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Solvent Evaporation in an Isolated Subsurface Structure: An Unrecognized and Underappreciated Risk

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Abstract: Isolated subsurface structures readily collect solvents spilled onto surrounding surfaces or poured into opening(s) in the manhole cover. Fatal overexposures and fires/explosions have occurred following these events. This work documents evaporation of 10 mL of lacquer thinner from a paper towel positioned near the base of a vertically oriented precast concrete chamber (volume = 2.5 m^3) and exchange through opening(s) in the manhole cover monitored using a Photoionization Device (PID) sensor. A sixth order polynomial fitted by Microsoft Excel best describes the process of evaporation and dispersion in the airspace and exchange with the external atmosphere. Restoration of the uncontaminated atmosphere can require 48 hours or more under these conditions. A manhole cover containing a single opening is most likely to retain vapor for the longest period, and one with two circumferential openings opposite each other is least likely. Results presented here argue for the involvement of individuals made knowledgeable by education, experience, and training in confined spaces to address this unrecognized and underappreciated risk. Optimizing ventilation induced by natural forces in isolated subsurface structures is a natural application of the NIOSH (National Institute for Occupational Safety and Health) Prevention through Design initiative.

Keywords: confined space; isolated subsurface structure; natural ventilation; solvent evaporation; vapor accumulation and dispersal

1. Introduction

Expansion of the subsurface infrastructure following increased urbanization throughout the 20th century has provided a solution to proliferation and congestion of utilities intended to service buildings located along streets. At the same time, isolated and networked structures have created the unintended consequence of confining gases and vapors that have migrated from the soil and vapors formed from evaporation of volatile liquids [1,2]. Ignitable and explosible concentrations of gases and vapors in the presence of sources of ignition have led to many fires and explosions [3–5]. More recent attention has developed because of concern about vapor intrusion into subsurface parts of buildings such as void spaces and parking garages [6–8].

The exposure of workers to vapors and gases confined in the airspaces occurs at the time of opening of manholes and hatches providing access to subsurface structures [9–11]. Many if not all of the structures mentioned in the previous discussion meet generally accepted criteria for classification as confined spaces [12]. Confined spaces typically are structures in which people do not or cannot routinely work and are not designed for entry and work. However, because of the need to perform activity in these structures, they become workspaces.

Preparation for entry into subsurface chambers poses considerable risk because associated activity involves partial or full removal of the manhole cover or access hatch and first contact with the atmosphere confined in the airspace of the structure [9]. An analogous situation involving tanks and similar structures occurs during hatch opening and sampling [13]. Workers entering previously closed structures must establish ambient conditions in the airspace as part of preparation. This can necessitate partial or full removal of the manhole cover or access hatch in order to insert the probe of the atmospheric testing instrument or in some cases the entire instrument in order to assess the condition of the atmosphere and the duct of the portable ventilation system. Availability of opening(s) in manhole covers and access hatches is essential to safety [10,11,14].

The literature contains little information concerning ventilation of isolated subsurface structures induced by natural forces prior to or during preparation for entry and work [9–11,14–19]. Investigators at the Bureau of Mines published the first articles using gas mixtures maintained under equilibrium conditions [15–18]. More recently, Wiegand and Dunne [9] examined ventilation of a subsurface structure induced by natural airflow through an open or partially open manhole.

McManus [10] and McManus and Haddad [11,20] studied ventilation induced by natural forces of a mixture of exhaust gases from a small engine and contained in a subsurface concrete vault through opening(s) in the manhole cover. These studies indicated that ventilation of such spaces through one or more openings in the manhole cover is a continuous, naturally occurring phenomenon. Results from these studies parallel those obtained by investigators at the Bureau of Mines [10,11,15–19]. In addition, the atmosphere in the airspace was rapidly and thoroughly well-mixed, as indicated by instrument readings [10,11]. The concentration of CO was almost identical at almost every moment in time at different levels in the structure, as measured once per minute by datalogging instruments. Video indicated that the atmosphere rotated in apparent circular motion within the airspace of the structure.

This study reports on evaporation of a lacquer thinner [21] introduced into the same isolated subsurface structure as might occur following a spill on the surface or surreptitious introduction. Several simultaneous processes follow: evaporation of the liquid to form vapor, migration and accumulation of vapor in the airspace, and transfer from the airspace to the external atmosphere. The preceding processes (evaporation, migration, and accumulation) accompany and may complicate the exchange of the atmosphere in the airspace with the external atmosphere [10,11,20]. Concentration of vapor in the airspace reflects the balance between vapor formation until exhaustion of liquid and vapor loss in air exchanged from the airspace. Usually, information concerning the composition, concentration, and consequence of the atmosphere that develops during these events only emerges in summaries following incidents [1,2,22–26].

