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**TASTE AND ODOUR IN LAKE ONTARIO
NEAR LAKEVIEW AND LORNE PARK
DRINKING WATER INTAKES,
AUGUST/SEPTEMBER 1999**

M.N. Charlton, B.G. Brownlee, G.A. MacInnis and J.E. Milne

NWRI Contribution Number 99-252

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**TASTE AND ODOUR IN LAKE ONTARIO NEAR LAKEVIEW AND LORNE
PARK DRINKING WATER INTAKES, AUG/SEPT, 1999**

BY

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**National Water Research Institute
Environment Canada**

NOVEMBER, 1999

**PREPARED AS PART OF A RESEARCH PARTNERSHIP WITH
ONTARIO CLEAN WATER AGENCY**

NWRI Cont. # 99-252

Management Perspective

Great Lakes 2000, Drinking Water Quality

A research partnership was formed with Ontario Clean Water Agency to investigate the source of taste and odour compounds in western Lake Ontario drinking water.

- Taste and odour episodes seem to be becoming more frequent and of longer duration. The main compound, geosmin, is produced biologically.
- A novel approach to laboratory analyses was effective at most concentrations found during the taste and odour episode in 1999.
- Most geosmin was found in surface water while a few samples indicated that the deep cold water may have non-problem levels of geosmin. Thus, this vexatious problem may be avoided with more expensive longer intake pipes.
- The popular belief that the taste and odour problem is due to some sort of "overturn" of the lake is not supported by our observations.
- More work is needed with larger vessels to confirm the spatial distribution and the vertical stratification to answer questions of availability of unaffected water and whether the problem might respond to enhanced nutrient controls.

Provide report for use of Ontario Clean Water Agency. Publish Manuscript in a scientific journal. Conduct session on Taste and Odour at upcoming CAWQ Symposium in Feb, 2000, collect experiences and plan for new work in 2000.

Sommaire à l'intention de la direction

Grands Lacs 2000, Qualité de l'eau potable

Un partenariat de recherche a été conclu avec l'Agence ontarienne des eaux afin de faire enquête sur la source des composés responsables du goût et de l'odeur désagréables de l'eau potable dans l'Ouest du lac Ontario.

- Les épisodes où l'eau a un goût et une odeur désagréables semblent de plus en plus fréquents et durables. Le principal composé en cause, la géosmine, est d'origine biologique.
- La nouvelle approche retenue pour les analyses de laboratoire a été efficace avec la plupart des concentrations décelées durant l'épisode de 1999.
- La plus grande partie de la géosmine a été trouvée dans l'eau de surface tandis que quelques échantillons indiquaient que l'eau froide profonde peut recéler des concentrations inoffensives de géosmine. Cet ennuyeux problème peut donc être évité si on a recours à des canalisations de prise d'eau plus longues mais plus coûteuses.
- La croyance populaire selon laquelle le problème de goût et d'odeur serait causé par une sorte de renversement des eaux du lac n'est pas confirmée par nos observations.
- Il faudra des travaux additionnels à l'aide de bateaux plus gros afin de confirmer la répartition spatiale et la stratification verticale pour répondre aux questions concernant la disponibilité d'eau non altérée et la possibilité de résoudre le problème en améliorant les mesures de contrôle des substances nutritives.

Fournir un rapport qui pourra servir à l'Agence ontarienne des eaux. Publier ce manuscrit dans une revue scientifique. Tenir une séance sur le goût et l'odeur lors du prochain symposium de l'Association canadienne sur la qualité de l'eau, en février 2000; colliger des expériences et planifier de nouveaux travaux en 2000.

INTRODUCTION

Taste and odour events have sporadically occurred in drinking water drawn from Lake Ontario. A particularly protracted event occurred in 1998. This event resulted in many complaints about the quality of drinking water. In 1999 a research partnership was set up between the Ontario Clean Water Agency and the National Water Research Institute for the purpose of investigating the formation of taste and odour compounds in the lake and to find out more about their variability in depth and distance from shore.

FIELD SAMPLING

Sampling was conducted in Lake Ontario in the vicinity of the intakes for the Lakeview and Lorne Park WTPs in the Region of Peel (Fig. 1). The sampling stations are designated LV for Lakeview and LP for Lorne Park. Samples extending lakeward from the Lakeview intake are expected to represent a large area of the lake. Details of the sampling station depths and locations are shown in Table 1.

Table 1: Depths and distance from shore of stations

Station	Station depth (m)	Distance from shore (km)
LV1	18	2
LV2	40	4
LV3	65-70	10
LV4	2	0.02
LP1	11	1.3

Stations LV1 And LP1 were sampled weekly from August 11 to Sept 13, 1999. LV2 was sampled weekly from August 11 to Sept 8, 1999. Sampling was conducted at deeper stations LV3 and LV4 and the shallow station LV4 on August 31 and Sept 7. The latter stations were added in an attempt to further delineate the extent of taste and odour compounds.

Samples were collected using a Canadian Coast Guard "P-class" vessel. Sampling was restricted to good to moderate weather conditions. High waves precluded sampling on some days. A profile of temperature, dissolved oxygen, conductivity, pH, and depth was obtained at each station using a Hydrolab™ H2O profiler. At LV3 and LV4 the Hydrolab cable was insufficient and a logger (OS200) was used to obtain temperature profiles. A VanDorn bottle was used to collect samples at 2m and bottom minus 2m (b-2) depths at each station. Water collected with the VanDorn bottle was used for geosmin and 2-methylisoborneol (MIB) analyses (two aliquots from the sampler at each depth), algal counting and identification, seston, and chlorophyll analyses. Sterilized, evacuated bulbs were used to collect water for actinomycetes analyses on August 11, 17, and 24. Sterilization facilities were not available for September 1, 7-8, and 13; a VanDorn sample

was preserved for actinomycetes. Secchi depth was recorded at each station. Results of the algal and bacterial analyses, seston, and secchi depths will be reported elsewhere.

EXPERIMENTAL

Materials

Geosmin (GSM) and 2-methylisoborneol (MIB) were obtained from Wako Chemicals, Richmond, VA, as a 100 µg/mL solution in methanol which was diluted to a working concentration of 100 ng/mL in methanol. Diphenyl-d₁₀ was obtained from MSD Isotopes, Montréal, QC. NaCl was heated for several hours at 450°C. Fibre assemblies and manual holders for solid phase microextraction (SPME) were purchased from Supelco (Sigma-Aldrich Canada, Oakville, ON). The fibre was coated with polydimethylsiloxane/divinylbenzene (PDMS/DVB). Aqueous standards were prepared by volumetric addition of a methanolic solution (25 µL) of MIB, GSM and diphenyl-d₁₀ to reagent water from a Milli-Q® system (Millipore Corp., Bedford, MA) to give a final concentration of 100 ng/L. Internal standard (diphenyl-d₁₀, 25 µL) was added to 25 mL of sample to give a final concentration of 100 ng/L.

