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Short communication

Determining breakthrough of the soil fumigant chloropicrin from 120 mg XAD-4 sorbent tubes

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Abstract

The emission to the atmosphere of soil fumigants such as chloropicrin represents a potentially important human exposure pathway. Commonly, determining the air concentration of fumigants is carried out by pumping air through sorbent tubes which chemically retain the fumigant. In order to obtain an accurate measurement, it is essential that the fumigant does not break through the sorbent tubes, since this would result in an underestimation. Using a simple apparatus, we tested the potential for chloropicrin breakthrough from 120 mg XAD-4 sorbent tubes. The effects of chloropicrin loading (0.33 and 3.3 mg) and air flow rate (50 and 1000 mL min^{-1}) on the transport of chloropicrin through six XAD-4 tubes (connected in series) were examined over time periods ranging from 1 to 360 min. The higher flow rate led to rapid and high breakthrough of the chloropicrin, especially at the longer time periods. At 360 min, all six tubes together retained only 46–54% (depending on initial loading) of the added chloropicrin. At the lower flow rate, essentially all of the added chloropicrin was always retained on the first two tubes. The effect of flow rate was greater than that of initial chloropicrin loading and sampling time. It is concluded that when 120 mg XAD-4 tubes are used in soil fumigant emission studies, it should be at low flow rates only and always with at least one back-up tube.

Keywords: Fumigant pesticides; Methyl bromide alternatives; Agriculture; Volatile organic compounds; VOCs; Ozone

1. Introduction

The soil fumigant chloropicrin is becoming more widely used in the wake of the 2005 ban on the use of methyl bromide as a pre-plant pesticide treatment. Primarily used in the production of high cash crops such as strawberries and carrots, chloropicrin has a broad efficacy in controlling nematodes, bacteria, fungi, insects and weeds. However, its use is regulated due to concerns over worker and public inhalation risks and because of the potential role of its constituent volatile organic compounds (VOCs) in the formation of near-surface photochemical smog. These concerns have led to an increasing need to research the emissions of chloropicrin from fumigated soil to the atmosphere. Such research, carried out in the field or using laboratory soil columns, often requires the use of sorbent tubes to trap emitted chloropicrin and thus

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determine its concentration in air. XAD-4 (a polymeric adsorbent resin) sorbent tubes are widely regarded as the most suitable for trapping chloropicrin, due to the affinity of the fumigant for the XAD resin, and have been successfully employed in recently published field experiments (Wang et al., 2005; Gao and Trout, 2007; Ou et al., 2007; Van Wesenbeeck et al., 2007). A critical factor in the use of sorbent tubes is ensuring that 'breakthrough' of the chemical in question does not occur (in which case, not all of the chemical entering the tube is retained on the sorbent). Conditions conducive to breakthrough are most likely high chloropicrin concentrations (leading to a saturation of adsorption sites on the XAD resin) and high rates/volumes of air flow through the tube (leading to physically enhanced transport of the chloropicrin through the XAD resin). Since breakthrough would lead to an underestimate of air concentrations, it is important to quantify the significance of these conditions on chloropicrin retention by the XAD-4 tubes. This was the aim of the work presented here.

2. Materials and methods

All experiments were carried out at 22 °C using the apparatus shown in Fig. 1. After cutting and smoothing their ends, up to six 120 mg XAD-4 sorbent tubes with dimensions of 70 mm × 6 mm (SKC, PA, USA) were connected in series using acetyl instant connectors (John Guest, Middlesex, UK). These connectors were found to produce a non-leak seal and avoided the use of highly sorbing (e.g. latex rubber tubing) or poorly sealing (e.g. Teflon tubing) materials for connecting the sorbent tubes to one another. The instant connector at the inlet end of the sorbent tube 'chain' was connected to a 6 mm Teflon tubing which had a hypodermic needle sealed into its other end. The instant connector at the outlet end of the sorbent tube chain was connected, via 6 mm Teflon tubing, to an electronic flow sensor (McMillan, TX, USA). All connections were found to be leak-proof. Both 'Type 4' and 'Type 7' flow sensors were used to establish flow rates of either 50 mL min^{-1} (Type 4 sensor) or 1000 mL min^{-1} (Type 7 sensor), through the sorbent tubes. Air flow was provided by the laboratory vacuum system. All flow sensors were pre-calibrated using a DryCal DC-Lite reference flow meter (Bios Int., NJ, USA).