2. Materials and Methods

This work occurred in the yard of a construction company located in Burnaby, British Columbia, a suburb of Vancouver, and involved an isolated, subsurface precast concrete box-like structure measuring about 1.5 m in height with a volume about 2.5 m^3 [10,11]. The yard also contained equipment and vehicles used by work crews. Construction crews left the yard in the vehicles and equipment early in the morning and returned late in the afternoon.

Air monitoring occurred using the Photoionization Device (PID) sensor in readily available, commercial four-gas testing instruments (GfG 460, GfG Instrumentation, Ann Arbor, MI, USA) [27–29]. The position of the instruments on the stand was 114 cm (45 in) and 38 cm (15 in) above the bottom, respectively. Hence, the instruments were about 76 cm apart from each other in the vertical direction. The sensors were calibrated using isobutylene and report concentration in "isobutylene units." Where the focus of the study is the process and not discrimination of specific contaminants as in this situation, detection of the signal is all that has importance. The datalogger stored measurements once per minute. Previous experience had shown the absence of abnormal atmospheric conditions in the absence of contamination [10,11]. The yard contained no sources of contamination near the test chamber. Measurement occurred at two heights in the airspace over the period of the test (Figure 1). The instruments were calibrated according to recommendations of the manufacturer.

Figure 1. Equipment used to measure evaporation of solvent. Equipment included two instruments containing Photoionization Device (PID) sensors and two instruments for measuring temperature and humidity. The aluminum pie plate containing the paper towel onto which is poured the lacquer thinner is also visible.

Temperature and relative humidity were measured using datalogging instruments (Reed ST-171 Data Logger, Reed-Direct.ca, Ste-Anne-de-Bellevue, QC). The dataloggers stored measurements once per minute. Air velocity (speed) and external temperature were measured just above the surface of the ground as described previously [10,11]. (Discussion of the latter results will occur in a subsequent study.)

Each test followed the level of vapor contained in the airspace of the structure during and following evaporation of 10 mL of lacquer thinner [21]. The lacquer thinner was poured onto a paper towel folded in four and positioned on an aluminum pie plate located near the bottom of the instrument stand (Figure 1) immediately prior to inserting the instrument stand into the space. The surface of the paper towel was about 15 cm from the position of the sensors in the lower instrument. The instrument stand was removed from the space 24 hours after the start of the test. Removal of the instrument stand permitted the chamber to self-ventilate for a minimum of 24 hours (depending on the calendar) prior to the start of the subsequent test. The instruments were recharged and the dataloggers downloaded.

The response chart for the PID sensor [29] indicates that vapor of toluene, MEK (methylethyl ketone), and acetone are detected. The relative response factors are 0.53, toluene; 0.9, MEK; and 1.2, acetone, respectively. The true concentration of a substance is the value presented by the instrument multiplied by the relative response factor. Hence, the concentration of vapor of pure liquid is the product of the (instrument reading) × (Correction Factor). Values of the Correction Factor <1 indicate that the molecule is more sensitive to detection by this method than is isobutylene. The Correction Factors for the ingredients in lacquer thinner indicate that this solvent is almost ideal for use in a study of evaporation into the airspace of an isolated subsurface structure.

This study commenced in early June 2016 and terminated early in August 2016—the warm months of the year. These dates provide points of reference within which discussion will occur. The tests started around 07:00 and progressed until the batteries in the instruments failed. The instruments operated up to 16 hours. The tests examined impact of number/area and spacing of openings in the manhole cover and ambient temperature on change in concentration of contaminant. A canopy was used to prevent entry of rain and exposure of the work area to the sun. The interior of the structure typically was dry during the tests. The instrument stand was removed from the space 24 hours after the start of the test. Removal of the instrument stand permitted the chamber to self-ventilate for a minimum of 24 hours (depending on the calendar) prior to the start of the subsequent test. The instruments were recharged, and the dataloggers downloaded.

The manhole access cover had seven openings—six around the circumference and one in the center. A single opening in the center and two openings (center and circumference or two circumferential openings opposite each other) were selectively plugged to investigate the role of the area of the openings on exchange of air and concentration of substance detectable by the PID sensors.