Extraction Procedure

The headspace SPME extraction used here is described in Watson et al. (in press). Briefly, a 25 mL sample or standard was placed in a 30 mL (1 oz) screw cap bottle with a pre-pierced (22 ga needle) teflon-silicone rubber septum and small magnetic stirring bar. NaCl (6 g) was added, and the bottle swirled gently to wash NaCl from the neck of the bottle. The bottle was placed in a water bath at 65°C on a hotplate-stirrer and the SPME fibre extended into the headspace above the sample. Stirring was started and maintained at a rate sufficient to give good mixing without vortex formation. After 1 h, the fibre was retracted, the holder was inserted into the injection port of the gas chromatograph-mass spectrometer (GC-MS) and the analytes desorbed for 1 min in splitless mode. The fibre was then retracted and "cleaned" by extending it for 8-10 min in an unused injection port of another gas chromatograph at 250°C.

Analytical Conditions

The GC-MS was a Hewlett-Packard 5890 Series II gas chromatograph with a 5971 mass selective detector operated in positive ion mode at 70 eV. The chromatographic column was HP-5MS, 30 m by 0.25 mm with 0.25 µm film thickness. The temperature program was 40°C initial for 2 min, then programmed at 4°C/min to 140°C, 10°C/min from 140-280°C and held at the final temperature for 5 min. The helium carrier gas was used at constant flow mode to provide a linear velocity of ca. 32 cm/s. Selected ion monitoring (SIM) was employed. In earlier samples a single ion was monitored for each analyte/standard: m/z 95 for MIB, m/z 164 for the internal standard (diphenyl-d₁₀), and m/z 112 for GSM. In later stages, five ions (m/z 112, 125, 126, 149 and 182) were

monitored for GSM to provide greater specificity. Chromatographic responses were integrated using Hewlett-Packard Chemstation (G1034C) software.

RESULTS

Samples were collected and analyzed weekly for six weeks starting on August 11, 1999. Lake conditions necessitated sampling on two days on Aug31/Sept1 and Sept7/Sept8; sampling was restricted on Sept 13. Initially, three sites were sampled weekly at surface and bottom minus 2m. The samples actually collected during the six weeks are catalogued in Table 2. Duplicate samples were taken from a single bottle cast in order to assess variability (*vide infra*). Samples were collected in 330 mL screw cap glass bottles with no headspace and analyzed the same day or next day. For short-term storage before or after analysis, samples were stored at 4°C in the dark. Some of the samples were re-analyzed, mostly in cases where the initial results for a set of duplicates gave results differing by more than *ca.* 10%. Re-analysis was carried out within one to two days of the initial analysis.

Samples were analyzed in batches consisting of a fibre blank, two standards, a reagent water blank to check for carryover of analytes from the standards, followed by the samples. Analyte carryover was negligible. The standards were used to calculate response factors of MIB and GSM relative to the internal standard (ISTD), diphenyl- d_{10} . The relative standard deviation (RSD) for these response factors was typically 1.4–4.5%. MIB was not detected (< 0.2 – 0.3 ng/L) in any of the samples.

Individual geosmin analyses ranged from 0.9 to 223 ng/L (Table 2). The six weeks of sampling captured the development of the taste and odour event from low levels of geosmin on August 11 to peak levels on August and back to lower levels by Sept 13. Sampling was added at the shallow nearshore station LV4 to find whether high concentrations would lend support to a notion that the geosmin was produced by benthic algae. These nearshore results were not much different from those offshore. Further analysis with biological data such as chlorophyll and actinomycetes numbers may shed some light on the source of geosmin in 1999.

DISCUSSION

Variability between duplicate samples and within samples upon re-analysis was quite high in some cases for the first two weeks (e.g., LV1 surface and bottom and LV 2 surface on August 11, and LV 2 bottom and LP1 surface on August 17). Results for subsequent weeks (coinciding with the onset of noticeable odours in tapwater from western Lake Ontario) generally showed very good agreement between duplicate samples. Two explanations which we initially considered for this variability in the earlier samples were: (1) GSM decomposed rapidly in these samples upon storage, and/or (2) some interfering substance was analyzing as GSM.

Table 2. Geosmin concentrations (ng/L) for duplicate samples from five Lake Ontario sites, August-September, 1999. Numbers in parentheses are repeat analyses. NS=no sample collected; NDS=no deep sample at this shallow site.

Date	Depth	Site				
		Lakeview 1	Lakeview 2	Lakeview 3	Lakeview 4	Lorne Park 1
		LV1	LV2	LV3	LV4	LP1
Aug 11	Surface	13.8 (2.5)	20.7 (8.3)	NS	NS	1.7
		1.7 (1.9)	2.4 (2.3)	NS	NS	1.7
	Bottom	2.0 (1.8)	0.9	NS	NDS	2.1
		26.3 (1.7)	1.0	NS	NDS	1.9
Aug 17	Surface	6.3	32.8	NS	NS	9.6 (19.0)
		6.7	23.1	NS	NS	29.1 (15.7)
	Bottom	3.9	14.4 (3.8)	NS	NDS	5.7
		3.9	1.7	NS	NDS	5.7
Aug 24	Surface	120	65.2	NS	NS	223
		114 (105)	63.6	NS	NS	208
	Bottom	72.0	15.3	NS	NDS	51.0
		56.7 (64.7)	11.4	NS	NDS	53.1
Aug 31/ Sep 01	Surface	59.1	46.6	55.5	55.2	60.8
		58.5	44.1	54.3	55.3	60.8
	Bottom	71.0	51.4	5.0	NDS	61.1
		72.2	48.5	8.1	NDS	59.9
Sep 07/ Sep 08	Surface	36.6	33.8	NS	24.4	30.6
		36.2	NS	NS	24.0	28.0
	Bottom	39.1	30.5	5.8	NDS	30.6
		38.7	30.8	6.3	NDS	30.1
Sep 13	Surface	17.8	NS	NS	NS	16.3
		16.4	NS	NS	NS	14.7
	Bottom	9.3	NS	NS	NDS	16.3
		10.7	NS	NS	NDS	14.1

Korth et al. (1992) observed that GSM disappeared at nearly 1% per hour from a sample of Murrumbidgee River water (Australia), so overnight storage prior to initial analysis could explain some of the variability, e.g., LV1 surface and bottom, and LV2 surface samples from August 11; and LV2 bottom sample from August 17. Two observations contradict this explanation: (1) one of the August 17 LP1 surface duplicates doubled from 9.6 to 19.0 ng/L after storage and re-analysis, and (2) this variability was no longer observed from the third sampling week onward, even though no procedural changes were made.

