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Identification of 1,3-Dioxanes and 1,3-Dioxolanes as Malodorous Compounds at Trace Levels in River Water, Groundwater, and Tap Water

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A study of organic compounds imparting odor problems in river waters and groundwaters has been conducted. The Tordera aquifer located in Barcelona and Girona (NE Spain) is the water supply reserve for many seasonally crowded villages on the coast. Closed loop stripping analysis (CLSA) and flavor profile analysis (FPA) have been employed as analytical tools to identify the compounds responsible for the odor complaints. The feasibility of purge-and-trap (P&T) has also been evaluated. The 2-alkyl-5,5-dimethyl-1,3-dioxanes and 2-alkyl-4-methyl-1,3-dioxolanes were the most significant compounds identified in river water and groundwater with a threshold odor of 10 ng/L for 2-ethyl-5,5-dimethyl-1,3-dioxane (2EDD), the most malodorous compound. The analyses were carried out by HRGC/MS, and the synthesized 1,3-dioxanes and dioxolanes were characterized by CI-MS and EI-MS/MS techniques. A company, currently manufacturing saturated and unsaturated polyester resins, located in the upper course of the river, produced these compounds as byproducts during the synthesis of resins. The pollution by dioxanes and dioxolanes affected all the aquifer and slowly diminished to the ppt levels when the company was forced to correctly treat their wastewaters. Additional examples of the presence of dioxanes and dioxolanes in wastewaters of other resin plants and also tap water of Barcelona are shown.

Introduction

Water companies devote considerable time and effort to the identification and treatment of compounds causing odors in water supplies. Consumer complaints concerning taste and odor problems deal with the public perception of an unsafe drinking water. Nevertheless, it must be noted that neither the presence of compounds imparting taste and odors to water implies that it is unsafe nor the absence of organoleptic effects guarantee the absence of undesirable pollutants (*1*).

The sources of contaminants producing taste and odors in water can be attributed to both natural and anthropogenic compounds. Geosmin, 2-methyl isoborneol (MIB), *trans*-2-*cis*-6-nonadienal, 2,3,6-trichloroanisole, dimethyl polysulfides, and isopropyl methoxy pyrazine, among others, are the most frequently reported compounds of biological origin causing off-flavors in water at nanogram per liter levels (*2*−*8*). Excellent reviews on this subject have been published (*9*, *10*). The AWWA taste and odor survey conducted in 1989 showed that the major odor problems reported by the utilities were characterized as chlorine, earthy, fishy, and medicinal, whereas taste problems were reported as sour, metallic, and chlorine (*11*). Disinfection byproducts formed in treatment plants such as iodinated trihalomethanes (*12*), short-chain aldehydes or fatty acids (*13*, *14*), and others have been identified as sources of taste and odor episodes. Leaching chemicals such as phenolic antioxidants from polyethylene pipes (*15*) or pipe joint lubricants used during the installation of plastic and ductile iron water mains (*16*) may also impart tastes or odors to water. Recently, several taste and odor threshold levels of common water contaminants have been reported (*17*). Industrial and sewage effluents and leachates from poor waste disposals or landfills are, among others, frequently mentioned as the source of tastes and odors from anthropogenic compounds (*18*, *19*).

Closed loop stripping analysis (CLSA) according to the method first described by Grob (*20*) and others (*21*, *22*) is by far the most reported analytical tool in the literature used to identify the compound or compounds responsible for taste and odor episodes. The CLSA technique is suitable for the analysis at nanogram per liter levels and can be used in combination with sensory GC techniques to discriminate compounds in complex chromatograms by their odor. Recently, this combination (CLSA and sensory GC) has allowed the identification of dicyclopentadiene, with an estimated threshold odor level of 10 ng/L, as the compound causing odor problems in groundwater (*23*).

Since October 1993, odor incidents had been noticed in river water and groundwater wells in the Tordera aquifer that is located in the Barcelona−Girona area (NE Spain). Many of these wells are used for drinking purposes in important tourist villages located near and along the coast. Preliminary analytical data showed the presence of antioxidants, aromatic solvents, and chlorinated solvents that due to their low concentration levels were discarded as the potential origin of the odor event as were a large number of unidentified compounds with no equivalents in mass spectral libraries. These compounds were further identified as 2-alkyl-5,5-dimethyl-1,3-dioxanes and 2-alkyl-4-methyl-1,3-dioxolanes (see acronyms in Table 1) after comparison of their mass spectra with the products published by Cocheo *et al.* (*24*) in the air around a polyester resin plant and by Preti *et al.* (*25*), who identified 2-ethyl-5,5-dimethyl-1,3-dioxane (2EDD) as the malodorous compound in the treated water of Philadelphia.

The 2-alkyl-5,5-dimethyl-1,3-dioxanes, 2-alkyl-4-methyl-1,3-dioxolanes, and 2-alkyl-1,3-dioxolanes (see Figure 1) are byproducts present in wastes from resin manufacturing plants that use glycols (i.e., neopentyl gycol, polypropylene glycol, ethylene glycol) as raw material for acid-catalyzed condensations. The presence of these compounds in water has only been reported to our knowledge in the incident of Philadelphia (*25*−*28*), Barcelona (*29*), groundwater (*30*−*32*),

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TABLE 1. Mass Spectra (EI, CI) of the Main Dioxanes and Dioxolanes[a]

compound	ions (m/z) (% abundance)
	2-Alkyl-5,5-dimethyl-1,3-dioxanes (EI)
R = H (DMD)	56(100); 41(32); 57(12); 86(9); 115(9) $[M - H]^+$; 69 (8)
= Me (TMD)	56(100); 41(31); 115(23); 43 (23); 69 (19); 129(14) $[M - H]^+$
= Et (2EDD)	56(100); 115(68); 69(48); 41 (45); 57(41); 143(9) $[M - H]^+$
= i-Pr (2iPMD)	56(100), 115(79); 41(79); 43(79); 69(73); 157(6) $[M - H]^+$
= i-But (2iBMD)	115(100); 56(81); 69(80); 41 (50); 85(32); 171(9) $[M - H]^+$
= But (2nBMD)	115(100); 56(88); 69(76); 41 (53); 85(31); 171(9) $[M - H]^+$
	2-Alkyl-5,5-dimethyl-1,3-dioxanes (CI)[b]
R = H (DMD)	117(100)$[M + H]^+$; 69(35); 99(25); 115(25); 87(18)
= Me (TMD)	67(100); 77(67); 83(59); 69(56); 79(49), 131(26) $[M + H]^+$
= Et (2EDD)	87(100); 115(73); 145(62) $[M + H]^+$; 69(43); 85(21)
= i-Pr (2iPMD)	115(100); 87(98); 159(92) $[M + H]^+$; 69(76); 71(25)
= But (2nBMD)	117(100); 72(85); 87(55); 145(14); 173(12) $[M + H]^+$
	2-Alkyl-4-methyl-1,3-dioxolanes (EI)
R = H	87(100)$[M - H]^+$; 44 (99); 58(57); 45 (27); 43 (27); 59(19)
= Me	87(100); 43(78); 58(53); 59(46); 41(32); 101(8)$[M - H]^+$
= Et (2E4MDL)	87(100); 59(67); 41(43); 57(39); 72(20); 115(2) $[M - H]^+$
= i-Pr	87(100); 59(41); 41(32); 56(20); 43(16); 129(2) $[M - H]^+$
= i-Bu	87(100); 59(36); 41(23); 85(12); 43(9); 143(2) $[M - H]^+$
= Bu	87(100); 59(35); 41(22); 71(10); 57(8); 143(2) $[M - H]^+$
	2-Alkyl-1,3-dioxolanes (EI)
R = H	73(100) $[M - H]^+$; 44 (48); 45(22); 43(19)
= Me	73(100); 43(73); 45(70); 58(30); 87(10)$[M - H]^+$
= Et	73(100); 45(32); 57(10); 42(7); 43(6); 101(4) $[M - H]^+$
= i-Pr	73(100); 45(24); 43(8); 56(7); 41(7); 115(2) $[M - H]^+$

[a] Acronyms of dioxanes and dioxolanes are in parentheses. [b] Only m/z >50 amu are represented.

