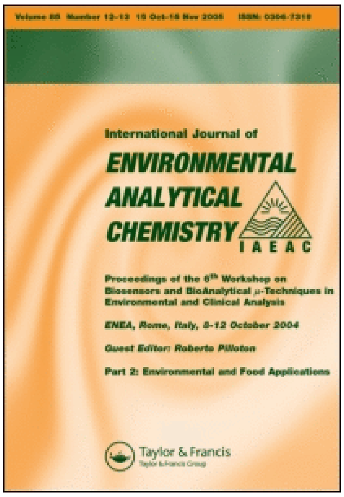

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OCCURRENCE OF GEOSMIN AND OTHER ODOROUS COMPOUNDS OF NATURAL ORIGIN IN SURFACE AND DRINKING WATERS. A CASE STUDY

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The concentrations of geosmin and other natural compounds in raw water from the Llobregat river and tap water from Barcelona (N.E. Spain) were measured by CLSA and GC-MS. From 1997 to mid 1999, average concentrations of 86 and 33 ng/l of geosmin were recorded in Llobregat river water at the entrance to the two main water treatment plants (WTP1, WTP2), whereas their treated waters contained 24 and <5 ng/l, respectively. Barcelona's tap water coming from the WTP3 supplied by Ter river had also an average value of <5 ng/l for geosmin.

The presence of geosmin in Barcelona's tap water can be attributed to the blending of the two Llobregat WTPs and also to the blending of Llobregat and Ter river treated waters. Geosmin is one of the compounds responsible for complaints from consumers. Neither 2-methyl-isoborneol (MIB) nor 2-alkyl-3-methoxypirazines were detected among other compounds with low odor threshold concentrations (OTC).

Keywords: Closed loop stripping (CLSA); geosmin; 2-methyl-isoborneol (MIB); odor; raw water; tap water

INTRODUCTION

Taste and odors in drinking waters are one of the major causes of consumer complaints. These are enhanced during drought when the quality of raw water is lower. Consumers usually associate a bad taste or smell with unsafe drinking water and these episodes damage the public image of the water company. Thus, a

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rapid response to identify the compound/s and an efficient treatment to remove them are required.

The association between algal blooms and episodes of unpleasant taste and odors has long been established; in particular, blooms of cyanobacteria have been held responsible for many incidents. The two main compounds from natural origin most frequently cited[1–3] as causing these taste and odor episodes are geosmin [1,10-*trans*-dimethyl-*trans*-(9)-decalol] and 2-methyl-isoborneol or MIB [(1R-exo)-1,2,7,7-tetramethylbicyclo(2.2.1)heptan-2-ol]. Both compounds infer a characteristic earthy/musty odor to water, and the lowest reported odor threshold concentrations (OTC) are 10 ng/l and 29 ng/l for geosmin and MIB, respectively[4,5]. Similar OTC levels (2–7 ng/l) have been reported for pyrazines and trichloroanisoles[6]. Dimethyl disulfide and dimethyl trisulfide, with a characteristic septic /swampy odor, are produced by bacterial degradation of algae[7] and decaying vegetation[8]among other sources. These compounds have published OTC values of <4000 and 10 ng/l, respectively[9].

Other commonly identified compounds in algal blooms such as β-cyclocitral, 6-methyl-5-hepten-2-one, *cis*-3-hexen-1-ol, *trans*-2-*cis*-6-nonadienal or geranylacetone can be considered as tracers of potential problems in water because they contribute to the overall odor of the sample.