Either 0.33 or 3.3 mg of 99.9% purity chloropicrin (CCl_3NO_2) obtained from Dow Agrosciences (IN, USA) was injected into a 160 mL glass bottle using a micro-syringe, and immediately capped with a Teflon-faced rubber septum and aluminum crimp seal. After 1 h of equilibration, the hypodermic needle connected to the sorbent tube chain inlet was inserted through the septum to initiate the drawing of the chloropicrin-laden air through the sorbent tubes. Simultaneously, a second hypodermic needle was inserted through the septum to allow air inflow to the glass bottle and avoid the formation of a vacuum within. The sorbent tube chains were removed after 1 (1000 mL min^{-1} only), 3 (50 mL min^{-1} only), 12, 30, 60, 180 and 360 min. For selected treatments, replicate determinations were performed in order to assess variability.

Removed tubes were individually capped and stored at −19 °C prior to extraction and analysis. Each XAD tube was extracted within 2 days by removing the glass wool holding the contents in place and carefully shaking the resin into a 20 mL

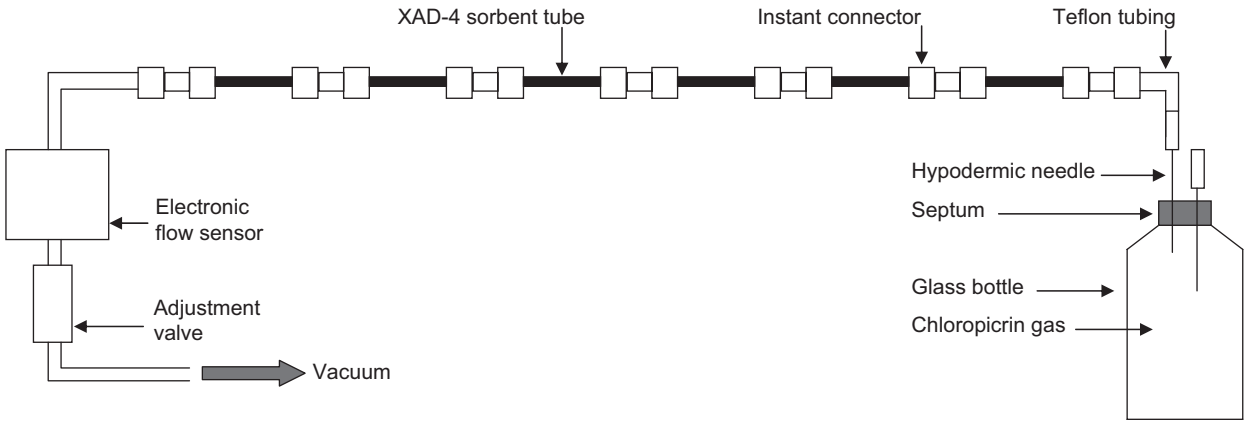

Fig. 1. Experimental set-up for chloropicrin breakthrough tests.