Statistical analysis occurred using IHSTAT, an application for Microsoft Excel (Microsoft Corporation, Redmond, WA, USA) developed and published by the American Industrial Hygiene Association [30]. IHSTAT determines whether samples are normally or lognormally distributed through goodness of fit tests for determining compliance with regulatory standards and guidance values. AIHA [31] recommends use of the lognormal distribution for data that appear to be lognormally distributed and for data that are better represented statistically as lognormally distributed or represented by both the normal and lognormal distributions. Data presentation in this document reflected this recommendation.

3. Results

Results obtained during these tests are divisible by the level of the detector in the space relative to the position of the pie-plate holding the evaporating solvent (Figure 1) and by the number and position of opening(s) in the manhole cover. Opening(s) in the manhole cover ranged from one (center only) to two (center and circumference or two circumferential openings opposite each other). The outdoor environment introduced considerable uncontrollable variability into the situation.

Figures 2 and 3 show the composite of the upper and lower level curves for one opening. Figures 4 and 5 show composite curves for two openings (center and circumference), and Figures 6 and 7 for two openings (circumferential openings opposite each other), respectively. The signal detectable by the instruments increased from zero, sometimes rapidly but more often gradually, then plateaued with a single peak, and gradually decreased. For a given day, the signal obtained from the lower instrument (the one closer to the source) consistently exceeded the signal obtained from the upper instrument during the period of operation. Similarly, the time at which the peaks occurred generally was similar for the two instruments. Upper level signals detected during testing of a single opening in the manhole cover were generally smooth, whereas those obtained using two openings, while sometimes smooth, often contained rapid fluctuations (choppiness). Choppiness occurred most consistently in measurements obtained during July. Choppiness in lower level measurements was less extreme than in upper level measurements. Battery life was insufficient to capture the signals during the final decrease to zero. The curves showed no obvious indicator about cessation of evaporation of solvent.

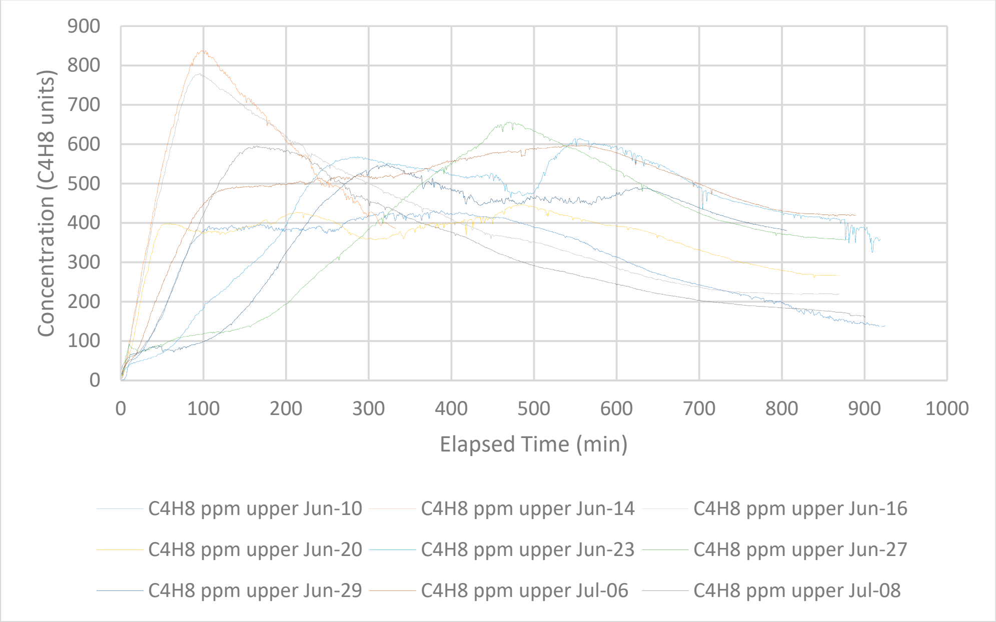

Figure 2. Upper level composite curves, single opening.

