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The analysis of volatile trace compounds in landfill gases, compost heaps and forest air

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Landfill gas, cryotrapped on a loop fashioned from a length of a capillary gas chromatography (GC) column, was examined for volatile organometallic compounds (VOMCs) and for volatile organic compounds (VOCs) by using GC–mass spectrometry (MS). A large number of organic components were present and many were identified, but the only VOMCs present in high enough concentrations to be detected were trimethylstibine and tetramethyltin. The use of inductively coupled plasma (ICP)-MS as an element-specific detector allowed the identification of a number of other organometallic species in the landfill gas, including trimethylarsine and trimethylbismuth, and, for the first time, butyltrimethyltin and dibutyldimethyltin. The presence of molybdenum hexacarbonyl was confirmed. Gas from a large-scale compost heap and from compost incubated in the laboratory contained iodomethane but no common VOMCs (GC–ICP-MS). Only VOCs were present in forest air (GC–MS). Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: GC–MS; GC–ICP-MS; organotin speciation; volatile organic compounds (VOCs); volatile organometallic compounds (VOMCs)

INTRODUCTION

Anthropogenic sources, such as landfills and anaerobic sewage sludge digesters, yield a number of volatile organometallic compounds (VOMCs) and hydrides of elements such as arsenic, antimony, bismuth, selenium, tellurium, mercury, lead, iodine, nickel, molybdenum, and tungsten.[1,2] Arsines have also been found in natural gas.[3] The usual method of sampling these gases involves collection into plastic Tedlar bags followed by pre-concentration into a cold trap.[4] The analysis of the concentrate is subsequently carried out by using a rudimentary packed gas chromatography (GC) column followed by element-specific detection of the separated species, using GC–inductively coupled plasma mass spectrometry (ICP-MS).[5] Identification is made on the basis of comparison with standards and/or calculated retention times.[6] Tedlar bags have the advantage that they are easy to use in the field and, unlike metal canisters, they do not adsorb organometallic species.[4] There are two main problems with this methodology. Firstly, the sample is usually kept at ambient temperature for at least a few hours prior to the pre-concentration step, and secondly, species identification is indirect and dependent on the availability of standards. Some investigators have resorted to trapping out particular gas fractions, identified by using GC–ICP-MS, and then transferring these fractions to a GC–MS system for species confirmation.[1] To circumvent these difficulties, a sampling method is needed that traps unstable species at low temperature, because some metal species are inherently unstable (some solid absorbents, such as Tenax, that are commonly used to trap VOMCs can react with some gases[7]). The associated analytical method should provide molecular information and be fast and convenient to use. To meet these requirements, we have studied the use of a cooled capillary trap to concentrate the sample, which, after collection, can be incorporated into the capillary column of a gas chromatograph–mass spectrometer for sample separation and identification. Although cryotrapping of gases has been widely employed before,[8,9] as has the use of capillary traps,[10,11] the novelty of the present method is the incorporation of the trap directly into the analytical gas chromatograph–mass spectrometer. We describe the application of the method to the analysis of landfill gas and to forest air.

We also describe the analysis of the gas produced in a

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large-scale compost heap by using the canister–GC–ICP-MS method.

EXPERIMENTAL

Landfill gas and forest air samples

The gas samples were analyzed by using GC–MS and by using GC–ICP-MS. The gas chromatograph–mass spectrometer was a Varian Saturn instrument fitted with a 30 m DB-5 (0.25 mm o.d., 0.25 µm i.d.) column. The GC–ICP-MS utilized the same column in a Hewlett Packard 5890 GC connected to a VG Plasmaquad PQ2 Turbo ICP-MS for element-specific detection. The connection to the inductively coupled plasma mass spectrometer was made through a length of capillary column inserted through a copper tube that was heated to 170 °C by using a heating cord.

The gas to be analyzed (first collected in a Tedlar bag in the case of the landfill gas) was sucked through a glass U-tube trap cooled to −5 °C followed by a glass tube containing either $CaSO_4$, to remove H_2O when sampling air, or NaOH pellets, to remove CO_2, H_2S, and H_2O when sampling an anaerobic environment. The clean-up trap was connected to an 80 cm piece of DB-5 capillary (0.32 mm i.d., 0.32 µm o.d.) immersed in a 1-propanol cooling bath at −120 °C. Independent tests showed that compounds with a boiling point above approximately −20 °C in a gas mixture are condensed in the capillary trap. This was done by injecting appropriate compounds into Tedlar bags and determining recoveries after sampling in the standard way. The connection between the glass tubes was made with very short pieces of Tygon and silicone tubing and capillary connectors. The volume of the samples was determined by using a bubble flow meter connected after the peristaltic pump. The samples were transported and stored, if necessary, at −78 °C; the two ends of the capillary were sealed in a capillary connector.