glass vial. The glass wool and the glass tube itself were also placed into the vial. Hexane (3 mL) was then added and the vial immediately capped with a Teflon-faced rubber septum and aluminum crimp seal. Vials were shaken for 30 min, allowed to settle briefly, and the supernatant solution (around 1.5 mL) transferred to a gas chromatography (GC) vial for analysis. GC analysis was performed using a Hewlett Packard HP6890 equipped with a micro-electron capture detector. The column was a J&W Scientific DB-VRX 30.0 m × 0.25 mm × 1.4 μm capillary column (Agilent Technologies) running at a flow rate of 1.4 mL min^{-1} and using He as the carrier gas. Analysis time for each sample was 18.3 min. Over the first minute, the GC oven temperature was held at 45 °C. Thereafter, it was increased to 80 °C at a rate of 2.5 °C min^{-1}. During this stage, chloropicrin was eluted, with a retention time of 13.2 min. The oven temperature was then increased to 120 °C at a rate of 30 °C min^{-1} and held for 2 min to facilitate column clean-up between samples. Finally, the oven was cooled to 45 °C in preparation for the next sample. The inlet temperature was 240 °C and the detector temperature was 290 °C.

3. Results and discussion

Percentages of the total chloropicrin addition subsequently recovered on each XAD-4 tube are shown in Table 1. For those treatments where replicate determinations were carried out, the mean followed by the range of values is given. The replicate data for the amount and (more importantly) the distribution of chloropicrin throughout the tube chain indicate that the method employed was reproducible. Differences between duplicate measurements ranged from 0.2% to 6.8%

Table 1
Percentage of added chloropicrin (CP) recovered on each XAD-4 tube

CP (mg)	mL min^{-1}	Tube#	Time (min)					
			1	12	30	60	180	360
0.33	50	1	–	93.0	88.8±0.4	96.1	95.5	93.8±1.5
		2	–	nd	nd	nd	nd	2.4±1.2
		3	–	nd	nd	nd	nd	0.2±0.2
		4	–	nd	nd	nd	nd	nd
		5	–	nd	nd	nd	nd	nd
		6	–	nd	nd	nd	nd	nd
		Total	–	93.0	88.8	96.1	95.5	96.4
3.3	50	1	–	85.3	89.3±5.7	84.6	72.6	49.6±6.8
		2	–	nd	nd	nd	8.4	35.3±4.1
		3	–	nd	nd	nd	nd	nd
		4	–	nd	nd	nd	nd	nd
		5	–	nd	nd	nd	nd	nd
		6	–	nd	nd	nd	nd	nd
		Total	–	85.3	89.3	84.6	81.0	84.9
0.33	1000	1	92.9	51.3	41.3±1.4	33.4	15.2	6.5±1.6
		2	15.8	27.6	24.3±1.4	24.3	16.5	9.9±2.1
		3	1.5	11.1	12.3±2.4	16.2	15.3	11.4±1.7
		4	0.1	3.9	5.6±1.0	9.2	13.8	11.2±1.6
		5	nd	1.2	2.3±0.3	5.3	10.0	9.7±1.2
		6	nd	0.3	0.9±0.2	2.5	7.3	5.3±3.6
		Total	110.2	95.4	86.7	90.9	78.1	54.0
3.3	1000	1	83.3	45.7	33.3±0.2	13.9	8.9	2.6±0.8
		2	18.7	28.2	33.9±4.6	24.2	13.6	4.7±1.2
		3	2.1	12.4	15.7±4.1	20.9	11.3	6.5±1.4
		4	0.2	3.6	9.3±0.6	13.8	13.2	7.8±1.2
		5	nd	0.3	3.6±0.9	5.3	12.0	8.8±0.9
		6	nd	0.1	1.2±0.5	3.1	9.8	9.6±0.6
		Total	104.1	90.3	86.1	81.2	68.8	46.1

Tube 1 was closest to the inlet source of chloropicrin. nd: not detected. ±: range for duplicate measurements.

(Table 1). Total recoveries, i.e. on all six tubes together, are also shown in Table 1. In instances where no chloropicrin was detected on the sixth XAD tube (indicating that no breakthrough from the chain of tubes occurred), total recoveries ranged from 81.0% to 110.2% (mean 92.4%). On this basis, it was assumed that all of the chloropicrin added to the glass bottle was delivered to the XAD-4 tube chain (i.e. that none remained in the glass bottle at the end of the experiment).