The determination of geosmin and other natural occurring compounds has traditionally been carried out by CLSA (closed loop stripping analysis)[6,9–17] and to a lesser extent by P&T (purge and trap)[18–20]; LLE (liquid-liquid extraction)[21–23], OLSA (open loop stripping analysis)[24], SDE (simultaneous distillation extraction)[9] and recently by SPME (solid-phase microextraction)[25,26]. CLSA, as originally developed by Grob[27], is frequently used to determine geosmin and other natural compounds. CLSA combined with GC-MS allows them to be determined at 2–5 ng/l, far below their OTC levels. A detailed description of the method can be found in the Standard Methods[28]. Geosmin and MIB have been found in surface waters worldwide: USA[6,22,29], Australia[30,31], Canada[32] and Japan[18,19]. Other compounds such as dimethyl polysulfides had been found in Australia[33,34], Israel[35,36] and other countries[20,37,38]; and trichloroanisoles have been detected in Canadian rivers[23]. Granular activated carbon (GAC) and powdered activated carbon (PAC) remove efficiently geosmin as well as other combinations as described elsewhere[3]

The aim of this study is to provide current data on the concentrations of geosmin and other natural compounds in Mediterranean rivers where data is sparse. A case study of Barcelona's drinking water, which is supplied by two rivers of different water quality, and the evolution of the geosmin levels in the different stages of the WTP2 is presented.

EXPERIMENTAL

Geographical situation

Barcelona's drinking water is supplied by Llobregat (45%) and Ter (55%) rivers, located south and north of Barcelona, respectively. These rivers have different water qualities due among other factors, to the presence of salt mining and densely industrialized and inhabitant areas along the banks of the Llobregat river. This salinity imparts a characteristic salty taste to treated water from WTP1 and WTP2 and is often a source of complaints from consumers.

Two water treatment plants Abrera (WTP1) and Sant Joan Despí (WTP2) are situated on the Llobregat river. The former is approximately 45 Km from the mouth and mainly serves water to the cities around Barcelona (0.5 million inhabitants) and also a small part to Barcelona. The WTP2 is 7 Km from the mouth of the river and mainly provides water to the city and the surrounding area (3 million inhabitants). On the other hand, Ter river is treated in a third WTP (Cardedeu, WTP3) and transported to Barcelona by a pipeline. Figure 1 shows the geographical situation of the different treatment plants. WTP1 and WTP3 consist of breakpoint chlorination, clarification, sand filtration, GAC filtration and postchlorination. The WTP2 follows the same scheme as described for the other WTPs but also includes an ozonation step after sand filtration and before GAC filtration.

The various consumption needs of the treated water in the city often require the blending of these waters. Thus, consumers can find four types of tap water in Barcelona: a) Ter treated water (from WTP3), b) Llobregat treated water (from WTP2), c) blended Llobregat treated water from WTP2 and small percentage of WTP1 and d) blended Llobregat and Ter treated waters in a wide range of percentages (from WTP1, WTP2 and WTP3).

Sampling

Samples from Llobregat river raw water in front of WTP1; different stages of the WTP2 (raw, sand filtered, ozonated, GAC filtered, treated) and tap waters from all types of blending were collected in 1L amber glass bottles with teflon septa and polypropylene screw caps, filled without overflow. Previously, the glass bottles had been washed in soapy water, rinsed in tap water, ultrapure water and finally reagent-grade acetone. They were then air-dried and baked overnight. After this procedure, they were covered with aluminum foil to preserve them from dust and other contaminants.