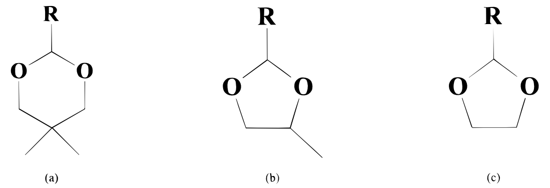


FIGURE 1. (a) 2-Alkyl-5,5-dimethyl-1,3-dioxanes; (b) 2-alkyl-4-methyl-1,3-dioxolanes; (c) 2-alkyl-1,3-dioxolanes.

and the effluent from a sewage treatment plant of a fibreglass and resin manufacturing company (*33*).

The aim of this paper is to elucidate the origin of the contamination of the Tordera aquifer by dioxanes and dioxolanes, its spreading along the river and groundwater, and also to assess its impact on the water quality during 2 yr. In addition, it is also shown for some examples how the unappropriate treatment by a waste management facility for industrial wastewaters coming from a resin plant can be a source of odor complaints in tap water. The analytical methodology consisted of CLSA and GC/MS identification of odorus compounds although the feasibility of purge-and-trap (P&T) was also proved. The synthesis of the main dioxanes and dioxolanes and their characterization by CI-MS and EI-MS/MS techniques was also performed to accurately quantify their presence in water.

Experimental Section

Description of the Site. The Tordera River is located 65 km northeast from Barcelona. From its source, it flows southeast for 60 km draining palezoic schists and granites and impermeable tertiary formations to the Mediterranean Sea. Its alluvial aquifer is the main water supply for the surrounding population (140 000 inhabitants in winter; 500 000 in summer) as well as for industries (mainly chemical plants) and agricultural areas. The aquifer system is formed by alluvial quaternary sediments. The middle and lower valley (500−1000 m wide) is filled with sand and gravel (5−30 m thick) laying on impermeable materials. These permeable unconfined deposits continue into the delta forming a lightly confined aquifer, which is separated from the upper unconfined layer by a thin silty-sand formation. The system thickness reaches 50 m near the sea. The aquifer permeability ranges from 170 to 400 m/d, and the specific flow of the deep aquifer varies from 10 to 43 L s^{-1} m^{-1}.

Figure 2 shows the geographical situation of the 48 sampling sites and the four river water samples analyzed. Twelve wells (4−8, 13, 15−18, 24, and 30) are used by industries; eight of them (23, 42, 45, 54, 60, 62, 66, and 71) are used for agricultural uses; two are piezometers (14 and 64), and the rest are used for drinking water purposes. The water demand can be evaluated as an average in 30, 36, and 55×10^3 m^3/d for agricultural, industrial, and drinking water, respectively.

Glassware. Amber glass bottles were washed with soapy water and rinsed with tap water, with Milli-Q water, and finally with reagent-grade acetone. Then, they were air-dried and baked at 180 °C for 1 h. After this procedure, their mouths were covered with aluminum foil to prevent the presence of dust or other contaminants.

Sampling. The samples from different wells (see Figure 2) were collected after water had run for several minutes in order to eliminate the stagnant water. Amber glass bottles (1 L) were rinsed several times with the water to be analyzed and were afterwards filled until overflow to prevent the loss of volatile compounds by the presence of headspace. The water samples were transported and stored at 4 °C until their analysis within 24−48 h.

The frequency of sampling for wells was initially every 2 weeks until June−July 1994 then was monthly until November 1994, and finally was bimonthly. Once factory A was identified as the origin of the odor events, the frequency of sampling for its wastewaters was weekly until they changed their wastewater treatment. After that, for several months, twice a week and then weekly samples from wastewaters of company A were analyzed until no significant variations in the concentration levels of dioxanes and dioxolanes were measured.

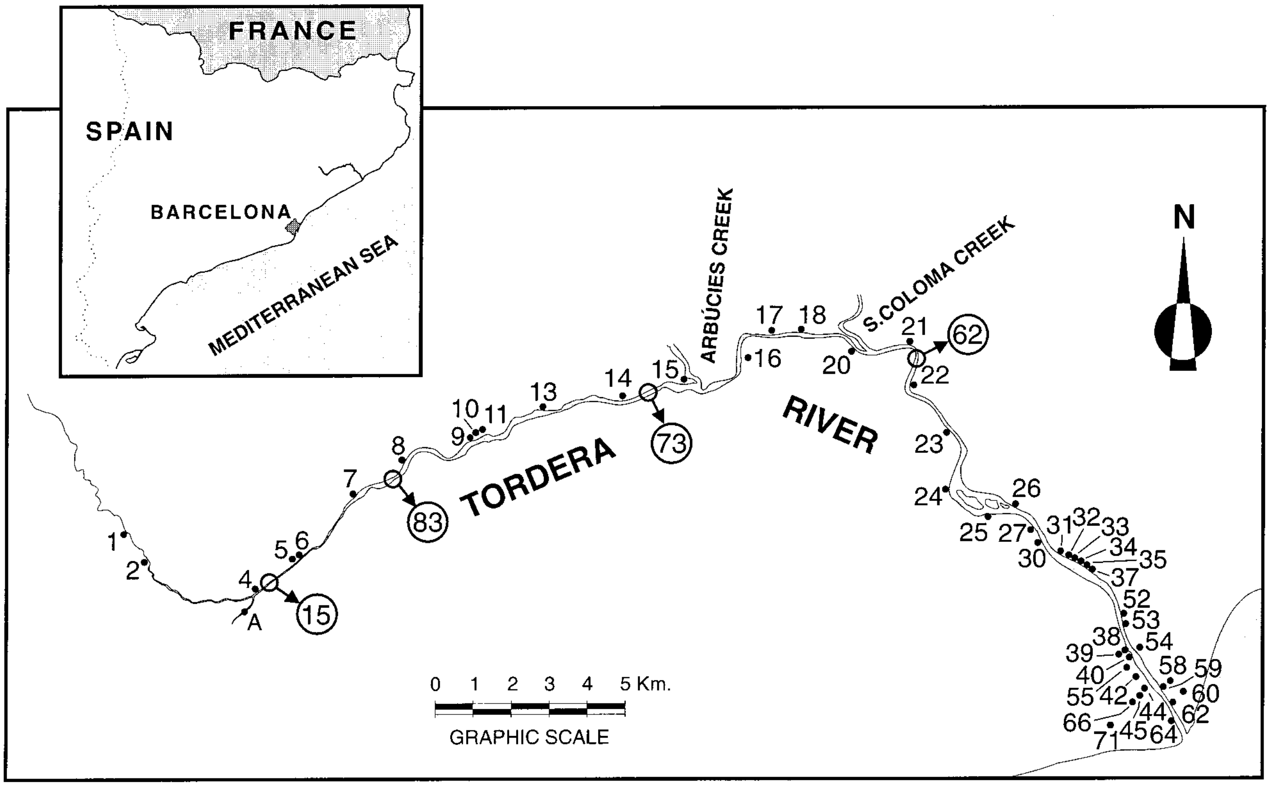


FIGURE 2. Study area and sampling site locations in the Tordera aquifer. Groundwater samples are numbered, and river water samples are encircled. Wells 4–8, 13, 15–18, 24, and 30 are used by industries; wells 23, 42, 45, 54, 60, 62, 66, and 71 are used for agricultural purposes; wells 14 and 64 are piezometers, and the rest are used for drinking water purposes.

River water samples from four different points taken along the river course (see Figure 2) were collected as described above for the wells. The unfiltered water samples were transported and stored at 4 °C until analysis. The frequency of sampling was irregular, but a set of samples was analyzed every 6 months.

Closed Loop Stripping Analysis (CLSA Method). Analyses were carried out in a commercial CLSA apparatus (Brechbüler, Switzerland) according to the method developed by Grob (*20*). Water samples (1 L or diluted with Milli-Q) were spiked with 1-chloroalkanes (C_5, C_6, C_{10}, C_{12}, C_{16}, and C_{18}) to give a final concentration of 800 ng/L for each compound. We used 5-mg activated carbon filters. The samples were stripped for 1 h. Temperatures of 45 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 of the spiked water samples. The filters were then extracted with 40 μL of CS_2 (20 + 20 μL).