At 1000 mL min^{-1}, chloropicrin was recovered from each of the first four tubes at the 1 min sampling time. It is clear that, even after this short time, significant breakthrough from the initial tube had occurred. Over time, the percentage of the fumigant recovered on the first tube declined dramatically, and at 360 min was just 2.6–6.5%, depending on the initial amount added. Furthermore, the amount recovered on all six tubes declined over time and at 360 min was just 54.0% (for the 0.33 mg addition) and 46.1% (for the 3.3 mg addition). Breakthrough of chloropicrin from the tubes was much less substantial at 50 mL min^{-1}, and only in one case was, albeit a small amount of, chloropicrin detected beyond the second tube. Nevertheless, recovery on the first tube tended to decline over time and, particularly at 360 min, significant breakthrough onto the second tube was observed. Consideration of the data in Table 1 shows that no breakthrough loss of chloropicrin from the chain of tubes was observed at 50 mL min^{-1}. However, as was also the case for the 1000 mL min^{-1} flow rate data, the initial amount of chloropicrin added did have an effect on breakthrough at 50 mL min^{-1}. For example, at 360 min, increasing the amount from 0.33 to 3.3 mg led to almost a halving of percentage chloropicrin recovery on the first XAD-4 tube (93.8% and 49.6% recovery, respectively).

Clearly, unless a large number of the 120 mg XAD-4 tubes is used, chloropicrin air concentrations would be significantly underestimated when a flow rate of 1000 mL min^{-1} is adopted. This would be particularly so when long sampling periods are used and high levels of chloropicrin are present. In the 'worst case' scenario here (1000 mL min^{-1}, 360 min sampling period and 3.3 mg chloropicrin addition), the recovery of just 46.1% of the chloropicrin (on all six tubes) suggests that, under such conditions, measured air concentrations would be less than half of the actual values. Under the same conditions, the data suggest that the use of a single tube would result in the measurement of only 2.6% of actual air concentrations. Subsequent errors in the calculation of chloropicrin emission losses from the soil would also, therefore, be substantial. Although all three factors (chloropicrin loading, flow rate and sampling time) exerted some control over chloropicrin breakthrough, it would appear that flow rate was most influential. For example, the data suggest that simply by using the lower flow rate, and at least one back-up sampling tube, the problem of breakthrough losses can be overcome, even with a 360 min sampling period and the high chloropicrin loading. Lowering the chloropicrin loading and reducing the sampling times did not, in themselves, produce such a strong effect under all conditions. For example, lowering the chloropicrin loading from 3.3 to 0.33 mg did not prevent breakthrough losses from the tube chain across all sampling times at 1000 mL min^{-1} (Table 1). Similarly, although reducing the sampling time did prevent breakthrough loss from the tube chain at 1000 mL min^{-1}, this occurred only when reduced to time periods of little practical use in soil-air emission studies (i.e. 1 and 12 min). As an alternative approach to preventing breakthrough losses, larger XAD-4 tubes, such as those with dimensions 150 mm × 8 mm and a sorbent mass of 600 mg (SKC, PA, USA), could be used. Their ability to mitigate breakthrough of chloropicrin at varying flow rates and sampling periods should be verified prior to use in soil–air emission experiments.

The effect of sampling time on retention of chloropicrin on the chain of XAD-4 tubes helps to elucidate the process by which breakthrough occurs. Ideally, the sorbent tubes would effectively adsorb chloropicrin and, even if the first tube became saturated with a given amount of chloropicrin, it would retain this amount and allow the excess to breakthrough to the second tube. Once this second tube became saturated, it would retain this amount and any excess would breakthrough to the third tube, and so on. However, here, such an effect is not observed. Rather, the six XAD-4 tubes appeared to act in a way analogous to a chromatography column, i.e. the chloropicrin passed through the chain of tubes as a pulse. This is particularly evident for the 1000 mL min^{-1} data, as shown in Fig. 2, where the amount of chloropicrin on each tube is expressed as a fraction of the amount on the most heavily chloropicrin-laden tube at each sampling period. It can be seen that the chloropicrin shifted, through the chain of tubes, from being primarily

