TRAPPING EFFICIENCY OF CIS-1,3-DICHLOROPROPENE BY XAD-4 SORBENT TUBES FOR EMISSION STUDIES

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Fumigants used for controlling soil pests are semi-volatile organic compounds. Measurement of emissions is necessary to evaluate the impact of soil fumigation on air pollution. Monitoring emissions often requires the use of sampling tubes filled with organic polymer sorbents to trap fumigants from gas samples, followed by extractions and analysis. Alternative fumigants to methyl bromide (MeBr) being increasingly used include 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate (MITC) generators (e.g., metam sodium). Charcoal is considered efficient in adsorbing 1,3-D, MITC, MeBr and methyl iodide (MeI). XAD-4 is effective in trapping (or adsorbing) chloropicrin, but some investigators consider XAD-4 not effective for 1,3-D and other compounds. Both 1,3-D and CP are often used in combinations for soil fumigation such as in Telone C35, Telone C60 or InLine. When emissions of the two compounds are monitored, two sampling tubes (i.e. charcoal for 1,3-D and XAD-4 for CP) are normally used. This two sampling tube design doubles the number of samples and work when compared to a single sampling tube design. In this study, we tested the efficiency of XAD-4 sorbent tubes for trapping cis-1,3-D from gas samples under various conditions in comparison with CP as well as charcoal tubes for 1,3-D and MeI. At controlled laboratory temperature, the main variables tested were flow rate and sampling time. Laboratory studies often use low flow rates (e.g., 100-200 mL/min) and field studies often require high flow rates (e.g., 1000 mL/min) for emission measurements.

Materials and Methods:

Sampling tubes tested included small XAD (ORBO 613, XAD-4, 6 x 75 mm, 80/40 mg, Supelco, Bellefonte, PA), large XAD (226-175, XAD-4, 8 x 150 mm, 400/200 mg, SKC, Eighty Four, PA), small charcoal (ORBO-32, activated coconut charcoal, 6 x 75 mm, 50 mg, Supelco, Bellefonte , PA), and large charcoal (226-09, Anasorb CSC coconut charcoal, 8 x 110 mm, 400/200 mg, SKC, Eighty Four, PA) sorbent tubes. Two set-ups were used for testing: closed containers and flow-through cells. For the containers method, the inlet of the gas sampling tube was attached to a static gas dilution bottle that contained a known amount of fumigant. The outlet of the gas sampling tube was attached to a gas tight syringe. A known volume of fumigant gas standard was withdrawn with a gas-tight syringe by passing through the sampling tube at low flow rates (~100 mL/min). For flow-through cell method, an air sampling pump was attached to the outlet of the gas sampling tube. The inlet of the gas sampling tube was attached to a 250 mL gas collecting tube (Wilmad LabGlass, Buena, NJ). A known amount of fumigant standard was injected into the gas collecting tube through a septum while a fixed flow rate was maintained. After trapping fumigants, all sampling tubes were extracted for fumigant analysis by a gas chromatograph equipped with an electron capture detector.

Results:

When equal sample volumes were withdrawn from closed containers filled with equal concentration of fumigants, we found that XAD-4 trapped 1,3-D and MeI as efficiently as CP (data not shown). This efficiency was also comparable with the trapping efficiency of MeI by small charcoal tubes. For this test, low flow rate (~100 mL/min) was used when withdrawing fumigant samples by syringe. Based on this information, we conducted flow-through cell tests on trapping efficiency of 1,3-D by XAD-4 tubes at both low and high flow rates.

Table 1 shows the trapping efficiency of 1,3-D by XAD-4 tubes in comparison with 1,3-D by charcoal tubes as well as CP by XAD-4 tubes for short sampling times (5-30 min). The data showed that XAD-4 can trap 1,3-D effectively (>92%) by 1 sampling tube at the amount of fumigants tested. The amount of fumigants trapped by the 2nd tube at lower flow rate (100-200 mL/min) was minimal. At high flow rates (500-1000 mL/min), large XAD-4 tubes can trap 1,3-D as effectively as charcoal tubes for the short sampling time. The trapping efficiency of 1,3-D by XAD-4 is also comparable with CP.

To verify the findings, we further tested the trapping efficiency of 1,3-D and CP by XAD-4 tubes for longer sampling times, up to 3 h (Figs. 1 and 2) at a flow rate of 1000 mL/min. Several tests showed that the XAD-4 tube recovered average 92% at 10 min sampling time indicating reasonable high trapping efficiency. Recovery of 1,3-D was much lower if the tubes were flushed for 3 h from 1st tube as indicated by the increasing amount of 1,3-D recovered from the 2nd tube. There was also a total net loss from the two sampling tubes tested. Similar findings were found for CP, i.e., subsequent fumigant loss was found from the 1st sampling tube for the 3 h sampling time, except that the recovery for CP was 5-20% higher than 1,3-D. The results indicate that 1,3-D trapping efficiency by XAD-4 sampling tubes may be generally lower than for CP especially for longer sampling periods. Longer sampling time (e.g., 3 h) lead to substantial fumigant loss from the sampling tubes regardless of the fumigants and flow rates (data not shown for low flow rates).