Purge-and-Trap Method. A commercial Tekmar 2000 apparatus (USA) was used. Volatile compounds in 5 or 25 mL were purged for 11 min with helium (40 mL/min) and adsorbed onto a Tenax column at room temperature. Organic compounds were desorbed at 180 °C during 4 min and transferred directly to the GC/MS system. Fluorobenzene, 1-bromo-4-fluorobenzene, and 1,2-diclorobenzene-d_4 (Aldrich, Germany) were used as internal standards.

Instrumental Conditions. Analyses of CLSA extracts were carried out on a Fisons 8560 (U.K.) gas chromatograph equipped with a FID detector. Injections (1 μL) were made cold on-column into a 50 m × 320 μm i.d. CP-Sil 19CB (0.25 μm film thickness) fused silica column (Chrompack, The Netherlands). A deactivated precolumn (2 m) was used. The GC temperature program was 30 °C (5 min) to 280 °C (10 min) at a rate of 3 °C/min. Helium was the carrier gas, and the linear velocity was set at 31 cm/s at 30 °C. Nitrogen was used as the make up gas (125 kPa). A DB-5 column (J&W Scientific, Folsom, CA) was used for drinking water samples containing high levels of trihalomethanes (i.e., chlorodibromomethane and bromoform) to avoid coelution with DMD and 2EDD, respectively.

P&T analyses were carried out on a Fisons MD800 mass spectrometer equipped with a Fisons 8060 gas chromatograph. Extracts were transferred directly to the chromatograph (transfer line 180 °C) onto a 75 m × 530 μm i.d. (3 μm film thickness) DB 624 fused silica column (J&W Scientific, Folsom, CA). The GC temperature program was 30 (5 min) to 275 °C (10 min) at a rate of 3 °C/min. Helium was used as the carrier gas, and the linear velocity was set at 71 cm/s at 30 °C. The mass spectrometer was operated in electron impact mode (70 eV). The source temperature was maintained at 200 °C. Mass spectra were acquired by scanning from 35 to 450 Da with 1 s/decade.

GC/MS analyses were carried out on a VG Trio-1000 mass spectrometer equipped with a Fisons 8060 gas chromatograph. The same chromatographic conditions as described above for CLSA extracts were used. The mass spectrometer was operated in electron impact mode (70 eV). Transfer line and ion source temperatures were maintained at 200 and 250 °C, respectively. Mass spectra were acquired by scanning from 35 to 450 Da with 1 s/decade.

GC/CI-MS analyses were performed on a VG TS-250 (VG Instruments, U.K.) double-focussing mass spectrometer coupled with a Konik (S. Cugat, Spain) KNK-3000 gas chromatograph. We employed the same chromatographic conditions reported before. The chemical ionization operating conditions were as follows: ion source and interface temperatures, 180 and 250 °C, respectively; ionization energy, 45 eV; trap current, 190 μA. Isobutane was used as reagent gas at an ion source manifold pressure of 1×10^{-4} mbar. The resolution was kept at 1000, and the mass spectra were acquired by scanning from 60 to 300 at 1 s/scan and a 0.2-s delay time.

EI-MS/MS analyses were performed on an AutoSpec-Q hybrid (EBEqQ) mass spectrometer (VG Instruments, U.K.) and the operating conditions were the following: ion source temperature, 200 °C; trap current, 300 μA; acceleration voltage, 8000 V; and ionization energy, 70 eV. For the MS/MS experiments, the instrument was calibrated with perfluorokerosene (PFK) by selected dissociation of precursor ions and the monitoring of product-Q ions on a quadrupole analyser. The product-Q ions spectra were obtained by selecting the precursor ion by MS1 with a resolution of ca. 1500. The precursor ion collided with xenon in the collision cell (R_f only quadrupole collision cell, q) and Q was scanned at 5 s/scan over the range m/z 45–450. For precursor-ion spectra, the product-Q ion was selected by MS2 with unit resolution and the magnetic field scanned at 5 s/decade. Xenon was used as the collision gas at a pressure of 4×10^{-6} mbar and optimized the collision energy to 50–60 eV.

Synthesis of 1,3-Dioxane and 1,3-Dioxolane Derivatives. The 2-alkyl-5,5-dimethyl-1,3-dioxanes were synthesized by condensation of *neo*-pentylglycol (NPG; 2,2-dimethyl-1,3-propanediol) with an excess of 10% of different aldehydes (*p*-formaldehyde, acetaldehyde, propanal, *n*-butanal, isobutanal, and *n*-pentanal) and concentrated sulfuric acid (0.5%) as acid catalyst (*34*). All the reagents were from Aldrich Chemie (Germany). The mixtures were refluxed 1 h at room temperature. Then water was decanted; the acetals were dried over sodium sulfate and filtered. Purity was 90–97% for different compounds. The same compounds were synthesized at microscale employing the same procedure as described by Staudte et al. (*26*), who used *p*-toluenesulfonic acid as the catalyst and acetonitrile as the solvent. Briefly, the glycol and the acid were weighted into a microreaction vial. Acetonitrile was added followed by the corresponding aldehyde, and the mixture held at 35 °C for 2 h. After coming to room temperature, an aliquot (ca. 10 μL) was diluted to 1 mL with acetone to be spiked into water for recovery studies.

The 2-alkyl-4-methyl-1,3-dioxolane and 2-alkyl-1,3-dioxolane compounds were synthesized using the same procedure as described above but using propylene glycol (PPG) and ethylene glycol (EG), respectively. Mixtures of *cis* and *trans* isomers (usually 60/40) were obtained for the different 2-alkyl-4-methyl-1,3-dioxolane derivatives.

Quantitation. Dioxane and dioxolane quantitation was performed by the internal standard method. For each compound, the response factor is calculated relative to 1-chlorohexane at four calibration levels. The calibration analyses were obtained by analyzing Milli-Q water samples spiked with 1-chlorohexane and different spiked solutions of each dioxane and dioxolane (0.01, 0.25, 1, and 10 μg/L). The unknown concentrations in the sample are then obtained from the mean response factors using the formula $C_z = A_zC_i/R_zA_i$ 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 is the response factor for the target compound.

Results and Discussion

Mass Spectrometric Characterization of 1,3-Dioxanes and 1,3-Dioxolane Derivatives. EI mass spectra of 2-alkyl-5,5-dimethyl-1,3-dioxane were previously described by Cocheo *et al.* (*24*) and Preti *et al.* (*25*). They are characterized by small $[M - H]^+$ ions and losses of the alkyl chain at position 2 (m/z = 115), both corresponding to the known well-stabilized oxonium ions (*35*). On the other hand, CI spectra clearly show intense $[M + H]^+$ ions and the other peaks already observed in the EI mode. Table 1 shows the most abundant ions in the EI and CI modes for these compounds as well as several 1,3-dioxolane derivatives.

TABLE 2. EI–MS/MS Mass Spectra of 2EDD[a]

m/z	Product-Q ions[a]	Precursor ions[b]
115	69	$[M]^{\bullet+c}$
69	41	115
56	41	73, 115, $[M - H]^+$

[a] Product-Q ion spectrum of the ion *m/z* 115. [b] Precursor-ion spectrum of *m/z* 69. (See text for experimental conditions). [c] Experiments were performed with $[M]^{\bullet+}$ = 144 for 2EDD and $[M]^{\bullet+}$ = 158 for 2iPMD.