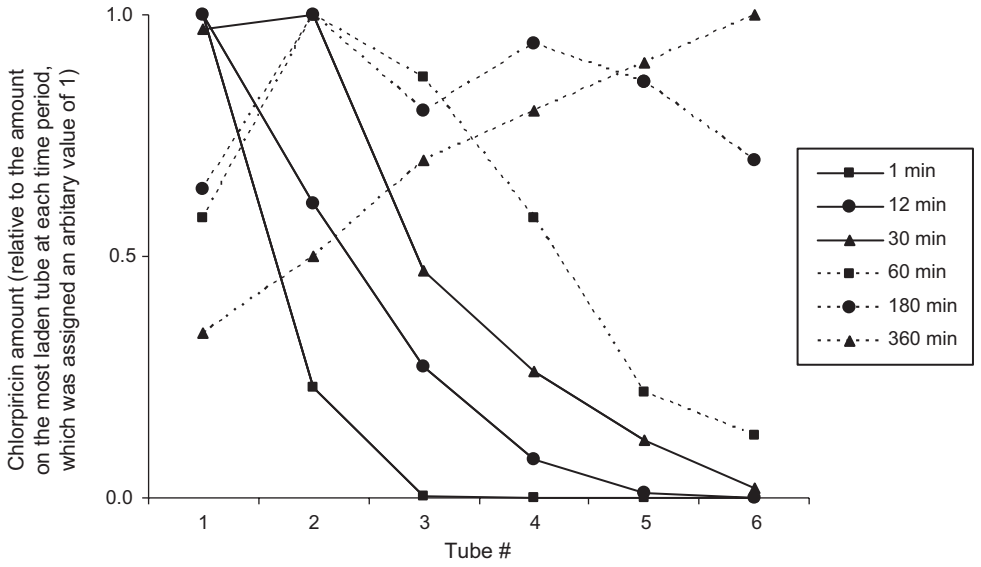

Fig. 2. Amount of chloropicrin on each XAD-4 tube (relative to the amount on the most heavily chloropicrin-laden tube at each time period) at the 1000 mL min^{-1} flow rate.

associated with the first tube in the early stages of the experiment, to being primarily associated with the sixth tube at 360 min. This indicates that a physical process, i.e. the flow of air, predominantly (but not exclusively since some, albeit reversible, sorption must have taken place) controlled the transport of chloropicrin through the tube chain.

In relating the current experiment to field or laboratory experiments designed to determine chloropicrin emissions, it should be remembered that here the fumigant was supplied to the tubes as a single spike, compared to the slower supply to be expected for emissions from a soil surface over time. Additionally, differences in environmental parameters between the breakthrough studies reported here and soil emission experiments may affect the performance of the XAD-4 tubes (e.g. differences in: ambient temperatures and moisture content of the XAD-4 resin). Nevertheless, in a laboratory soil chamber experiment, which determined emissions of chloropicrin from bed-furrow systems under realistic environmental conditions (unpublished data), we observed that collecting emissions over a 360-min period, using a single 120 mg XAD-4 tube and a flow rate of 1000 mL min^{-1}, trapped $<2\%$ of the chloropicrin initially added to the soil. At 50 mL min^{-1}, the use of a single tube trapped around 30%. At 50 mL min^{-1} but with three XAD-4 tubes connected in series, around 65% of the chloropicrin was trapped and no breakthrough onto the third tube was observed, indicating that all the chloropicrin emitted from the soil was trapped on the first two tubes (the remaining 35% was degraded in the soil). The low recoveries for single tubes at 50 and, particularly, 1000 mL min^{-1} further illustrate, under somewhat more realistic conditions than the breakthrough study, that care should be taken when choosing flow rates and sampling periods for the 120 mg XAD-4 tubes.

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