To test the second possibility, several of the August 17 samples were re-analyzed by monitoring five ions in the GSM window. Extracted ion chromatograms for one of the LP1 surface samples are shown in Fig. 2A, and for GSM standard in Fig. 2B. The chromatographic peak at 24.78 (± 0.01) minutes gave nearly identical ratios for all five ions thus minimizing the likelihood that an interference at the same retention time as GSM was responsible for the observed variability.

Another possibility is that the small sample sizes (6-40 mL) routinely used for SPME of these compounds (Bao et al. 1999, Lloyd et al. 1998, McCallum et al. 1998), in the present case 25 mL, do not permit representative subsampling if a major portion of the analytes is in the particulate fraction. This may be especially pronounced if geosmin-producing actinomycetes are present in the samples (S. Watson, University of Calgary, personal communication). From the experience gained in the present study, if precise results are crucial, especially during a period preceding a geosmin episode, then a method employing larger sample sizes (e.g., Bao et al. 1997, Palmentier et al. 1998) may be preferable.

The taste and odour event in Lake Ontario in August and September of 1999 may have been the worst ever. The highest geosmin concentrations in 1999 exceeded those previously recorded (Table 3).

Table 3: Geosmin concentrations in Lake Ontario

Concentration	Date	Type	Reference
10 - 70 ng/L	July/Aug 1983	tap water	Brownlee et al. (1984)
10 - 70 ng/L	1994	lake water	Palmentier et al. (1998)
<0.5 - 20 ng/L	Sept 1996	lake/St. Lawrence R.	Ridal et al. (1999)
3 - 110 ng/L	Aug 1998	tap water	Watson et al. (in press)
35 ng/L	Aug 1998	lake water	unpublished data
0.9 - 223 ng/L	Aug/Sept 1999	lake water	this study

Anecdotally, this was one of the longest events in memory. Many complaints were received by water treatment agencies. Geosmin was pervasive in the air near the lakeshore. In addition, the odour was present during a crossing of the lake between Toronto, Ontario and Wilson, New York by M. Charlton on Sept 1.

Concentrations of geosmin in surface waters were similar between sites on each sampling day. The apparent difference between LV1 and LP1 on Aug 24 may have been ephemeral and does not represent any systematic difference judging from the remainder of the data in Table 2. The sample at the LV4 site in very shallow water was similar to others on that day and provided no support for the notion that the geosmin originated from decomposing benthic algae near shore.

The thermal stratification of Lake Ontario may provide some respite from the offending compounds albeit at considerable expense. The lake stratifies into a warm upper layer (epilimnion), a transition zone (thermocline), and a cold bottom layer (hypolimnion) in the summer. Stratification begins in June and ends in October. The taste and odour events occur when the lake is stratified near the end of the summer in August and September. Profiles of temperature versus depth (Figs 3 - 7) show that the profundal hypolimnion temperature was about 5°C at LV3 while the epilimnion temperature was around 20°C. From the LV3 station to the intakes at LV1 and LP1 the hypolimnion became thinner or disappeared entirely. Thus, although there might be sporadic upwellings of hypolimnion water, the two intakes were drawing essentially surface epilimnion water most of the time. Figures 3-7 show the geosmin concentrations at the sample depths. There was a higher probability of finding hypolimnion water further from shore. The coldest and deepest hypolimnion water tended to have fundamentally less geosmin than the surface water. Apparent contradictions in data from LV2 are likely due to the thinness of the hypolimnion there and the difficulty in sampling precise depths from a drifting boat. Also, there is not necessarily any horizontal continuity between deep and shallow water at a station; different masses of water can be moving in different directions. The further offshore the more reliable is the thermal stratification and access to true hypolimnion water. The two deepwater samples at LV3 show that it is possible to obtain water from the lake with geosmin levels near the detection threshold by withdrawing hypolimnion water. Of course, Fig 1 shows that a pipeline would have to be about three times the length of the existing Lakeview intake to access the hypolimnion water; further limnological and engineering studies are needed.

The source of the geosmin in 1999 and in other years remains an open question. The stratification of the lake thermally and the corresponding stratification of geosmin concentrations suggests the geosmin comes from surface waters. Although we cannot eliminate the possibility, we did not find evidence that surface waters were being loaded with geosmin from decomposing benthic algae near shore. Indeed the lakewide extent of the odour in early September supports the idea that the geosmin is formed in the surface water. More sampling is needed with larger vessels to confirm the lakewide distribution of geosmin. If the distribution of geosmin does not parallel the distribution of nutrients that are more abundant near shore then it is unlikely that further management of nutrient loads would ameliorate the problem. Algal abundance data from water intakes, do not show blooms of taxa thought to be capable of producing geosmin at the time of taste and odour events (K.H. Nicholls, and L. Heintsch, Ontario Ministry of the Environment). This leads to the notion that the geosmin was produced by benthic algae. Clearly from these results

the benthic algae would have to be in the shallower water out of the hypolimnion. Then we would expect some sort of inshore - offshore gradient which we did not find. The results are not consistent with the popular notion that a "turnover" event brings the taste and odour compounds up from deep water. Again, the presence of geosmin odour across the whole lake points to a planktonic source. We speculate that the synthesis of geosmin may be triggered at a time of maximum temperature and maximum rate of change (negative) in daylight. Blooms of geosmin producing algae may not be necessary. At the same time, there is an amount of benthic algae and planktonic algae available to decompose at the end of summer with the possibility of geosmin production by actinomycetes.

SUMMARY

- 1) Headspace solid-phase microextraction coupled with gas chromatography - low resolution mass spectrometry was an effective method for analyzing geosmin in Lake Ontario waters. Prior to the onset of the "episode", however, relative analytical variability was high, possibly due to the small sample size used; methods employing larger samples should be considered for low concentration samples.
- 2) Weekly sampling of water near Peel Region drinking water intakes showed the development of a geosmin taste and odour event.
- 3) Peak concentrations of 223 ng/l of geosmin were higher than other previously reported concentrations in Lake Ontario. MIB (2-methylisoborneol) was not detected.
- 4) Deep (70m) hypolimnion water tended to have much less geosmin than surface water and thus, may be a better source for drinking water supplies; at stations closer to shore there were few differences between surface and bottom water.
- 5) Clarification of the sources of geosmin and predictability of taste and odour events, their distribution and relationship to nutrients requires more work.