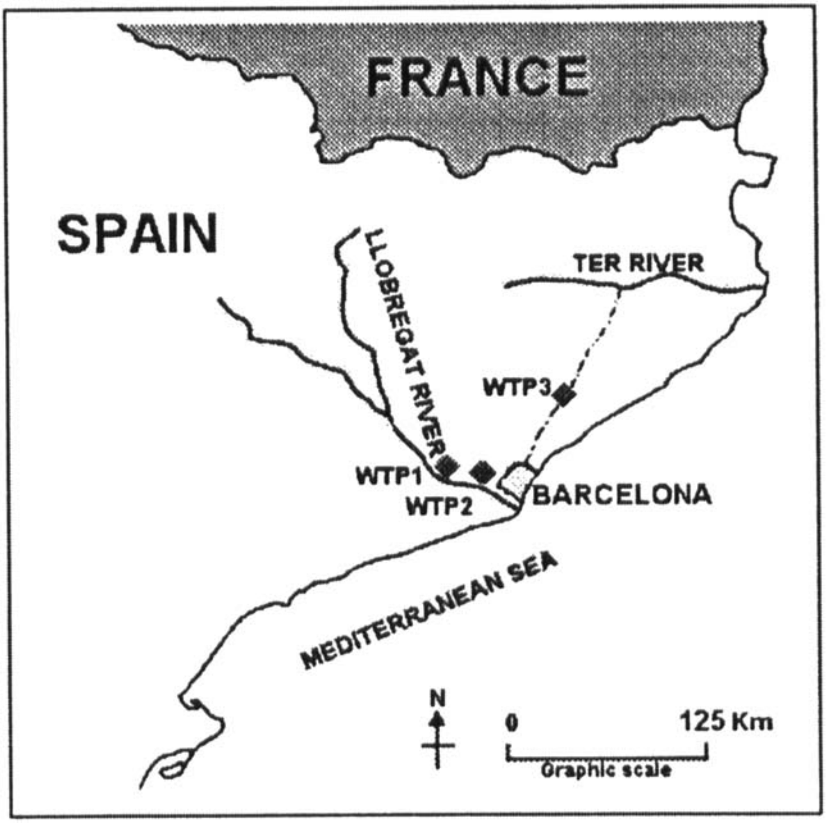

FIGURE 1 Map of the study area showing the locations of the sampling sites. Llobregat river: WTP1 (Abrera); WTP2 (Sant Joan Despí); Ter river: WTP3 (Cardedeu). Pipeline (···) from Ter river to WTP3 and then to Barcelona

A volume of 2 mL of a freshly prepared 0.142 M ascorbic acid solution was added to each bottle prior to sampling to reduce any free chlorine present in treated waters.

Closed-Loop Stripping Analysis (CLSA)

Analyses were carried out in a commercial CLSA apparatus (Brechbüler, Switzerland) according to the method developed by Grob[27]. Several 1-chloroalkanes (C_5, C_6, C_{10}, C_{12}, C_{16} and C_{18}) were added to the water samples as surrogate standards at a concentration of 800 ng/L for each compound. We used

1.5 mg-activated carbon filters. The samples were stripped for 1.5 hours. Temperatures of 45 °C and 55 °C were used for water-bath and carbon filter, respectively. After stripping, the carbon filters were spiked with C_8 and C_{14} 1-chloroalkanes at the same concentrations as the spiked water samples in order to control the filter elution. The filters were then extracted with 20 μL of CS_2 (10 μL + 10 μL).

Recovery efficiencies of 100% were obtained for geosmin, MIB and 2,3,6-trichloroanisole; 55% for 2-isopropyl- and 2-isobutyl-3-methoxypyrazines and 30% and 100% for dimethyldisulfide and dimethyltrisulfide, respectively. For the rest of the compounds, we obtained 100% recovery for 6-methyl-5-hepten-2-one; *trans*-2-*cis*-6-nonadienal and geranylacetone; 93% for β-cyclocitral and 5% for *cis*-3-hexen-1-ol.

Quantitation of geosmin and the other compounds was performed by the internal standard method. For each compound, the response factor is calculated relative to 1-chlorohexane. The unknown concentrations in the sample are obtained using the formula $C_z = A_z C_i / R_z A_i$ where C_z and C_i are the concentration of the unknown compound and the internal standard; A_z and A_i are the peak areas of the unknown and the internal standard, respectively; and R_z the response factor for the target compound.

Instrumental conditions

Analyses of CLSA extracts were carried out on a Fison 8560 gas chromatograph. Injections (1 μL of CS_2 extracts) were made cold on column into a 50 m × 320 μm i.d. (0.2 μm film thickness) CP-Sil 19-CB column (Chrompack, The Netherlands). The GC temperature program was 30 °C (5 min) to 285 °C (10 min) at a rate of 3 °C/min. Helium was used as the carrier gas (60 kPa). Samples with geosmin concentrations ≥ 5 ng/l were always confirmed by GC/MS. A Fisons Trio 1000 mass spectrometer equipped with a Fisons 8060 gas chromatograph was employed. The chromatographic conditions were the same described above. The mass spectrometer was operated in electron impact mode (70 eV). The source temperature was kept at 300 °C. Mass spectra were acquired by scanning from 35 to 450 Da with 1s/decade.