In order to transfer the stored samples (−78 °C) to the gas chromatograph, the trap temperature was reduced to −120 °C (propanol cooling bath). The trap was inserted with the aid of connectors between the injector and the separation column. The whole column was flushed with helium for 3 min and the separation was initiated by removing the trap from the cooling bath, hanging it in the oven, and starting the temperature program described in the figure captions.

Compost heap gas samples

The city of Vancouver started a garden-waste composting program in 1989. Grass trimmings, leaves and other plant waste are brought to the Vancouver landfill where the material is sorted to remove foreign matter and is ground such that the maximum length of the material is 7 cm. The plant material is then mixed with water and piled into windrows. The windrows are turned at regular intervals to ensure that the optimum temperature, moisture, and oxygen levels are maintained. After 3 months in windrows, the compost is stored in curing piles for a further 9 months. The final compost is sold primarily for use as landscaping mulch or, after blending with other materials, for use as topsoil.

A new windrow, piled 6 h prior to the start of the experiment, was chosen because the composting process is most active during the first 2 weeks after the windrow is created. The temperature of this windrow was 48 °C. A gas collector, consisting of an inverted plastic dish 20 cm in diameter and 10 cm in height with a 4 mm i.d. outlet, was placed 10 cm below the surface of the pile.

After 1 week, the outlet of the gas collector was connected to a 1 l evacuated glass chamber and the gas in the collector was sucked into this chamber. The temperature in the compost pile had increased to 61 °C.

The gas in the glass chamber was purged, in the laboratory, with helium, into a U-shaped glass tube (6 mm o.d. × 22 cm) filled with chromatographic column packing material (10% Supelcoport SP-2100 on Chromosorb, 45–60 mesh) and cooled in a dry-ice–acetone bath.[12] The contents of the tube were analyzed by using GC–ICP-MS[9] for volatile arsenic, antimony, bismuth, tellurium, tin, lead, mercury, cadmium and iodine.

Compost fermentation

Compost (1 kg) was collected from 10 cm below the surface of the pile for analysis for use in fermentation experiments and for total arsenic analysis. A series of 1 l Erlenmeyer flasks was prepared as described in Table 1. Compost (100 g) was placed in each flask and a purge-and-trap head was attached to each flask.[12]

The blanks, flasks A and B, were autoclaved at 121 °C for 20 min. The flasks that were incubated aerobically were purged with air from a compressed-gas cylinder for 30 min at 100 ml min^{-1}. The flasks that were incubated anaerobically were similarly purged with a mixture of 85% nitrogen, 10% CO_2 and 5% hydrogen from a compressed-gas cylinder. The inlet and the outlet tubes on the heads were closed with hose clamps and the flasks were incubated at 61 °C for 2 weeks.

The headspace of the flasks was analyzed for VOMCs by purging the flasks into U-tubes, as described above. Again, the contents of the U-tubes were analyzed by using GC–ICP-MS.

Table 1. Compost incubation conditions

Flask	Sterilization	Type of incubation
A	Yes	Aerobic
B	Yes	Anaerobic
C	No	Aerobic
D	No	Aerobic
E	No	Anaerobic