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FIGURES

Figure 1: Chart of sampling area

Figure 2A. Extracted ion chromatograms for Lorne Park surface sample collected August 17.

Figure 2B. Extracted ion chromatograms for geosmin standard.

Figures 3 to 7: Temperature profiles and geosmin concentrations at each station. Geosmin concentrations are means rounded to the nearest digit. Means marked ** are from highly variable data.

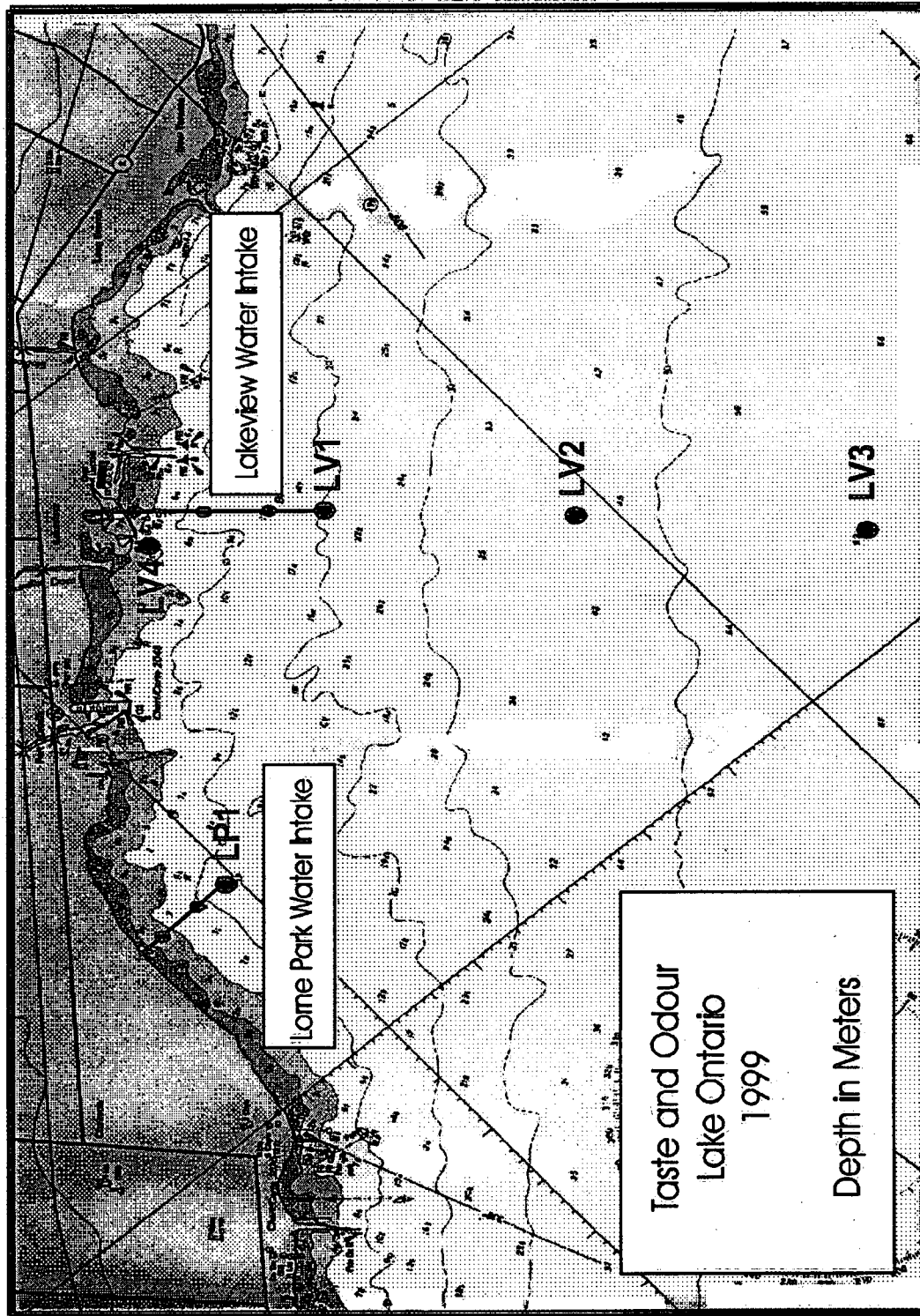


Figure 1

Figure 2A

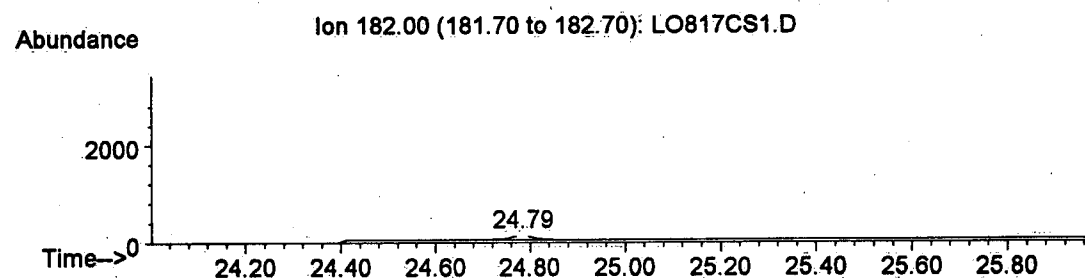
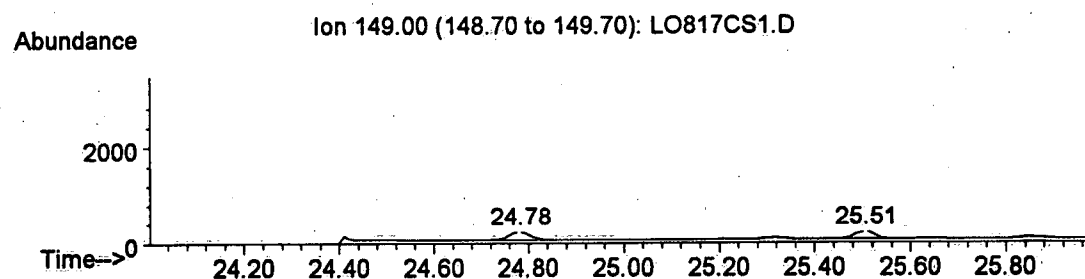
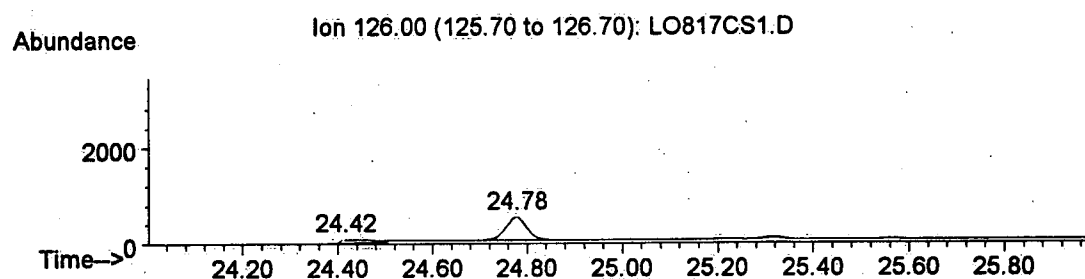