Summary:

XAD-4 sampling tubes can be used for trapping 1,3-D from gas samples with greater than 90% recovery at both low and high flow rates (up to 1000 mL/min) for short sampling time (5-30 min). However, longer sampling times lead to significant loss (>10% for 3 h sampling time) of fumigants from the first XAD-4 sampling tubes regardless of flow rates and fumigants. Short sampling intervals or a series of sampling tubes may be used to achieve high trapping efficiency of fumigants by XAD-4 sampling tubes. Otherwise, loss of fumigants from the sampling tubes should be considered and adjusted to avoid underestimation of emissions especially under long sampling time measurements.

Table 1. Trapping efficiency of XAD-4 tubes for cis-1,3-ichloropropene (1,3-D) in comparison with chloropicrin (CP) and charcoal tubes for short sampling times.

Sampling tubes*	Chemical (amount)	Flow rate (mL/min)	Sampling time (min)	Recovery (%) Average	Std. dev.
Small XAD in series	Cis-1,3-D (0.275 mg)			(n=2)	
1		100	10	98.9	5.2
2				0.0	0.0
1			20	96.7	1.4
2				0.0	0.0
1			30	98.7	9.9
2				0.1	0.1
1		200	10	94.9	10.9
2				0.1	0.1
1			20	93.7	6.3
2				0.3	0.1
1			30	97.3	4.8
2				0.6	0.1
Large XAD	Cis-1,3-D (0.550 mg)			(n=3)	
1		500	10	94.8	6.5
1			20	92.9	4.2
1		1000	5	97.5	1.8
1			10	94.5	8.1
Large XAD	CP (0.640 mg)			(n=3)	
1		500	10	97.2	1.8
1			20	97.4	5.3
1		1000	5	87.8	10.7
1			10	90.4	11.0
Large charcoal	Cis-1,3-D (0.648 mg)			(n=3)	
1		500	10	96.4	4.8
1			20	91.4	7.1
1		1000	5	97.1	3.8
1			10	94.6	9.0

* When used in series, the tubes were connected in order of the no.

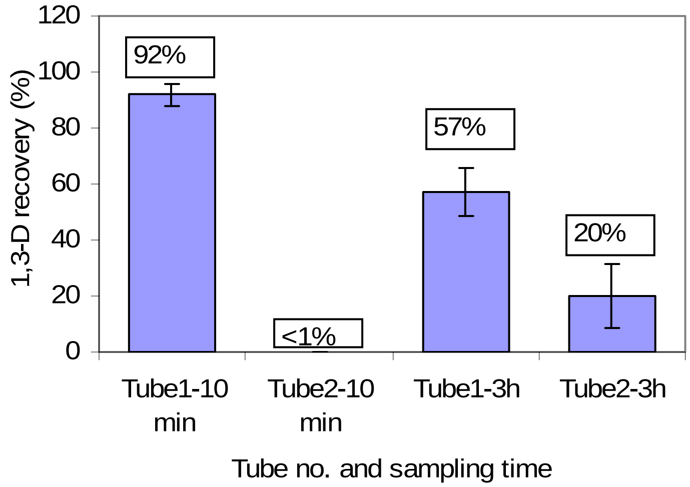

Figure 1. Cis-1,3-dichloropropene (1,3-D) trapping efficiency by XAD-4 tubes (tube1=large XAD and tube2=small XAD, connected in series) at 1000 mL/min for 10 min and 3 h sampling time (n=6). The amount of cis-1,3-D tested was 0.688 mg.

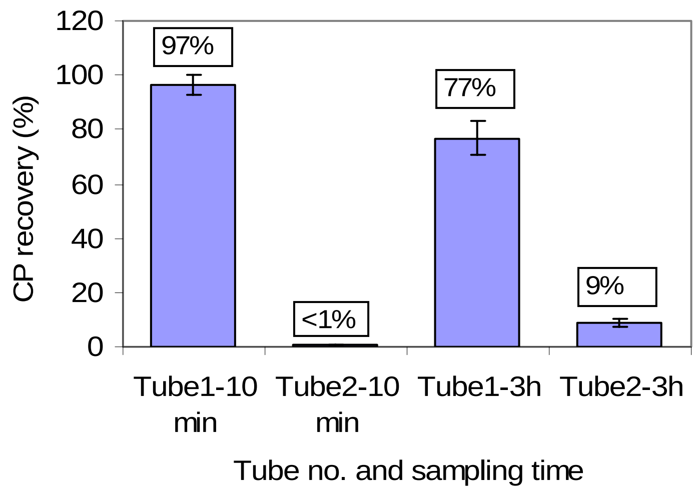

Figure 2. Chloropicrin (CP) trapping efficiency by XAD-4 tubes (tube1=large XAD and tube2=small XAD, connected in series) at 1000 mL/min for 10 min and 3 h sampling time (n=3). The amount of CP tested was 0.715 mg.