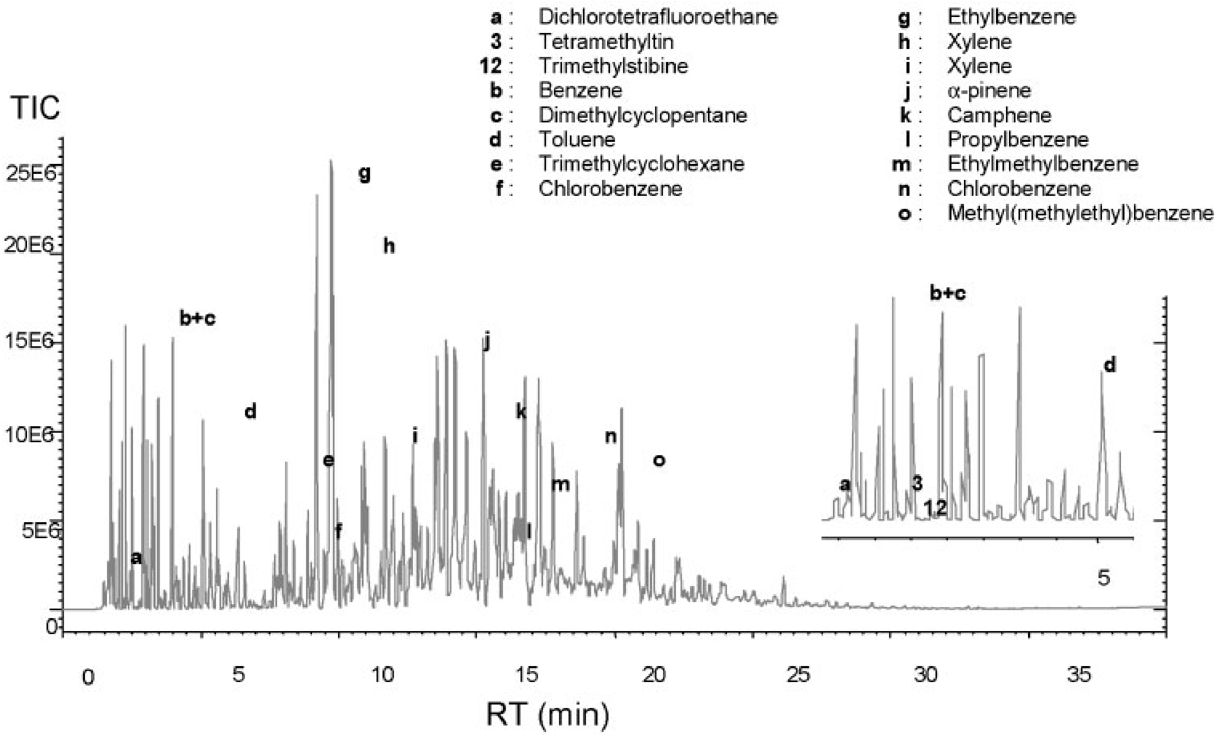

Figure 1. GC–MS chromatogram of 20 ml landfill gas. Trapping flow rate: 3 ml min^{-1}. GC program: 5 min at 40 °C, 25 min at 2 °C min^{-1}, 2 min at 5 °C min^{-1}, 3.6 min at 25 °C min^{-1}, 5 min at 190 °C.

RESULTS AND DISCUSSION

The landfill gas from the Vancouver site has been the subject of earlier investigations. For example, Wreford *et al.*[13] investigated the major components, CH_4 and CO_2, and Feldmann and Cullen studied the VOMCs.[2] The present study focuses on the simultaneous determination of VOMCs and volatile organic compounds (VOCs).

The GC–MS analysis of the landfill gas, Fig. 1, revealed a very complex mixture made up of organic compounds, some of which were identified by matching spectra with those in the Saturn library. The large number of VOCs is typical.[14] One recent study reported a total of 140 compounds identified from seven UK sites, of which 90 were common to all sites.[15] The only VOC that was identified in the Vancouver gas, but not widely reported,[16,17] is dichlorotetrafluoroethane, a chemical that is regulated in many countries. Only two of the anticipated organometallic compounds, tetramethyltin (**3**) and trimethylstibine (**12**), were detected and identified by using GC–MS. These are, together with trimethylarsine and trimethylbismuth, the major VOMCs in the Vancouver landfill gas[2] and in gas from other such sites.[18] Trimethyl-arsine and -bismuth were masked by the VOCs in the present study.

The VOMCs detected in landfill gas in these previous studies were analyzed by using ICP-MS for element-specific detection. This method was applied to the present samples in order to establish if the same sampling procedure could be coupled to the GC–ICP-MS detection system to permit the identification of other VOMCs. The landfill gas samples were screened for a range of metals and metalloids. Some element-specific chromatograms are shown in Fig. 2.