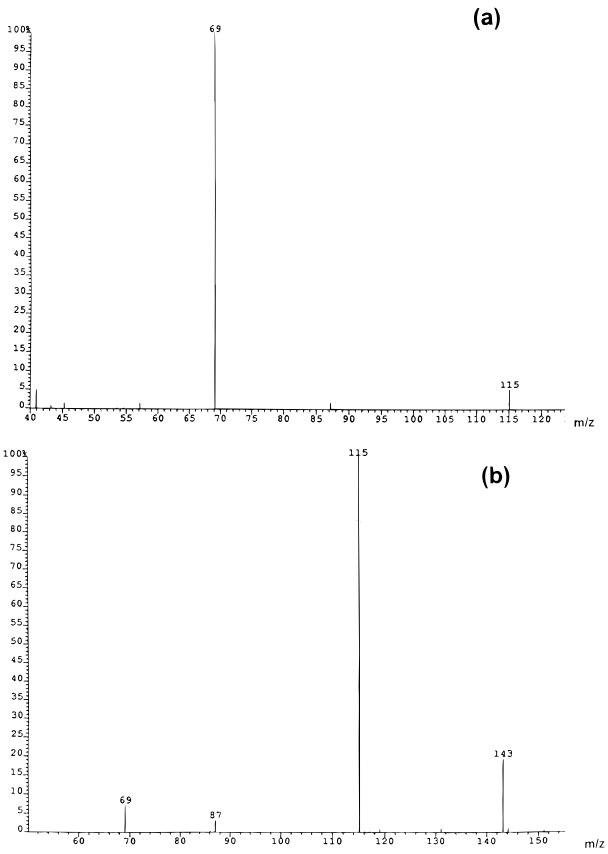


FIGURE 3. EI-MS/MS of 2EDD. (a) Product-Q ion spectrum of *m/z* 115. (B) Precursor-ion spectrum of *m/z* 69. See text for experimental conditions.

A proposed fragmentation pathway provided by the MS/MS experiments described in Table 2 was obtained from the product-Q ion spectrum of m/z 115 and the precursor-ion spectrum of m/z 69 from 2EDD (see Figure 3). The origin of the ions m/z 56 (base peak) and 69 is depicted in Figure 4. Thus, the m/z 69 ion is generated through m/z 115 from consecutive losses of CO and H_2O. The base peak m/z 56 is generated by oxonium ions (a,b) via m/z 73 ion, although the exact fragmentation mechanism is unknown, the most probably pathway is through a stabilized tertiary carbonium ion C_5 (*36*, *37*).

Study of Recovery Efficiencies. Once the different compounds were synthesized, a study of the recovery efficiencies by CLSA and P&T methods was performed in order to obtain a more accurate determination of concentration levels and the feasibility of the two procedures. The recoveries from Milli-Q water spiked with 0.25 ppb of each compound using the CLSA method are displayed in Table 3.

The 2-alkyl-5,5-dimethyl-1,3-dioxanes had a range of 13–100% recovery for different compounds using the CLSA method, being higher for the derivatives with longer alkyl chains as expected by their log K_{ow}. An acceptable recovery of 57% was obtained for 2EDD. On the other hand, the 2-alkyl-4-methyl-1,3-dioxolanes showed lower recoveries

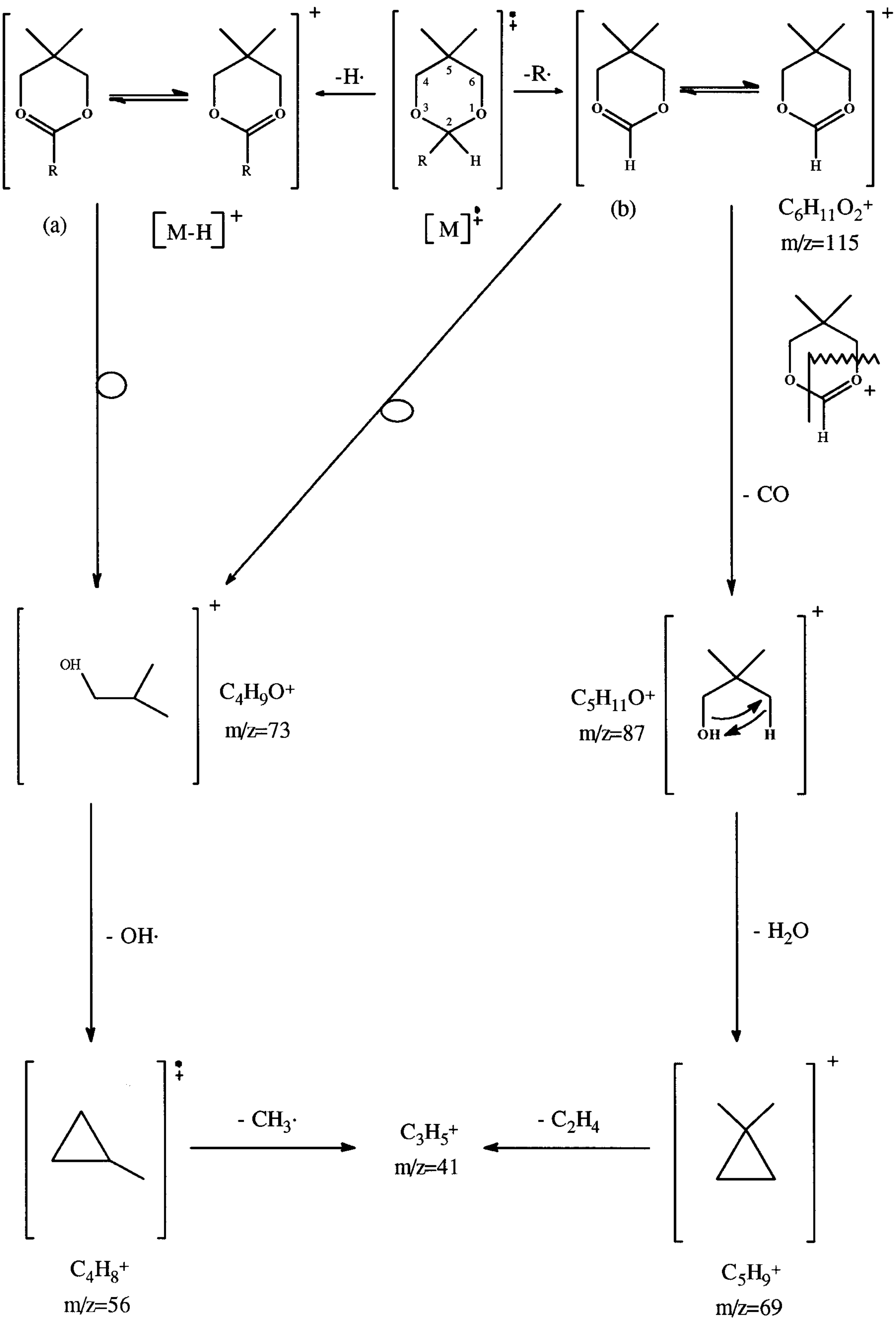
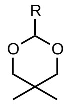
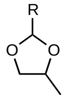
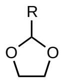


FIGURE 4. Proposed fragmentation pathway for mass spectra of 2-alkyl-5,5-dimethyl-1,3-dioxanes.

than their homologue 1,3-dioxane derivatives. The most abundant compounds in real samples, the *cis* and *trans* isomers of 2E4MDL, were recovered in a limited extent (26%). The worst recoveries by CLSA were obtained for 2-alkyl-1,3-dioxolanes being the isopropyl, the only tested compound that showed a relative good performance.