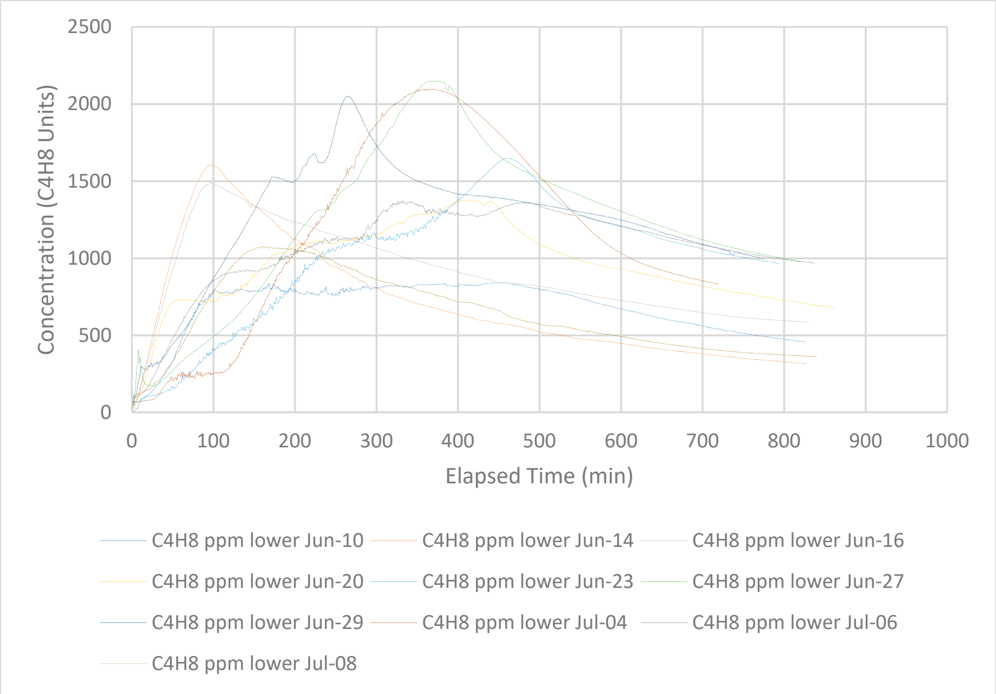

Figure 3. Lower level composite curves, single opening.

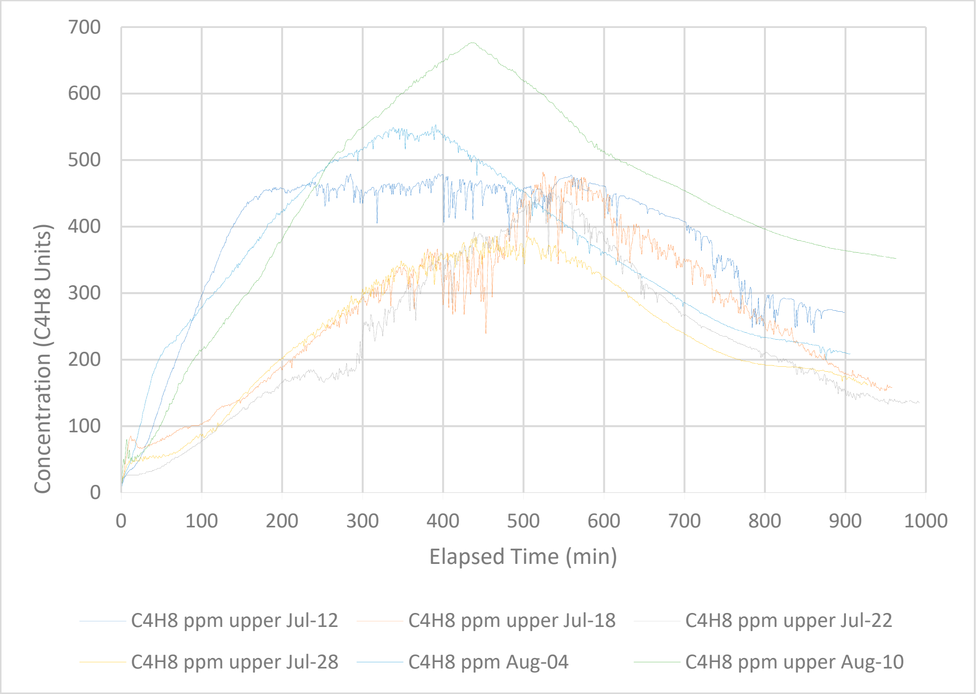

Figure 4. Upper level composite curves, center and circumferential openings.

