, the most popular and shows good analytical potential to analyse these compounds, it is obviously that sensory methods are the least expensive and can give the fastest response [29, 30]; but also, it's the most susceptible technique.
Quantitative concentration determination was performed by an internal standard method. For each compound, the response is calculated relative to 1-chlorooctane. Table 2 (a, b and c) lists the identified compounds and their

concentrations after the analysis of the samples collected at 3, 8 and 14 metres. The results of this analysis show that the concentration of the identified compounds was low; it does not exceed some ppb. The main compounds isolated from the water at 3 m depth are limonene, benzoic acid ethyl ester and 4-methylundecane; while benzaldehyde and diisopropylphenol are the main constituents detected at 8 m depth. At 14 m depth, 1-ethyl-2-methylbenzene, decane, toluene and *p*-xylene are best represented. Phthalates found in most analyzed water samples are generally contaminants and come from laboratory consumables [31].

Table 2b: Compounds identified by GC/MS at different depths in the SMBA dam.

Chemical compound			*Compound concentration (ng/L)*										
			Depth (m)										
Classe	Identity	Odour	3	5	6	7	8	9	10	11	12	13	14
Benzenic compounds	benzaldehyde	*	21	x	x	x	48	x		x	x	x	
	benzoic acid		88	x		x		x		x		x	
	benzoic acid ethyl ester		611	x	x								
	camphene	*										x	7
	1,2-dichlorobenzene (*o*-dichlorobenzene)	*					16		x			x	85
	1,3-dimethylbenzene						22		x				27
	1,2-dimethyl-3-ethylbenzene		19	x		x		x	x	x			
	ethylbenzene	*							x				43
	isobutylbenzene	*	60	x		x	18	x		x			
	isopropylbenzene (cumene)	*	5	x		x		x	x	x		x	
	1-ethyl-2-methylbenzene		44						x				142
	1-methyl-4(1-methylethyl) benzene		49	x		x		x		x		x	27
	1-methyl-2-propylbenzene								x				
	propylbenzene	*						x	x			x	23
	1,3,5-trimethylbenzene	*						x	x			x	11
	1,2,3-trimethylbenzene	*	7	x		x	17	x		x		x	99
	1,2,4-trimethylbenzene (pseudocumene)	*							x				x
	1,3,5-trimethylbenzene (mesitylene)	*			x				x				39
	styrene	*	116	x	x	x	20	x	x	x	x	x	18
	toluene	*			x	x			x			x	105
	m-xylene	*			x		21		x			x	
	p-xylene			x	x							x	100

*: compound having taste and/or odour.
X: unquantified compound or quantity isolated at the indicated depth.

The various volatile substances present in water at different depths of the SMBA dam were sorted according to their vertical distribution in water. A number of compounds (styrene, borneol, benzaldehyde, tetradecane and 1,2,3-trimethylbenzene) have a constant distribution and are present at virtually all depths, some as bornyl acetate and cyclohexanol have a specific distribution and exist only in a given depth while others (nonane, 1,2-dichlorobenzene and mesitylene) have a more or less random distribution.
The list of the compounds isolated from the water of SMBA dam was compared to that described by Young *et al.* [32]. It appears from this comparison that the compounds common to both studies are: 1,2-dichlorobenzene, isopropylbenzene, styrene, naphthalene and toluene. Among these compounds, only styrene was found in the dam water at a concentration where its odour can be detected. Styrene has rubber, paint or sulphurous odours.
VOCs isolated from the SMBA dam water have biological or chemical origins; they include volatile compounds derived from biological pollution from aquatic microorganisms or plants. Chemical pollution, less important than the first, is of diverse nature and comes from oil, coal tar and some substances used in agriculture.
These results suggest that the odour problem in the dam water is not due to specific compounds but rather to the association of several odour compounds.

The results of this study could be used to prevent the incidence of identified odorous compounds on the quality of drinking water by monitoring their presence in the water of SMBA dam. Further investigation on odour producing aquatic microorganisms growing in the lake is needed.

Table 2c: Compounds identified by GC/MS at different depths in the SMBA dam.

Chemical compound			*Compound concentration (ng/L)*										
			Depth (m)										
Classe	Identity	Odour	3	5	6	7	8	9	10	11	12	13	14
Terpenes	borneol	*	184	x		x	29	x	x	x	x	x	24
	bornyl acetate		82										
	camphor	*				x						x	29
	limonene	*	1786	x		x		x		x			
	α-pinene	*	37	x		x		x					
	α-terpineol	*	38	x		x							
Miscellaneous	cypermethrin						17						
	1,2-diethylcyclobutane										x		
	1-butoxy-2-propanol												25
	2-ethyl-1-hexanol								x		x		
	2-butyl tetrahydrofuran			x							x		
	cyclohexanol	*			x								
	pentylcyclopropane								x		x		
	phthalates		x	x	x	x	x	x	x	x	x	x	x
	hexacosane				x		29						
	Methyl-6,8-dodecadienyl ether										x		
	naphthalene										x		
	Diisopropylphenol						47						

*: compound having taste and/or odour.
X: unquantified compound or quantity isolated at the indicated depth.

Conclusion

Off-flavour problem in the water of the SMBA dam was more important during the hot season and was accompanied by excessive growth of algae. This deterioration of water quality was due to the presence of odorous compounds. This study showed that neither geosmin nor 2-methylisoborneol were present in detectable amounts in all the water samples analyzed; however, borneol has been identified in most water samples. The compounds responsible for taste and odour are present in small quantities and are of different chemical natures. They have mainly a biological origin and are mainly terpenes and benzenic compounds.

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