The partition coefficients for the 2-alkyl-5,5-dimethyl-1,3-dioxanes were calculated by means of a commercial

TABLE 3. Recovery Efficiencies for 1,3-Dioxane and 1,3-Dioxolane Derivatives by CLSA and P&T Techniques

		CLSA				
		recovery ± SD				
		used filter[a]		new filter[b]		P&T[c]
compound		unsalted	salted	unsalted	salted	recovery ± SD
2-alkyl-5,5-dimethyl-1,3-dioxanes	R = H	13 ± 5	17 ± 5	37 ± 2	52 ± 6	28 ± 3
	Me	33 ± 5	40 ± 7	60 ± 4	90 ± 8	26 ± 1
	Et	57 ± 8	61 ± 13	88 ± 6	103 ± 9	42 ± 3
	i-Pr	95 ± 7	95 ± 9	108 ± 10	103 ± 10	71 ± 8
	Pr	79 ± 9	nt[e]	105 ± 9	101 ± 5	72 ± 2
	i-Bu	100 ± 12	100 ± 11	107 ± 9	104 ± 9	92 ± 2
	Bu	99 ± 13	101 ± 8	104 ± 3	114 ± 5	124 ± 5
2-alkyl-4-methyl-1,3-dioxolanes[d]	R = H	nr[f]	nt	2 ± 1	3 ± 1	15 ± 1
	Me	nr	nt	12 ± 1	17 ± 3	15 ± 1
	Et	26 ± 3	31 ± 5	62 ± 4	82 ± 8	33 ± 1
	i-Pr	73 ± 3	nt	100 ± 7	103 ± 9	63 ± 2
	i-Bu	88 ± 8	nt	97 ± 2	109 ± 3	nt
2-alkyl-1,3-dioxolanes	R = H	nr	nt	nr	nr	8 ± 1
	Me	<1	nt	nr	nr	16 ± 2
	Et	3 ± 1	nt	15 ± 2	20 ± 4	nt
	i-Pr	33 ± 5	nt	68 ± 5	89 ± 13	nt

[a] Average of six determinations at 0.25 ppb level. [b] Average of three determinations at 0.25 ppb level. [c] Average of four determinations. Range 1−100 ppb. Purge vessel 5 mL. [d] Recoveries for both *cis* and *trans* isomers. [e] nt, not tested. [f] nr, not recovered.

computer program (*38*) that breaks down the molecule and assigns a value to each fragment according to its data base. The final value is the sum of the partial values with a final correction after considering the structure of the molecule. All compounds showed values of log $K_{ow} < 3$, which is assumed to have a low probability for a bioaccumulation potential (*39*). The calculated values ranged from log $K_{ow} = 0.82$ (DMD) to 2.90 (2iBMD), being 1.86 for 2EDD. These differences can explain the wide range of recoveries found. The partition coefficients for 2-alkyl-4-methyl-1,3-dioxolanes were lower than their homologue 2-alkyl-5,5-dimethyl-1,3-dioxanes. As an example, 2E4MDL had a calculated log $K_{ow} = 0.82$, which explains its moderate recovery.

The results described above were obtained from several used carbon filters that we considered as representatives of still-in-use filters. However, when new, non-used carbon filters were employed, recoveries of both dioxanes and dioxolanes increased markedly, but their efficiency quickly dropped to the values cited previously. The salted CLSA according to the method described by Hwang *et al.* (*22*) was also performed with both new and used filters. This method enhanced recoveries of all compounds related to the unsalted procedure, being, as expected, more significant with the new filters. In comparing both methods, DMD, TMD, and 2E4MDL were significantly better recovered by the salting-out method among the compounds found in real samples by using either new or used filters. Nevertheless, we discarded the use of the salted method due to the large number of samples analyzed and the potential problems associated with this method (excessive amounts of sodium sulfate, tedious preparation, clogging, etc.).

We also studied the matrix effects by spiking dioxanes and dioxolanes into river water. The obtained results—not shown—did not present significant differences with the values displayed in Table 3 for Milli-Q water being the maximum difference less than a 10% lower recovery.

The same group of compounds was studied by P&T. Recoveries were performed in the 1−100 ppb range using a 5-mL purge vessel, being practically constant in this interval. Comparing both methods, it seems that dioxanes and dioxolanes with small alkyl chains (R = H, Me) are better recovered by P&T. However, CLSA is preferred for compounds with a longer alkyl chain. The recovery for 2EDD by P&T was 42%, slightly worse than CLSA. Taking into account the compounds present in the real samples, both methods are feasible but CLSA shows better recoveries for the identified compounds.

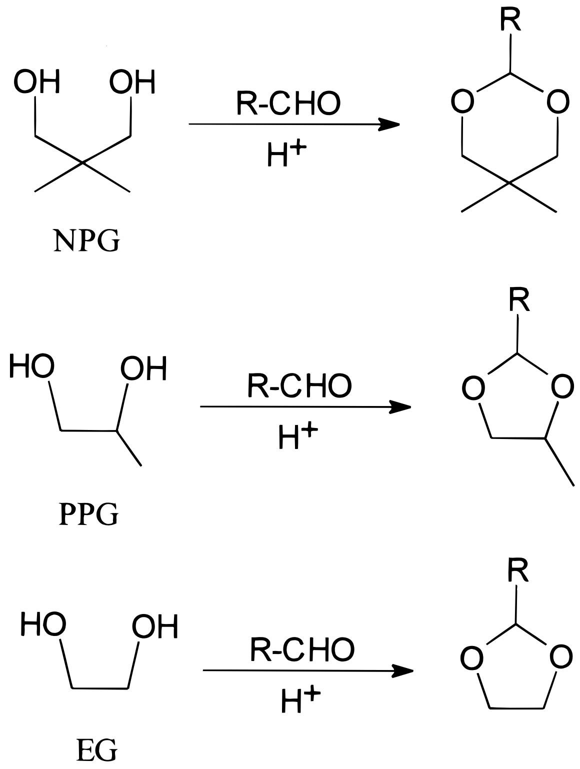


FIGURE 5. General scheme of the formation of 1,3-dioxane and 1,3-dioxolane derivatives.

Dioxanes and Dioxolanes in Waters. *Organic Compounds in the Wastewater of Company A.* The wastewaters from company A were regularly analyzed from November 1993 to June 1996. The identified compounds by GC/MS of CLSA extracts were dioxane and dioxolane derivatives and large amounts of terpenes coming from rosin oil residues

TABLE 4. Concentration Range, Mean Values, and Frequency of Appearance of Relevant 1,3-Dioxanes, 1,3-Dioxolanes, and 1,4-Dioxanes from Wastewaters of Company A[a]

compound	mean	max−min	frequency
5,5-dimethyl-1,3-dioxane	2293	16320−<0.01	82.8
2,5,5-trimethyl-1,3-dioxane	68.7	1390−<0.01	48.6
2-ethyl-5,5-dimethyl-1,3-dioxane	129.6	3900−<0.01	71.4
2-iso-propyl-5,5-dimethyl-1,3-dioxane	954.5	27500−<0.01	71.4
2-*n*-propyl-5,5-dimethyl-1,3-dioxane	0.2	7−<0.01	2.8
2-iso-butyl-5,5-dimethyl-1,3-dioxane	0.7	20−<0.01	5.7
2-*n*-butyl-5,5-dimethyl-1,3-dioxane	<0.01	<0.01	0
2,5-dimethyl-1,4-dioxane[b]	16.7	228−<0.01	51.4
2,6-dimethyl-1,4-dioxane[b]	9.3	99−<0.01	48.6
1,4-dioxane	6400	31400−<100	48.6
2-ethyl-4-methyl-1,3-dioxolane[b]	2985	86000−<0.01	88.6

[a] Results are expressed in μg/L. Data from January 1994−July 1995 ($n = 35$). [b] Expressed as sum of *cis* and *trans* isomers.

TABLE 5. Percentage of Concentrations of Individual Dioxanes and Dioxolanes from Wastewaters of Company A[a]

	range (μg/L)			
compound	<0.01−1	1−100	100−1000	>1000
5,5-dimethyl-1,3-dioxane	17.1	37.1	14.3	31.4
2,5,5-trimethyl-1,3-dioxane	65.7	25.7	5.7	2.9
2-ethyl-5,5-dimethyl-1,3-dioxane	82.9	8.5	5.7	2.9
2-iso-propyl-5,5-dimethyl-1,3-dioxane	88.5	2.9	2.9	5.7
2-*n*-propyl-5,5-dimethyl-1,3-dioxane	97.1	2.9	0	0
2-iso-butyl-5,5-dimethyl-1,3-dioxane	94.3	5.7	0	0
2-*n*-butyl-5,5-dimethyl-1,3-dioxane	100	0	0	0
2,5-dimethyl-1,4-dioxane	62.9	31.4	5.7	0
2,6-dimethyl-1,4-dioxane	68.6	31.4	0	0
1,4-dioxane	nd[b]	nd	51.4	48.6
2-ethyl-4-methyl-1,3-dioxolane	14.3	42.8	28.6	14.3

[a] Data from January 1994−July 1995 ($n = 35$). [b] nd, < 100 ppb for 1,4-dioxane.

that are largely used in lacquers, inks, adhesives, etc. The most abundant products were 2-alkyl-5,5-dimethyl-1,3-dioxanes (R = H to i-But) and 2-alkyl-4-methyl-1,3-dioxolanes (R = Et). Additional minor compounds were observed by P&T such as 2-alkyl-1,3-dioxolanes (R = Me and Et), 2-alkyl-4-methyl-1,3-dioxanes (R = H, Me), and miscellaneous compounds such as 1,4-dioxane, 1,3-dioxolane, 2,4,4-trimethyl-1,3-dioxane, 2,4,4,6-tetramethyl-1,4-dioxane, and 2,4,8,10-tetraoxaspiro[5,5]undecane (a condensation product of pentaeritrithol).