RESULTS AND DISCUSSION

Table I shows the average, maximum and minimum concentration levels of different natural compounds liable to be responsible for taste and odor events during the last two years (Feb. 97-June 99) in the Llobregat river. The sampling points analyzed are: raw water in front of the WTP1; raw water entering to WTP2 and its treated water. The analysis of geosmin was also performed in the different stages of this WTP.

TABLE I Concentration levels (ng/l) of geosmin and other compounds of natural origin in Llobregat raw water and WTP2. (February 1997- June 1999)

Compound	*N*[a]	*Average*	*Maximum*	*Minimum*	*>OTC*
Geosmin					
Llobregat river-Abrera[b]	20	86	200	<5	80
Entrance WTP2	122	33	160	<5	71
Sand filtered	59	28	130	<5	63
Ozonated	55	13	80	<5	42
GAC filtered	58	<5	12	<5	5
Treated	124	<5	18	<5	1.5
2-methyl-isoborneol					
Llobregat river-Abrera	20	<10	20	<10	
Entrance WTP2	100	<10	20	<10	
Treated	100	<10	<10	<10	
Dimethyl disulfide					
Llobregat river-Abrera	20	<100	<100	<100	
Entrance WTP2	100	<100	170	<100	
Treated	100	<100	<100	<100	
Dimethyl trisulfide					
Llobregat river-Abrera	20	<50	<50	<50	
Entrance WTP2	100	<50	<50	<50	
Treated	100	<50	<50	<50	
2-isopropyl- (and 2-isobutyl)-3-metoxypyrazines					
Llobregat river-Abrera	20	<10	<10	<10	
Entrance WTP2	100	<10	<10	<10	
Treated	100	<10	<10	<10	
6-methyl-5-hepten-2-one					
Llobregat river-Abrera	20	30	170	<20	

Compound	*N*[a]	*Average*	*Maximum*	*Minimum*	*>OTC*
Entrance WTP2	100	50	250	<20	
Treated	100	<20	60	<20	
β-cyclocitral					
Llobregat river-Abrera	20	<20	<20	<20	
Entrance WTP2	100	<20	<20	<20	
Treated	100	<20	<20	<20	
Geranyl acetone					
Llobregat river-Abrera	20	30	120	<10	
Entrance WTP2	100	20	200	<10	
Treated	100	<10	60	<10	
2,3,6-trichloroanisole					
Llobregat river-Abrera	20	<10	<10	<10	
Entrance WTP2	100	<10	<10	<10	
Treated	100	<10	<10	<10	

a. Number of samples analyzed.
b. Llobregat river raw water in front of WTP1 (approx. 40 km north of WTP2). >OTC: percentage of samples with levels higher than the odor threshold of geosmin (10 ng/l).

Geosmin

The presence of geosmin is a common cyclic episode in N.E. Spanish rivers caused among other factors by high temperatures, nutrients, etc, and enhanced by drought and lower flows of the river. During these odor events, values between 50–150 ng/l of geosmin can be recorded in Llobregat river. Figure 2 shows a chromatogram of a CLSA extract from raw water entering the WTP2.

Llobregat river in front of the WTP1 has a percentage of 80% of analyzed samples with geosmin concentrations above its OTC with a maximum measured value of 200 ng/l (see Table I). This percentage of samples with higher OTC values remains practically similar (71%, >OTC) when the raw river water enters the WTP2 which is located approximately 40 Km downstream of the WTP1. The maximum geosmin concentration recorded at this point was 160 ng/l but the average geosmin level in the river fell from 86 ng/l to 33 ng/l between the two WTP.