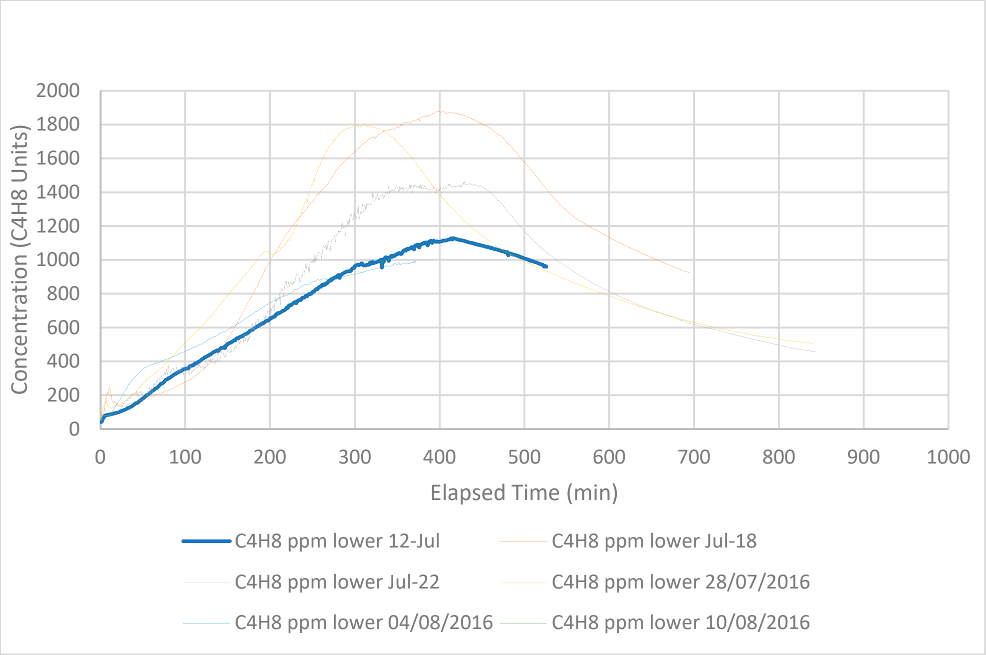

Figure 5. Lower level composite curves, center and circumferential openings.

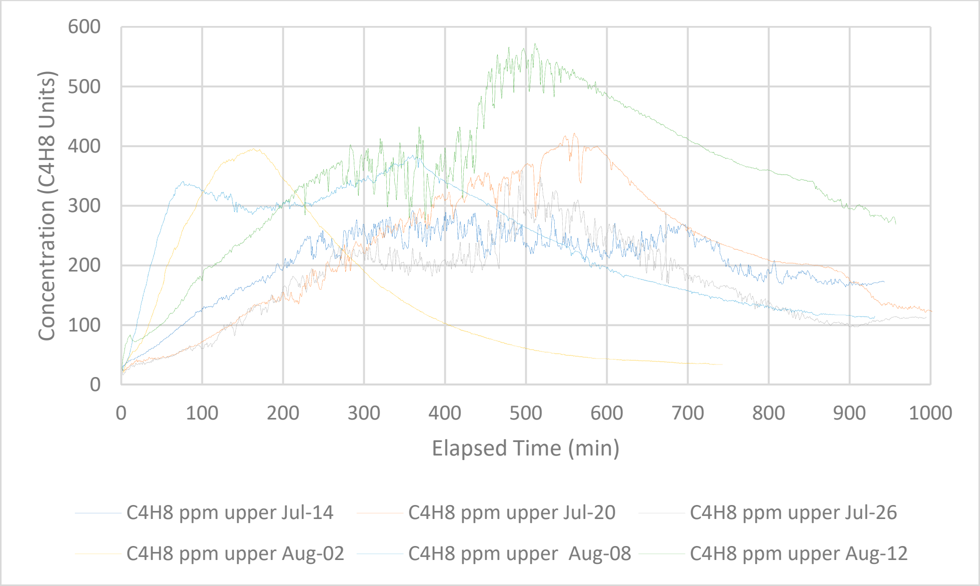

Figure 6. Upper level composite curves, two circumferential openings opposite each other.