The company A produces both saturated and unsaturated polyester resins. Polyester resins are produced by polymerization of different glycols in acid-catalyzed condensations. Saturated resins are mainly formed by condensation of NPG or PPG with terephthalic acid. Its production has an approximate ratio of 6:1. The company also produces minor amounts of other resins with some modifications (i.e., ethylene glycol, adipic or isophthalic acids). The unsaturated polyester resins in company A are formed by condensation of PPG and maleic anhydride. Modifications using diethylene glycol and phthalic or isophthalic or adipic acids are used in minor amounts.

The formation of byproducts such as 1,3-dioxanes and 1,3-dioxolanes could be explained by the reaction of different glycols and the aldehydes formed by dehydration of vicinal diols in acidic medium. The general scheme of the formation of these byproducts is depicted in Figure 5. Thus, 2-alkyl-5,5-dimethyl-1,3-dioxanes, 2-alkyl-4-methyl-1,3-dioxolanes, and 2-alkyl-1,3-dioxolanes come from the condensation of the different glycols (NPG, PPG, and EG) and aldehydes. Cocheo *et al.* (*24*) hypothesized the origin of the most common compounds. Thus, 2E4MDL is formed by condensation between two molecules of PPG; TMD is formed by condensation of NPG and EG, while 2EDD is the result of the condensation between NPG and PPG. Finally, DMD and 2iPMD are formed by the condensation of NPG with its disproportionation products.

Table 4 displays the concentration levels (in μg/L) of relevant 1,3-dioxanes, 1,3-dioxolanes, and 1,4-dioxane from the wastewaters of the company A and their frequency of appearance during January 1994−July 1995. This period covers several months before and after the company began to treat the wastewaters to reduce the amounts of compounds dumped into the river. The displayed results and the following were corrected for recovery efficiency.

From the table, it is inferred that the most concentrated compounds were usually in the ppm range during the odor incidents. These levels were dramatically reduced to the low ppb level when the company was forced by the administration to treat its wastewaters. However, for some months the results were sharply different. Thus, whereas some samples showed a total absence of dioxanes and dioxolanes, others contained low-medium ppb levels of 2EDD and higher values for DMD and TMD. These unexpected results reflected the variety of treatment procedures performed in the factory (i.e., adsorption onto GAC, ozone oxidation with Fenton's reagent, UV/H_2O_2) to reduce the levels of dioxanes and dioxolanes dumped into the river.

Table 5 displays the percentage of concentrations of individual dioxanes and dioxolanes in the wastewaters of the company for the same period. Concentrations were grouped in four groups (<0.01−1, 1−100, 100−1000, and >1000 μg/L). The table shows the improvements made by A. Thus, except for DMD and TMD, which present significant percentages in the range 1−100 ppb (37.1 and 25.7%, respectively), all the other compounds were bracketed into the <0.01−1 ppb range. These average values are practically 1000-fold less concentrated than the maximum concentrations measured during the beginning of the incidents in October 1993.

TABLE 6. Levels (in μg/L) of Dioxanes and Dioxolanes in Groundwaters (April 1994−July 1995)[a]

	concentration range (μg/L)								
sample	DMD	TMD	2EDD	2iPMD	2iBMD	2,5DMD	2,6DMD	2E4MDL	2iP4MDL
1	nd[b]	nd	nd	nd	nd	nd	nd	nd	nd
2	nd	nd	nd	nd	nd	nd	nd	nd	nd
4	124−2111	4.8−112	27.1−673	101−457	nd−6	2.0−35	0.2−29	61−3405	nd−3
5	nd−1.39	nd	nd−0.28	nd−0.01	nd	nd−0.04	nd−0.04	nd	nd
6	nd	nd	nd	nd	nd	nd	nd	nd	nd
7	2.6−26.7	nd−0.36	0.29−7.07	0.44−4.88	nd	nd−0.33	nd−0.05	2.14−20.30	nd−0.19
8	nd−tr	nd	nd	nd	nd	nd	nd	nd	nd
9	1.59−45.59	nd−0.72	nd−4.91	nd−7.38	nd	0.01−0.34	nd−0.12	0.46−7.63	nd
10	12.55	0.76	0.94	2.16	0.04	nd	nd	2.52	nd
11	1.12	0.19	4.30	1.86	nd	tr	tr	0.92	nd
13	nd−4.27	nd−0.23	nd−0.65	nd−1.37	nd	nd	nd	nd−7.03	nd
14	tr	nd	nd	nd	nd	nd	nd	tr	nd
15	nd	nd	nd	nd	nd	nd	nd	nd	nd
16	5.91	0.38	0.70	0.82	nd	tr	tr	3.85	nd
17	2.01−20.60	nd−1.60	0.26−7.40	0.38−3.21	nd	nd−0.70	nd−0.50	3.75−50.60	nd
18	6.93	0.45	1.27	2.27	nd	nd	nd	5.60	nd
20	1.72−8.70	0.07−0.53	0.08−7.77	1.82−2.31	nd	0.04−0.70	0.03−0.50	12.02−68.47	nd
21	0.04−2.65	nd−0.32	0.03−0.12	0.18−0.78	nd	nd−0.36	nd−0.35	2.11−29.52	nd
22	nd	nd	nd	nd	nd	nd	nd	nd	nd
23	nd	nd	nd	nd	nd	nd	nd	nd	nd
24	5.30	nd	0.23	0.38	nd	nd	nd	1.05	nd
25	4.84−19.26	0.04−1.27	0.10−2.52	0.18−1.17	nd	0.03−0.96	nd−0.85	7.14−66.73	nd
26	1.12	0.34	0.08	0.08	nd	nd	nd	4.97	nd
27	2.14	0.24	1.10	1.21	0.03	tr	tr	4.20	nd
30	3.20−14.26	nd−1.25	0.42−1.76	0.28−1.47	nd	nd−0.85	nd−0.91	5.32−38.28	nd
31	3.37	0.28	0.21	0.85	nd	0.03	0.03	2.94	nd
32	2.58−11.11	nd−0.75	0.26−0.62	0.35−0.89	nd	nd−0.49	nd−0.38	6.37−32.95	nd
33	0.79−8.98	nd−0.72	0.48−1.13	0.37−1.20	nd	nd−0.40	nd−0.32	nd−16.60	nd
34	6.30	0.48	0.33	1.19	nd	nd	nd	1.40	nd
35	4.20−6.27	0.24−0.55	0.40−0.86	0.30−0.55	nd	0.01−0.31	nd−0.23	6.80−15.79	nd
37	6.53−7.11	nd−0.13	0.76−1.85	0.35−1.12	nd	nd−0.15	nd	5.32−11.55	nd
38	5.81	0.38	0.51	0.53	nd	0.03	0.03	2.59	nd
39	2.34	0.20	0.39	0.50	nd	0.01	0.01	1.40	nd
40	2.94−16.63	nd−0.19	0.18−1.36	0.35−1.07	nd	nd−1.08	nd−0.90	3.71−36.23	nd
42	3.12−18.14	0.01−1.16	0.09−2.05	0.11−1.75	nd	nd−0.56	nd−0.41	3.17−14.67	nd
44	1.24−7.01	nd−0.67	0.06−0.51	0.05−0.33	nd	nd−0.42	nd−0.31	1.60−8.05	nd
45	5.40	0.38	0.12	0.13	nd	0.04	0.04	2.94	nd
52	5.30	0.34	0.27	0.35	nd	0.04	0.04	2.59	nd
53	0.64−3.47	nd−0.20	nd−0.72	nd−0.19	nd	nd−0.17	nd−0.26	nd−1.60	nd
54	2.75	nd	0.12	0.42	nd	nd	nd	3.15	nd
55	1.43	nd	0.11	0.23	nd	nd	nd	0.98	nd
58	1.43	nd	nd	nd	nd	nd	nd	0.21	nd
59	1.03−9.08	nd−0.40	0.02−1.04	0.03−0.36	nd	nd−0.27	nd−0.24	1.05−6.60	nd
60	0.87	0.13	nd	0.02	nd	nd	nd	0.15	nd
62	0.35−2.95	nd−0.10	nd−1.63	nd−0.50	nd	nd−0.03	nd−0.02	nd−2.14	nd
64	0.68−14.54	nd−0.73	0.05−1.13	0.08−0.53	nd	nd−0.45	nd−0.45	nd−17.99	nd
66	nd	nd	nd	nd	nd	nd	nd	nd	nd
71	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a] Data from April 1994−July 1995. Number of analysis: $n = 7$ for samples 4, 7, 9, 17, 20, 21, 25, 42, 44, 53, 59, and 64; ($n = 5$) for samples 35 and 40; ($n = 4$) for samples 2, 13, 32, 33, and 62; ($n = 3$) for samples 1, 5, 8, 15, and 30; ($n = 1$), for remaining samples. [b] nd, <0.005 μg/L. tr, trace.