There are, at least, nine organotin compounds in the gas and these comprise the major organometallic species. Chromatograms **B** and **C**, in Fig. 2, represent the tin compounds in two different landfill gas samples taken on the same day. Compound **2** is only present in sample **B** and compound **10** is only present in sample **C**. Both show similar intensities, and it is possible that one is a decomposition product of the other. The major species proved to be tetramethyltin, as would be expected from the GC–MS results described above. Previous studies of the Vancouver and other landfills suggest that the unidentified tin compounds are organotin hydrides. However, the presence of methylbutyltin compounds could be anticipated as products of biological processes involving anthropogenically introduced butyltin compounds. Indeed, all the compounds Bu_nSnMe_{4-n}, $n = 0–3$, have been found in coastal sediments and water (but not in air)[19] and Bu_3SnMe is produced in *in vitro* experiments that used natural sediments.[20]

In order to confirm the presence of dibutyldimethyltin and

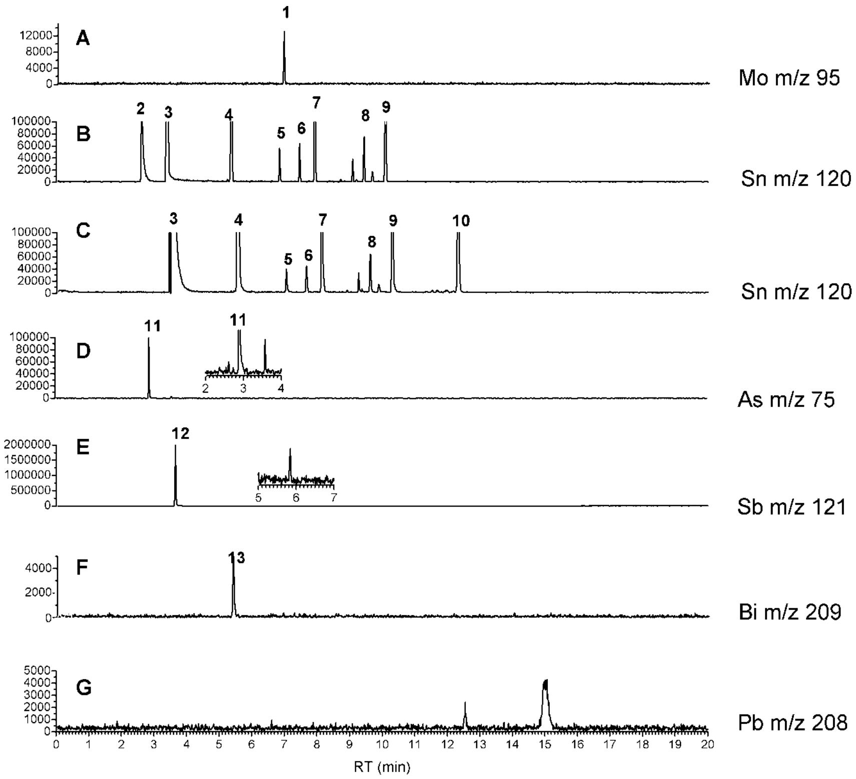

Figure 2. Element-specific chromatograms of 20 ml of landfill gas. Trapping flow rate: 3 ml min^{-1}. GC program: 5 min at 40 °C, 10 min at 15 °C min^{-1}, 5 min at 190 °C.

tributylmethyltin in the landfill gas, the compounds were synthesized from methylmagnesium iodide and the appropriate butyltin chloride in diethyl ether.[19] For identification, 1 μl of the reference tin solution was directly injected into the cooled trap capillary that also contained, in one case, the landfill sample. The trap capillary was connected to the peristaltic pump to pull in the injected reference sample. The chromatograms, shown in Fig. 3, confirm the presence of the two compounds.

One molybdenum compound is found in chromatogram **A**, Fig. 2. This compound proved to have the same retention time as a reference sample of molybdenum hexacarbonyl, as illustrated by Fig. 4. This compound was first detected in samples collected in a Tedlar bag from the same landfill gas in 1997,[2] and the molybdenum concentration in air was then estimated to be in the range 0.2–0.3 μg M^{-3}. Tungsten hexacarbonyl, which was previously found at a lower concentration, was not detected in the present investigation.

The other VOMCs, trimethyl-arsine, -antimony, and -bismuth, as well as tetramethyllead, were identified on the basis of their known retention times. Trimethylantimony was also confirmed by using GC–MS, as described above. Chromatogram **D**, Fig. 2, shows the presence of an, as yet, unidentified arsenic compound that is less volatile than trimethylarsine. A similar arsenic compound was found among the VOMCs in the environment of hot springs.[21]

COMPOST HEAP

Rather surprisingly, little attention has been paid to the VOCs from compost heaps, and studies have focused on the production of gases such as CH_4, CO_2, NH_3, N_2O, and H_2S.[22–24] The possible presence of metals in the compost has been acknowledged,[25,26] but VOMC emission has not been considered.