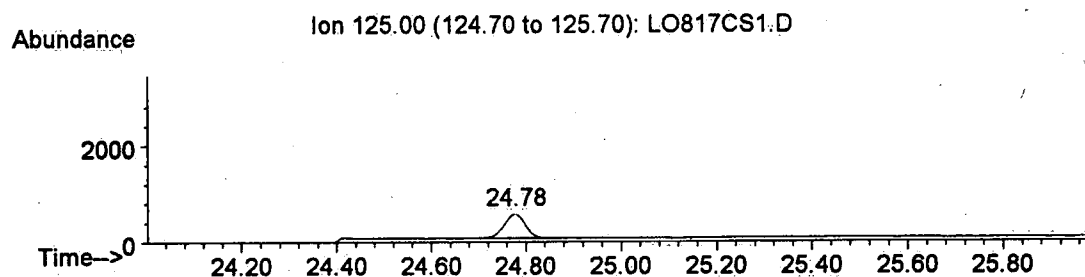
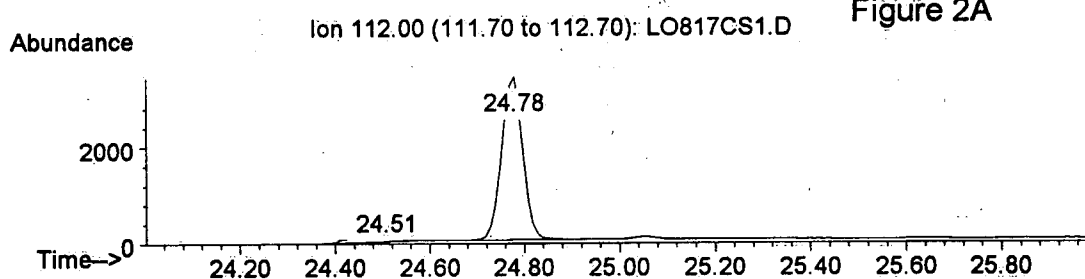
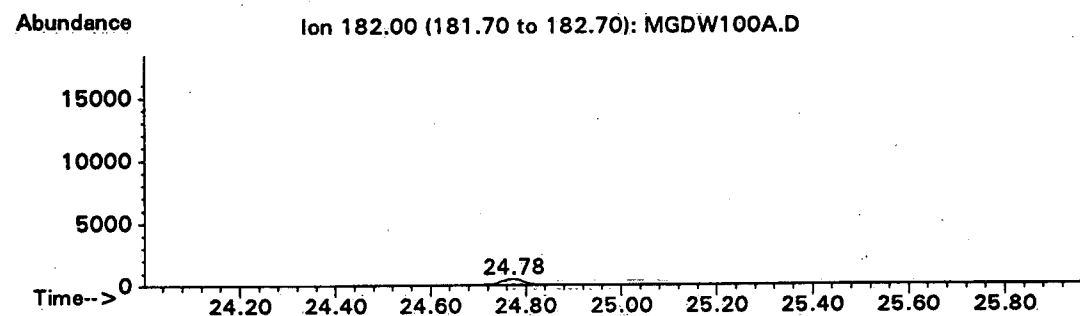
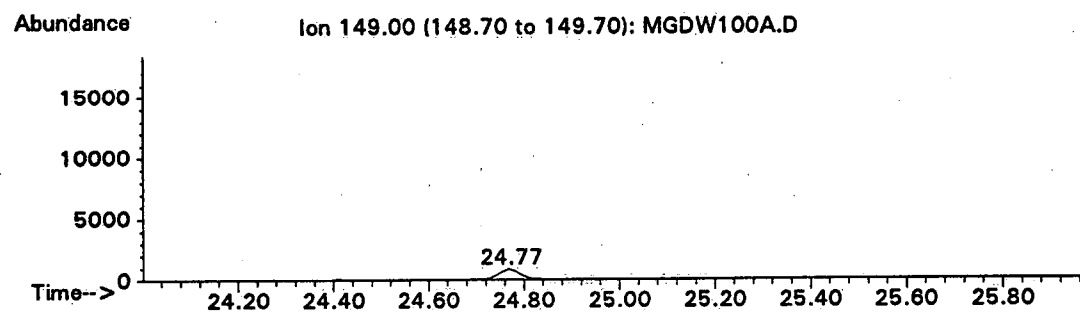
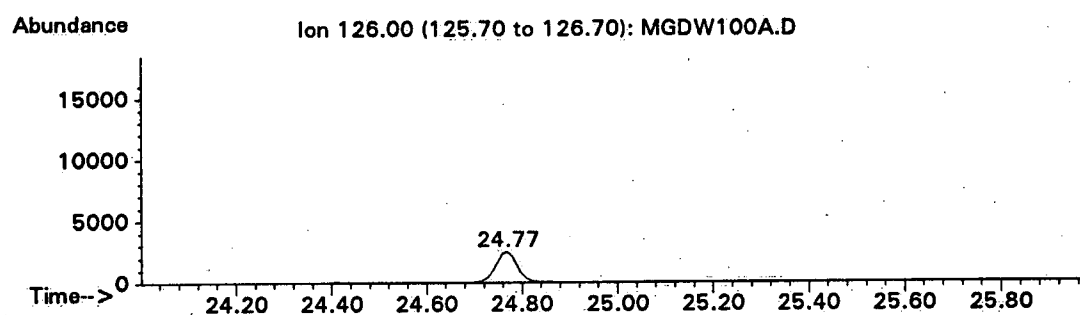
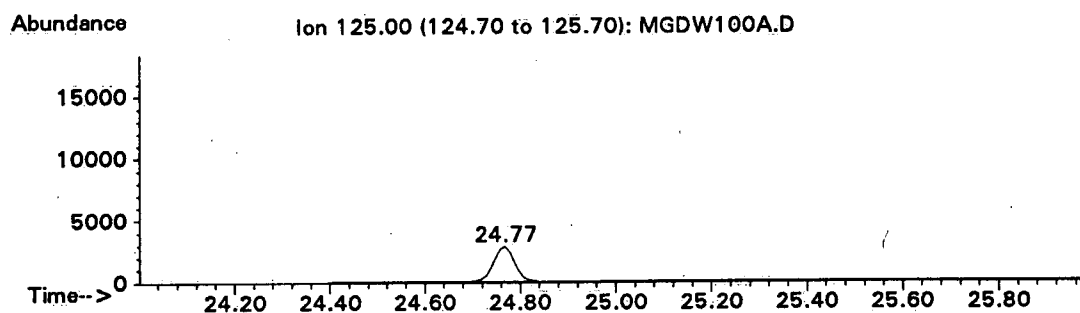
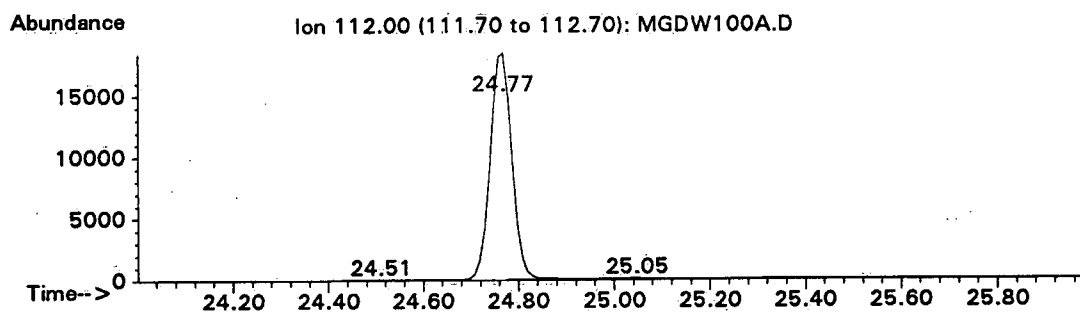
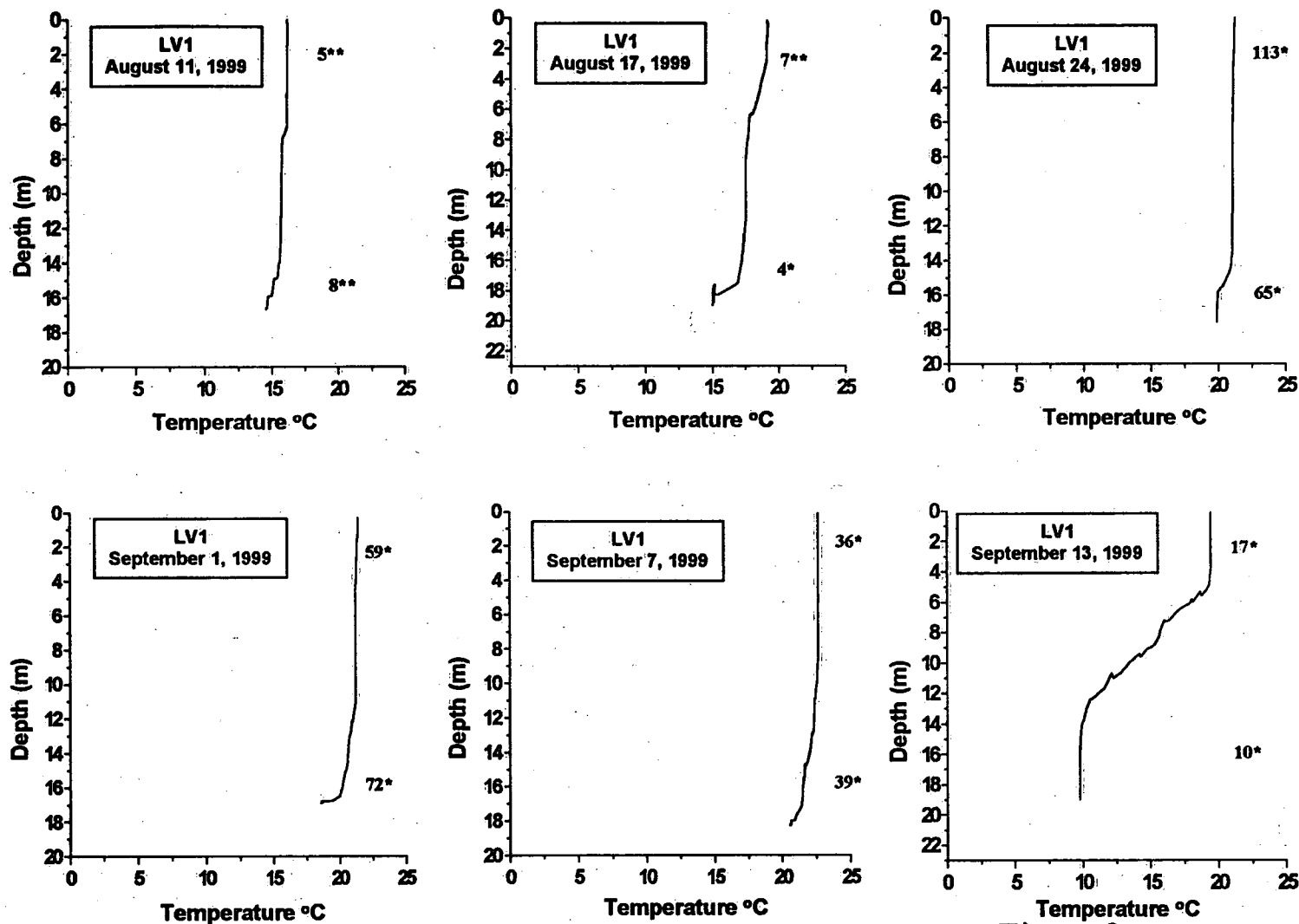