Groundwaters. Forty-eight different groundwater supplies collected on the left and right sides of the Tordera River were analyzed. Sampling points are shown in Figure 2. The results displayed in Table 6 correspond to April 1994−July 1995, the most intensive sampling period. The number of analysis for each point reflects both the importance of the well and how the variation of the dioxanes dumped by company A affected the closer wells.

Several water samples were analyzed by flavor profile analysis (FPA) according to the method described elsewhere (*40*). The obtained results were in agreement with those reported by Philadelphia's researchers that established a threshold odor of 5−10 ppt for 2EDD (*25*), although in our case the trained panelists described the odor of the samples and 2EDD as olive water.

The identified compounds in the groundwaters were the same byproducts of company A. The 2-alkyl-5,5-dimethyl-1,3-dioxanes (DMD, TMD, 2EDD, and 2iPMD) were identified in almost all samples. The 2-alkyl-4-methyl-1,3-dioxolanes were exclusively (2E4MDL) *cis* and *trans* isomers with very few samples containing the isopropyl derivative. The third group of compounds were both 2,5- and 2,6-dimethyl-1,4-dioxanes (2,5DMD and 2,6DMD) *cis* and *trans* isomers. As CLSA is not adequate for the determination of 1,4-dioxane at low ppb levels (recovery $<1\%$), the results for this compound are not displayed. As an example, Figure 6 shows the GC chromatogram of a CLSA extract from groundwater.

Table 6 contains the minimum and maximum concentration levels (expressed in μg/L) for each compound during the campaign. This allows the knowledge of levels of dioxanes and dioxolanes at each point before the company A had begun to treat their wastewaters and to know how this treatment lowered the concentration of these compounds. This reflects the direct influence of these dumpings into the aquifer.

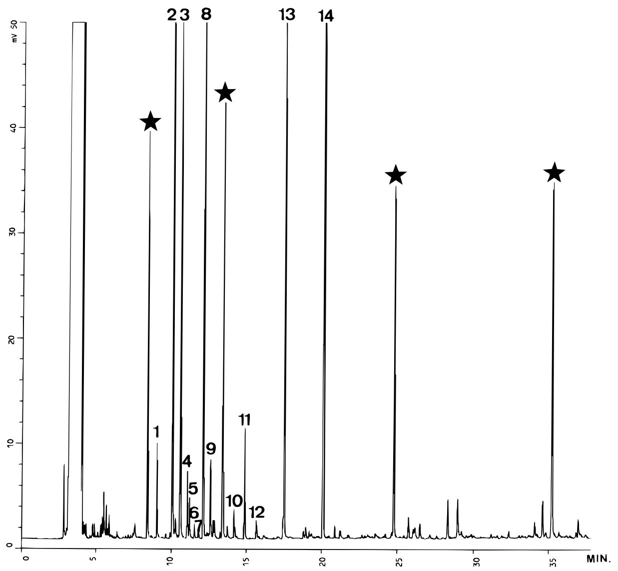


FIGURE 6. GC chromatogram of a CLSA extract from groundwater (well 9). The numbered peaks correspond to the following identified compounds: (1) toluene, (2) *cis*-2E4MDL, (3) *trans*-2E4MDL, (4) *cis*-2,5DMD, (5) *cis*-2,6DMD, (6) *trans*-2,5DMD, (7) *trans*-2,6DMD, (8) DMD, (9) TMD, (10) ethylbenzene, (11) *m*+*p*-xylene, (12) *o*-xylene, (13) 2EDD, and (14) 2iPMD. An asterisk (*) denotes internal standards (1-chloroalkanes C_5, C_6, C_8, and C_{10}).

Concentration levels were usually at the low ppb level except for sample 4, which is the closer well to the dumping and where the maximum concentration of 2EDD (673 μg/L) was reached. This compound (2EDD) was positively identified in almost all samples with maximum levels of 7.77 ppb (sample 20) and in the 1−2 ppb range for the farthest samples from the dumping. The seasonal variation of 2EDD in several wells located along the river course is depicted in Figure 7. The figure clearly shows that the amount of 2EDD into the aquifer dramatically diminished after November 1994 in all wells studied. DMD also shows the same trend described for 2EDD in agreement with their common origin.

The most abundant compound in all samples was 2E4MDL with a maximum measured value of 3405 μg/L in sample 4. The concentration range of 2E4MDL from the remaining samples varied from the low ppb level to 68.5 ppb (sample 20). The seasonal variation of 2E4MDL for the same wells did not follow the same general trend described before for DMD and 2EDD. Significant differences for each well were observed. Thus, 2E4MDL decreased markedly between June and November 1994 in well 7 and then almost a steady state was reached. The concentration levels in wells 42, 59, and 64 presented their maximum in November 1994; after this date, a moderate decrease was measured but less marked than that observed for 2EDD and DMD. The behavior of 2E4MDL in well 17 was quite different; it showed their maximum concentration during January−March 1995 to decrease to the same levels measured at mid-1994. These results represented a mixed behavior between those observed in well 7 and wells 42, 59, and 64. The values obtained for sampling point 20 increased from June to November 1994. During the period March−May 1995, the concentration levels remained practically constant, and finally a significant decrease was detected in July 1995. An unexpected low level of 2E4MDL as compared with those usually found in this sample was measured in January 1995. We did not find any explanation for this result because the other dioxanes and dioxolanes did not show the same concentration shift.

The difference in behavior in the aquifer between 2EDD, DMD, and 2E4MDL can be atributed to several factors such as higher solubility or mobility of 2E4MDL. In addition, the amount of 2E4MDL (mid ppb level) dumped into the aquifer by the treated wastewaters of company A was significantly superior than 2EDD (low ppb level) and could explain the slow decrease of 2E4MDL.

The wells near the mouth of the river and farthest from the dumping are the most used for drinking purposes. They presented significant variations of contaminant concentrations either along the studied period or between them, even for wells a few hundred meters appart. This can be attributed to a different piezometric levels of wells and a difference in the degree of pumping. No trends for a different distribution in both sides of the river could be observed from these results although samples far from the river banks showed the lowest values.

River Water. Four selected points (15, 83, 73, and 62, encircled in Figure 2) of the Tordera River were analyzed twice a year from October 1993 to October 1996. Table 7 shows the concentration ranges for the most relevant compounds. The higher levels were measured, as expected, in the closest point to the dumping (15). The maximum value for 2EDD (173 ppb) was determined in June 1994, decreasing dramatically from this value to levels <2 ppb in the last two years. The same trend was observed for 2iPMD with a maximum of 3030 ppb in June 1994 to 33 ppb, which was last measured October 1996. This represents a reduction higher than 99% for these two significant dioxanes into the river. Conversely, DMD (84 ppb in June 94), although presented the same tendency as described for 2EDD and 2iPMD, showed a less marked decrease. The limited number of analyzed samples does not allow us to generalize on the behavior of these compounds, but it seems that they follow the same trends as those observed in groundwaters.