The present study was conducted because the feed for the Vancouver compost originates mainly from tree leaves that are known to contain significant concentrations of arsenic compounds. In fact, the arsenic concentration in the final product is 3 ± 1 ppm. Thus, the production of volatile arsenic compounds during the composting process is a distinct possibility.

For this study, a polycarbonate bowl was buried 50 cm below the surface of the compost. After 1 week, the gases trapped in the dish were transferred to an evacuated glass container.[27] The canister sampling method was chosen because we wished to sample the gas that had been built up in a specific region of the compost heap. ICP-MS was chosen as the detection method. The chromatograms resulting from the GC–ICP-MS analysis of the gases collected from the compost heap showed only one peak. This peak was for iodine ($m/z = 127$) and the retention time matched that of iodomethane.

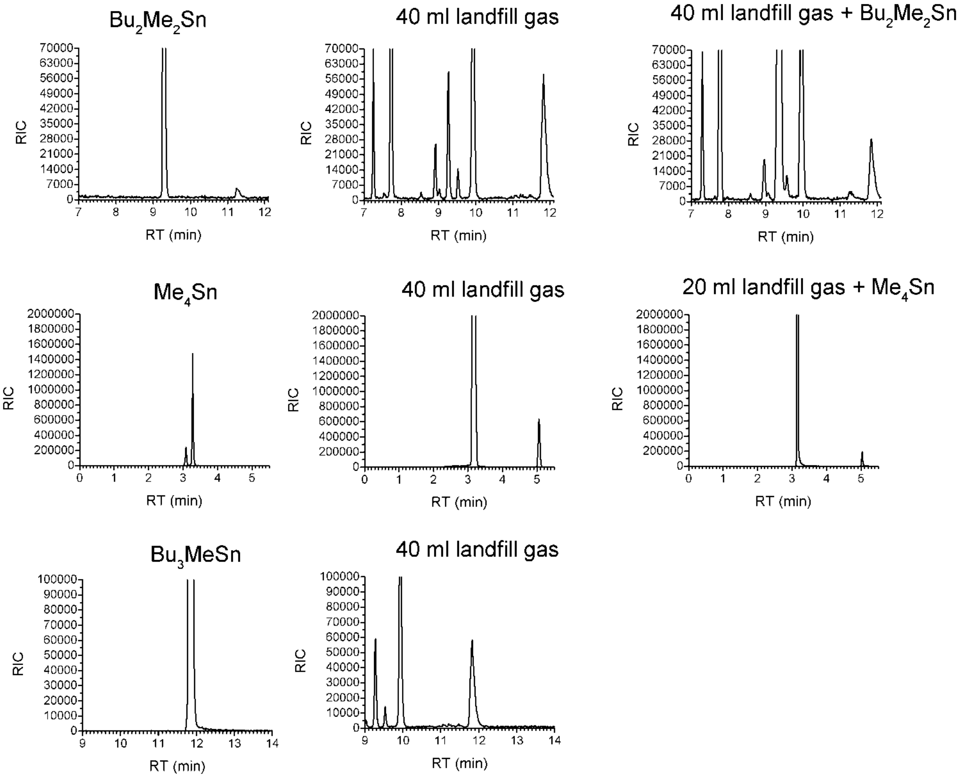

Figure 3. Identification of some tin compounds contained in the landfill gas.

In order to gain a little more insight into the composting process, 2-week-old compost was incubated in the laboratory under controlled conditions, anaerobically and aerobically. Here again, iodomethane was the only gas detected by GC–ICP-MS analysis of the collected headspace gases, but it was also found in the gas above the sterilized controls. Iodomethane was not present in the gas mixtures used to supply the atmosphere for the incubation experiments, so it is possible that it is formed by a chemical rather than a biological process.

FOREST AIR

In order to ascertain if metals could be volatilized in more natural surroundings, forest air samples were taken at two different locations in a forest on the University Campus: 30 cm above the ground (Fig. 5A) and underneath a 1 cm layer of leaves (Figure 5B). The chromatograms shown are representative examples from a number of determinations. Individual chromatography peaks were identified with the aid of the Saturn database. No VOMCs, particularly trimethylarsine, were detected. There are fewer VOCs. The presence of chlorocarbons is not unexpected; a number were found in the ambient air of a forest near Kyoto, Japan,[28] although those authors did not find any 1,1,1-trichloroethane.