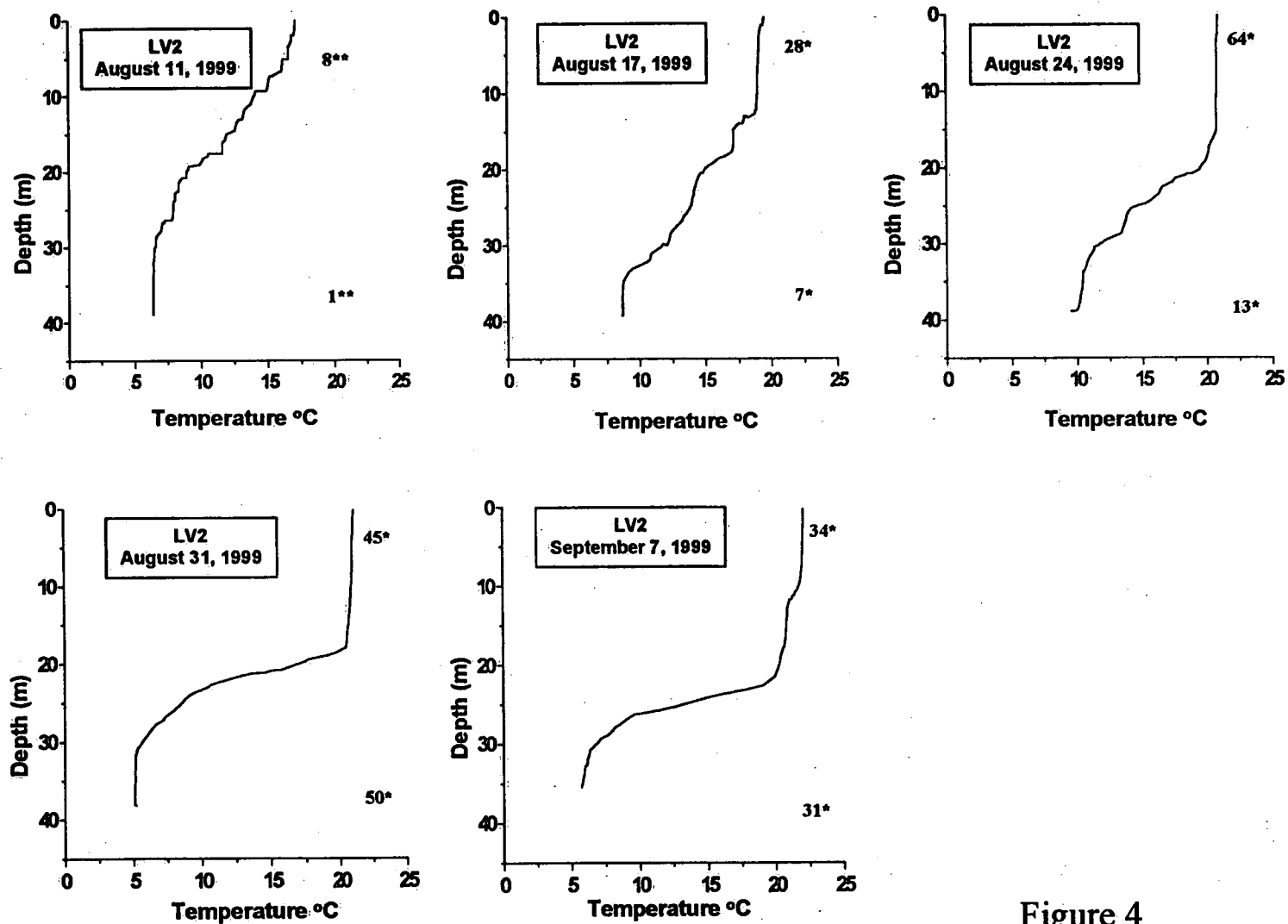
Figure 2B





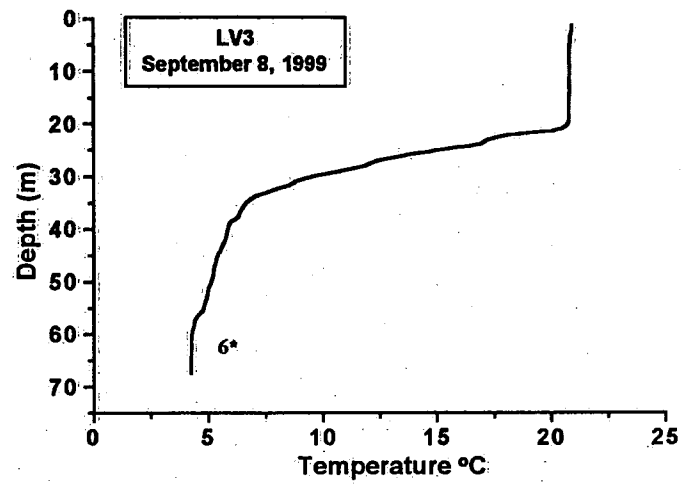
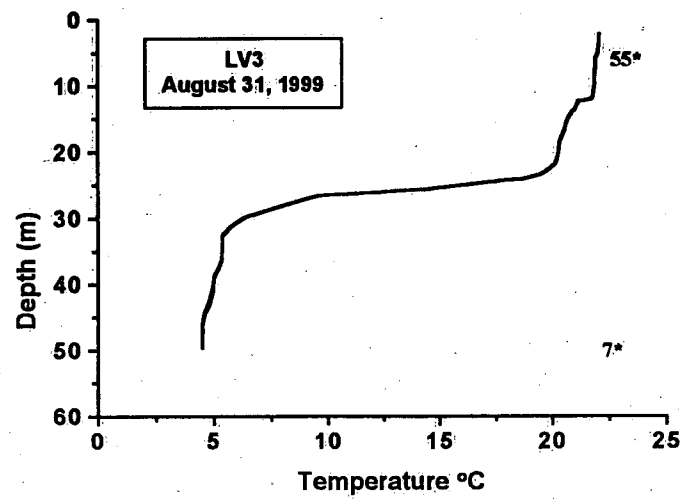
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Figure 3