Resin Manufacturing Plants. We were interested in knowing if two other resin manufacturing plants (B and C) not related to this incident and located on the banks of other two rivers generated the same byproducts detected in the wastewater of company A and therefore if they could be a potential source for odor complaints. In the wastewaters of both factories dioxanes and dioxolanes could be detected. Therefore, we concluded that these compounds can be considered as markers of pollution for resin plants. The concentration levels were as follows: DMD (44 ppb), TMD (11 ppb), 2EDD (73 ppb), 2iPMD (1411 ppb), 2nPMD (6 ppb), 2iBMD (227 ppb), and 2E4MDL (227 ppb) in the wastewaters of company B. We could only measure the amount of 2EDD (1513 ppb) in company C since the presence of large amounts of aromatic solvents prevented the accurate quantification or the presence of other dioxanes and dioxolanes. The levels detected in company B (grab sample) were lower than those usually found in company A and reflect a different production (i.e., 2iPMD and 2iBMD were the main compounds, the latter was not found in company A) of both companies and probably a better treatment of their wastewaters.

Barcelona's Tap Water. Odor incidents were detected in the raw water entering the water works plant of Barcelona, and some complaints from consumers of Barcelona's tap water were noticed in November 1994 and January−February 1995. The odor present in tap water was unanimously described as "olive water", a closer reference for mediterranean people than the varnish/chemical descriptor reported by Philadelphia's consumers (*25*−*28*). Several tap water samples showed levels of 2EDD ranging from 8 to 49 ng/L in this period whereas up to 312 ng/L was detected at the entrance of the water treatment plant. These results were unexpected because there are no resin manufacturing plants along the Llobregat River, which supplies raw water to Barcelona. Also, there were no connections between these samples and those of the Tordera River located more than 60 km away. The origin of the malodorous raw water in the water treatment plant of Barcelona was established when

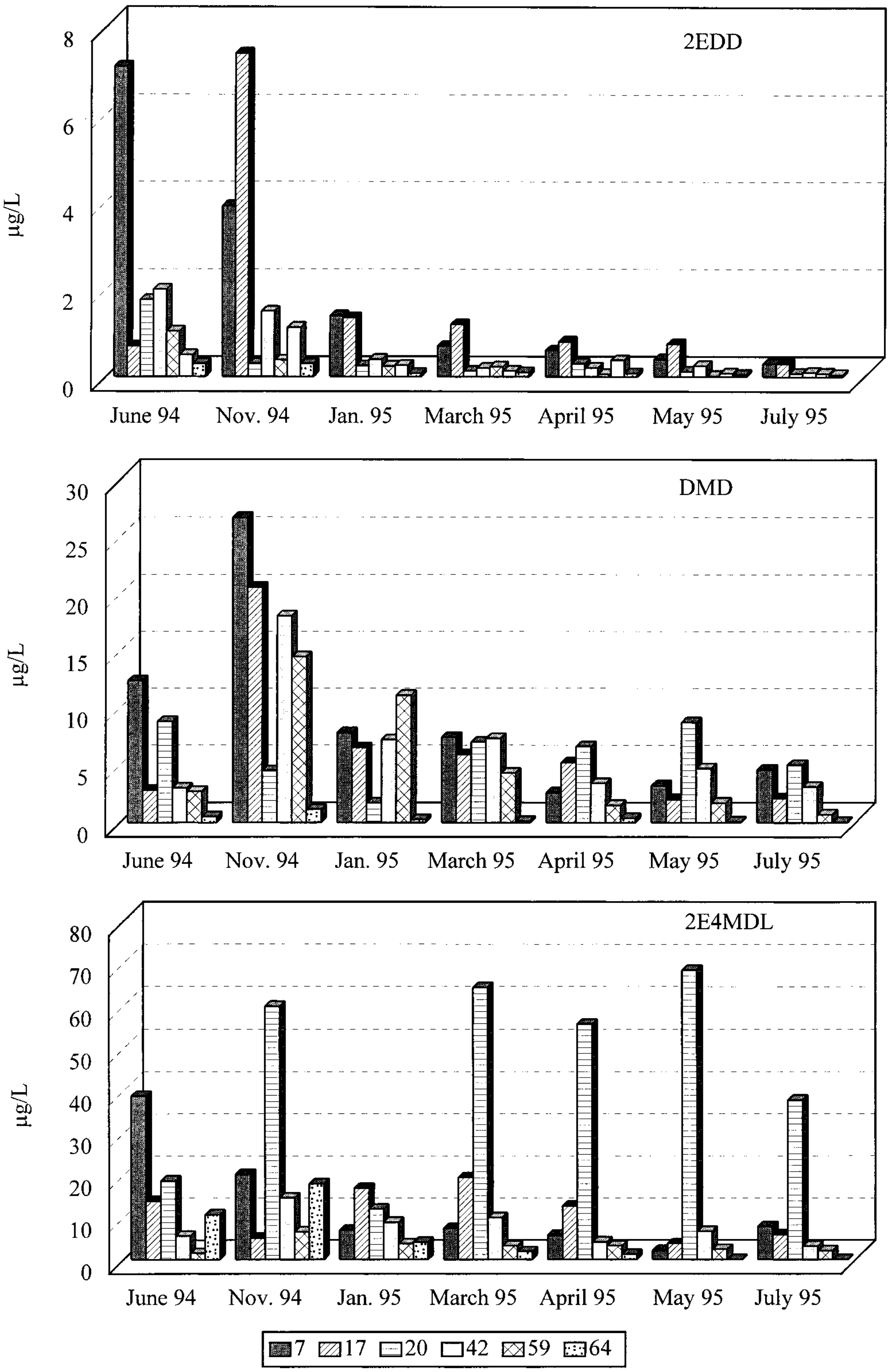


FIGURE 7. Seasonal variation of selected dioxanes and dioxolanes in several wells along the Tordera River.

samples collected along the Llobregat River course during an odor event led us to a sewer of a waste management facility located approximately 15 km away from the water treatment plant. This factory was devoted to the treatment and elimination of industrial residues. The main identified compounds in this sewer were 2EDD (17.3 ppm), 2E4MDL (16.7 ppm), DMD (0.5 ppm), TMD (0.5 ppm), and 2iPMD (0.1 ppm). We believe that these results can be explained when wastewaters from a polyester resin manufacturing plant were carried by tanker truck to the waste management facility located on the banks of Llobregat River. Once the origin was detected, corrective measures such as cleaning of the sewers and prohibition to treat this type of waste were enough to solve the problem.

The results shown here prove that the presence of dioxanes and dioxolanes in water can be a source for complaints from consumers due to their extremely low threshold odor. The most malodorous compound (2EDD) has been identified in river water, tap water, wastewater, and groundwater; it is a characteristic byproduct from resin plants. This compound

TABLE 7. Concentration Levels (in μg/L) of Dioxanes and Dioxolanes in River Water (October 1993−1996)[a]

river sample	concentration range (μg/L)					
	DMD	TMD	2EDD	2iPMD	2iBMD	2E4MDL
15	2.6−99	nd−20	0.30−173	4.8−3030	nd−22	39−152
83	3.6−104	nd−4.9	0.32−123	3.6−41	nd−0.12	34−122
73	4.5−32	nd−2.1	0.08−10	0.21−19	nd−0.43	12−34
62	nd−30.4	nd−0.70	0.08−4.0	nd−1.78	nd−0.29	17−20

[a] Data from October 1993−1996. For 2E4MDL only results from June and October 1996 are displayed. Number of analysis, $n = 7$. nd, <0.005 μg/L.

has one of the lowest threshold odor values reported in the literature for anthropogenic compounds and makes the water unacceptable for drinking purposes when 2EDD concentration levels are higher than 5−10 ng/L.

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