The samples taken underneath a layer of leaves contain many trace compounds (peaks 10–18 in Fig. 5B) not seen in samples taken above the ground. The mass spectra of these compounds did not match any in the database (sample spectra are available from the authors).

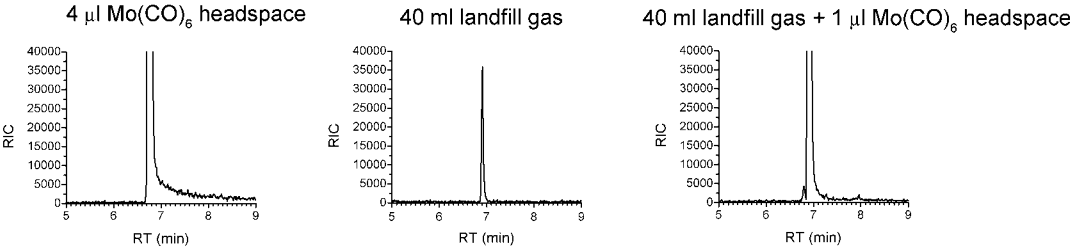

Figure 4. Identification of a molybdenum compound contained in the landfill gas.

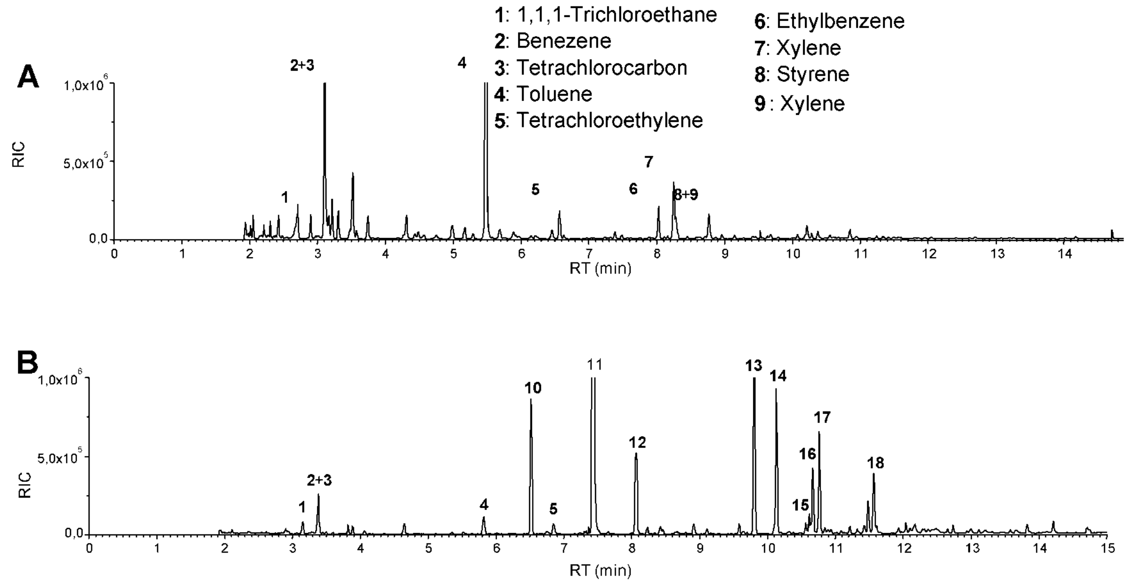

Figure 5. GC–MS chromatogram of trace compounds in 1 l of forest air taken: (A) 30 cm above the ground; (B) underneath $\sim$1 cm layer of leaves. Trapping flow rate: 20 ml min^{-1}. GC program: 5 min at 12 °C min^{-1}, 2 min at 20 °C min^{-1}, 5 min at 190 °C.

SUMMARY

The multiplicity of VOCs present in landfill gas and their high concentration seems to be a constraint on the use of GC–MS for the identification of any VOMCs that might be present. Only specific compounds present in higher concentrations or eluting in otherwise clear windows of the chromatogram are likely to be detected. Thus, in most instances, the identification of VOMCs remains a problem and requires methodology employing sensitive element-specific detection. The GC–MS method outlined above could be useful for the investigation of less biologically complicated sites, such as hot springs, wetlands, soils, and sediments. Although the diameter of the capillary trap and the efficiency of removal of H_2O and CO_2 by the clean-up trap limit the flow speed of the gas, several samples can be collected at once by using a multi-channel peristaltic pump. Cryogenic sampling into the capillary loop allows mild and unselective trapping of VOCs and VOMCs.

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