Figure 3 illustrates the seasonal behavior of geosmin in the WTP2 over the last two years. Prechlorination and sand filtration did not significantly diminish geos-

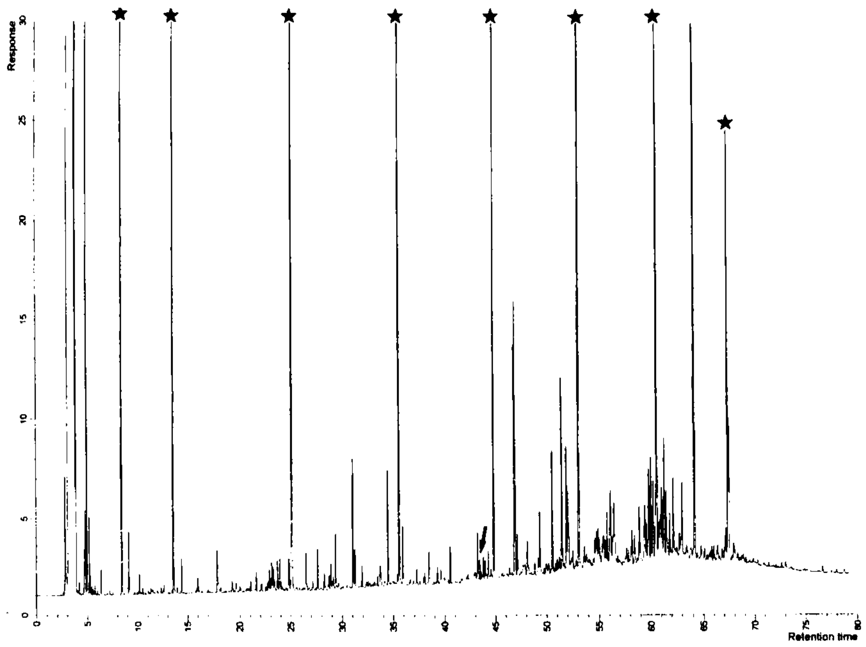

FIGURE 2 GC chromatogram of a CLSA extract from Llobregat river entering to the WTP2.*denotes internal standards (1-chloroalkanes). Geosmin is marked with an arrow (↓)

min (63%, >OTC), as expected. The ozonated samples showed much lower (42%, >OTC) geosmin levels. We attribute this decrease more to the fact that sand filtered water is diluted with variable amounts of groundwater before the ozonation step rather than to the ozonation process itself. This assumption was supported by the previous results of undiluted ozonated samples. At present, the addition of groundwater is necessary to improve water quality during drought. The most marked reduction of geosmin levels was observed in GAC-filtered samples, where only a small fraction (5%, >OTC) can present taste and odor problems. The treated water leaving the WTP2 only showed two samples with values higher than 10 ng/l from the 124 analyzed. They corresponded to a short period in the WTP with lower residence time of water in the GAC filters.

The combination of dilution of water before the ozonation process and, mainly, GAC filtration elliminates more than 95% of the geosmin entering the WTP2. Table II shows the geosmin levels in Barcelona's tap water according to its different origins. The treated water from the WTP1 presented high concentrations of geosmin with a large number of samples (62%) exceeding its OTC. The average

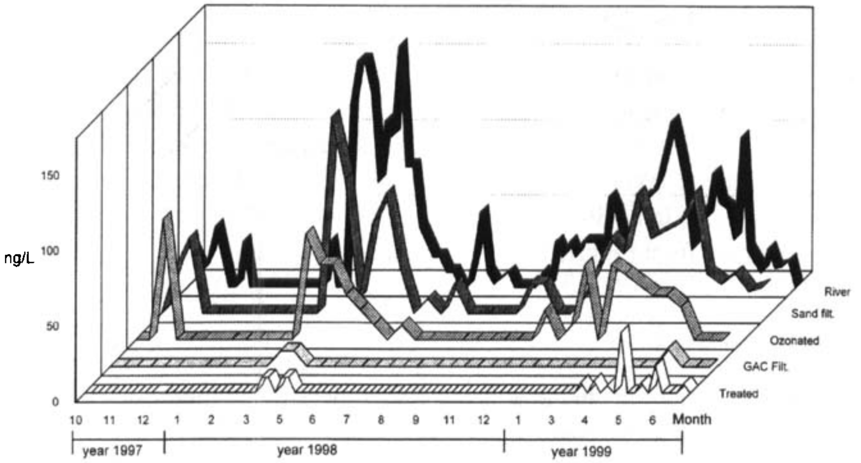

FIGURE 3 Seasonal variations of geosmin (ng/l) in raw water entering the WTP2 and its behavior at different stages of the treatment process