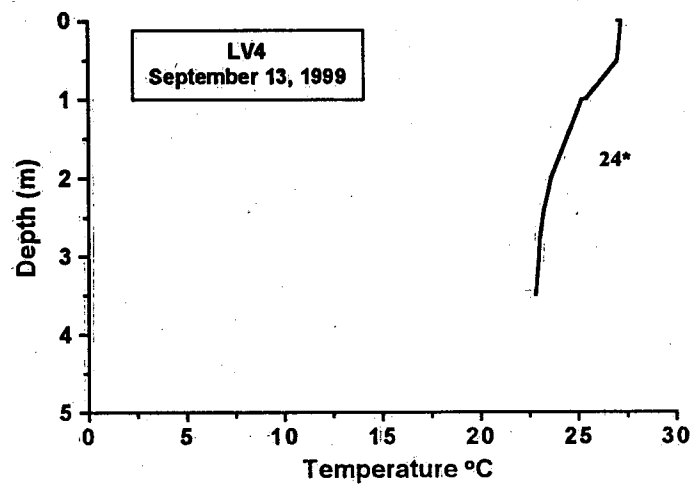
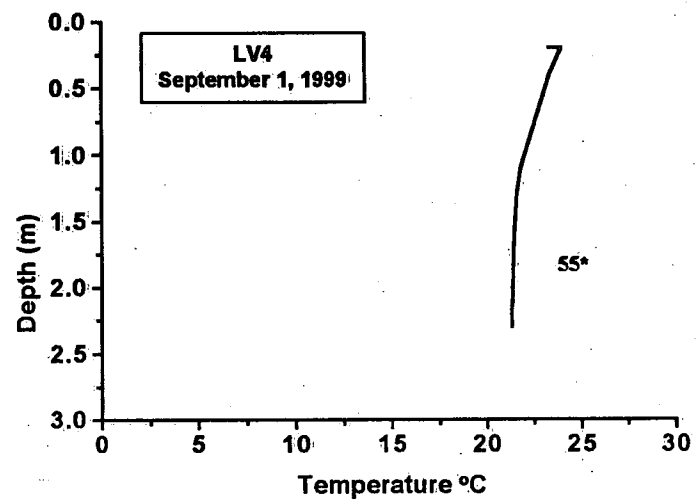
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Figure 4



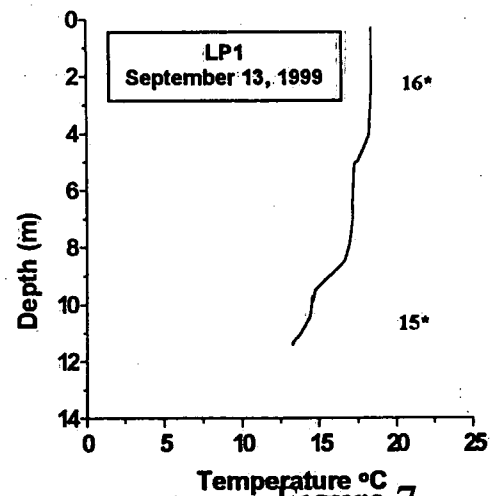
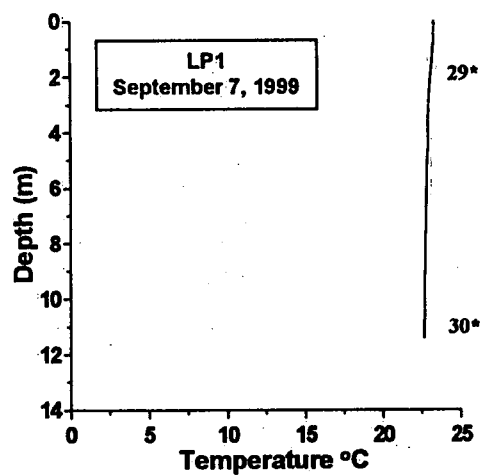
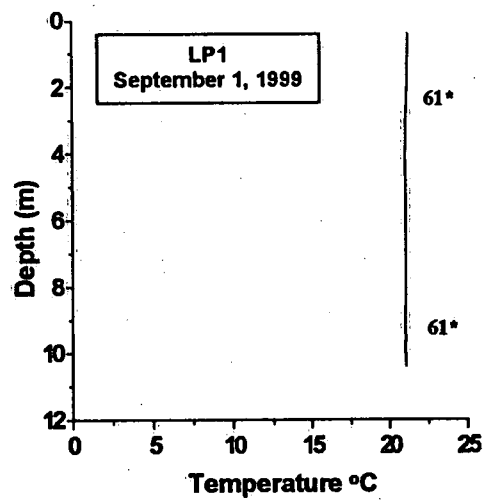
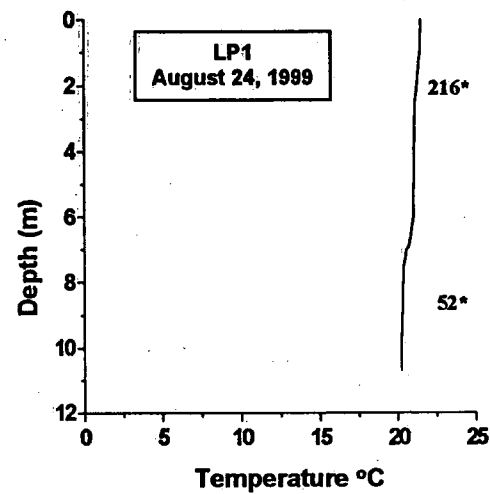
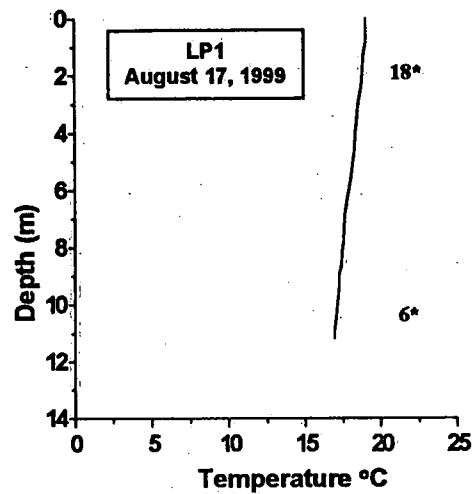
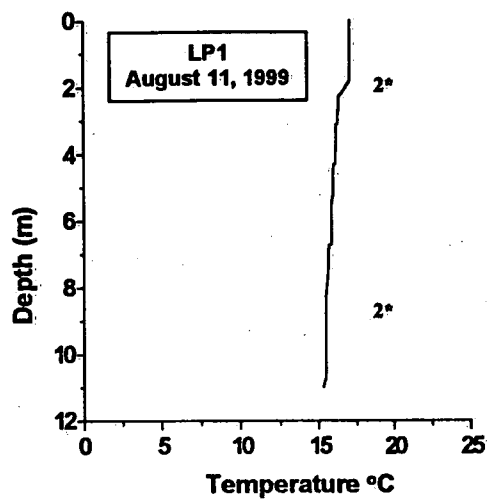
*mean Geosmin concentration (ng/L) 2m and b-2m

Figure 5



*mean Geosmin concentration (ng/L) 2m and b-2m

Figure 6



*mean Geosmin concentration (ng/L) 2m and b-2m

Figure 7

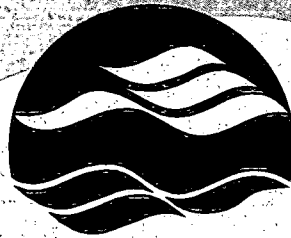
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