level was 24 ng/l for the last two years, with significant differences during the year, but peak levels were usually measured between March and May.

TABLE II Concentration levels of geosmin (ng/l) in Barcelona's tap water according to their origin. (July 1997-June 1999)

Compound	*Median*	*Maximum*	*Minimum*	*N*[a]	*>OTC*
Geosmin					
Treated WTP1[b]	24	100	<5	48	62%
Treated WTP2[b]	<5	18	<5	122	1.5%
Tap Llobregat[c]	<5	30	<5	49	17%
Tap Ter[d]	<5	30	<5	50	14%

a. number of samples analyzed.
b. Exclusively from Llobregat river.
c. Treated water from WTP2 blended with a variable percentage of treated water from WTP1.
d. Exclusively from WTP3.

As explained above, treated waters from different origins are usually blended. This would explain why 17% of the samples of Llobregat tap water, which is practically geosmin free when it leaves the WTP2, had concentration levels of geosmin higher than its OTC due to blending with treated water from WTP1. On the other hand, 14% of samples of tap water coming exclusively from the Ter river (WTP3) had geosmin levels higher than 10 ng/l.

2-methyl-isoborneol (MIB); 2-isopropyl- and 2-isobutyl-3-methoxypyrazines; 2,3,6-and 2,4,6-trichloroanisoles

The second natural metabolite most frequently cited (MIB) as the compound causing taste and odor episodes has not been reported in these rivers. It was only measured once at concentration levels near its detection limit. Other analyzed samples from other parts of Spain that presented odor problems also revealed the absence of MIB. In addition, neither pyrazines nor anisoles were detected in any of the samples from Llobregat or Ter rivers.

Dimethyl polysulfides

Dimethyl disulfide was found at low concentrations in the Llobregat river water entering the WTP2. We mainly identified this compound in effluents of wastewater treatment plants and also in a tributary of the Llobregat river (Rubí creek). This river is always diverted from the Llobregat due to its high degree of urban and industrial pollution but during storms it overflows and their waters are then mixed. We also have recorded these polysulfides in sand filtered samples when the WTP2 is not operating due to the low raw water quality.

Other compounds related to algal blooms

Geranyl acetone and 6-methyl-5-hepten-2-one were usually detected at low ppt levels. The maximum concentrations measured were 250 and 200 ng/l, respectively. These values are far below their OTC (50 and 60 µg/l, respectively). Other compounds such as β-cyclocitral were usually present at levels near their detection level, like for the other compounds cited above, far from their OTC (19 µg/l). We believe that these compounds contributed in a limited extent to the overall odor of the samples but were not responsible for the odor events. Other compounds such as *cis*-3-hexen-1-ol and several diunsaturated aldehydes (i.e. *trans*-2-*cis*-6-nonadienal) were not identified in the period studied.

CONCLUSIONS

Taste and odor events in Barcelona's drinking water caused by naturally occurring compounds are associated with the presence of geosmin. This compound can be measured from medium to high ppt levels when it enters the WTP1 and WTP2 on the Llobregat river. The presence of geosmin in Barcelona's tap water came from the blending of treated water from the WTP1 with the practically geosmin free treated water from the WTP2. The contribution of the other source (WTP3) from Ter river is small but significant (14%).

We did not identify either MIB or other odorous compounds such as pyrazines or trichloroanisoles. Other compounds related to the presence of algal blooms are present at concentrations far below their published odor threshold levels.

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