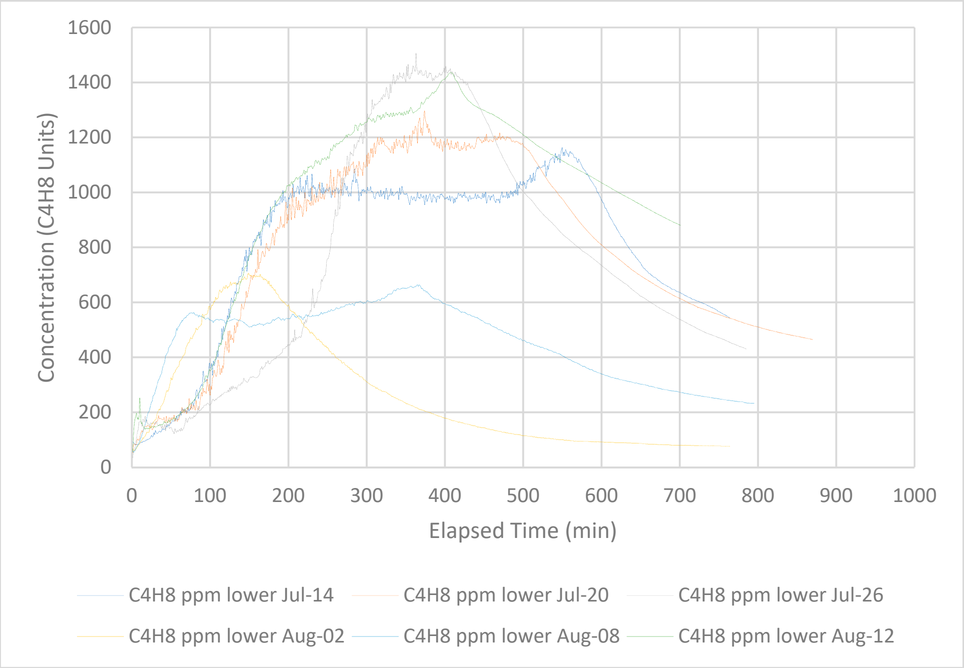

Figure 7. Lower level composite curves, two circumferential openings opposite each other.

Inspection of the curves suggested that the signal could persist for at least 24 hours. A faint aromatic odor was sometimes detectable the following morning (24 h after the start of the test) in about 70% of the situations when a single opening was present. When two openings were present, the faint odor was detectable in about 30% (center and circumference) and 50% (circumferential only), respectively. The faint aromatic odor was sometimes detectable 48 hours after the start of the test when the instruments were reinserted for the subsequent test. During preparation of the equipment, an aromatic odor was detectable only at the time of pouring the lacquer thinner onto the paper towel.

The readily detectable aromatic odor indicated the presence of toluene. The odor threshold for toluene is as low as 0.16 ppm with a mean of 1.6 ppm [32]. A person with normal ability to detect aromatic odor likely would have little difficulty detecting the presence of toluene vapor during these activities. These observations suggest that toluene was present during most if not all of the process studied here. Emission of the atmosphere from the interior of a subsurface chamber occurs on opening the manhole cover [9–11].

Figures 2 and 3 (single opening) show apparent superimposition of more than one type of behavior. In the first type (Figure 2), the signal increased rapidly, formed a sharp peak at 100 minutes of elapsed time, and decreased gradually. More typically, the upper composite curves (Figure 2) increased gradually from zero to a broad peak and then decreased gradually toward zero. The lower composite curves for the single opening (Figure 3) initially rose rapidly from zero and then rose less rapidly to a defined peak and decreased gradually toward zero. More typically, the behavior of the curves was considerably less predictable starting with the upper composite curves. Location of the peaks of concentration shifted by day.

The upper composite curves for the center and circumferential openings (Figure 4) initially rose gradually from zero or sometimes rapidly and then rose less rapidly to a sharp or broad peak or to a plateau and decreased gradually toward zero. The upper composite curves exhibited choppy behavior during the month of July. The lower composite curves for the center and circumferential openings (Figure 5) rose gradually from zero to a broad peak and decreased gradually toward zero. The shapes of the curves were approximately symmetrical.

The upper composite curves for the two circumferential openings opposite each other (Figure 6) rose gradually or sometimes rapidly from zero to a broad peak and decreased gradually toward zero. One of the samples showed distinctly different behavior from the others. The lower composite curve for the two circumferential openings opposite each other (Figure 7) rose rapidly from zero to a broad peak or a plateau and decreased gradually toward zero.

Figures 8 and 9 show the composite curves calculated using the arithmetic and logarithmic average, respectively, of the data points for a particular moment of elapsed time during all of the days. Under both calculation schemes in Figures 8 and 9, the upper composite curve for each of the conditions rose gradually to a broad flat peak and decreased gradually. Under both calculation schemes in Figures 8 and 9, the lower composite curve for each of the conditions rose gradually to a broad peak and decreased gradually

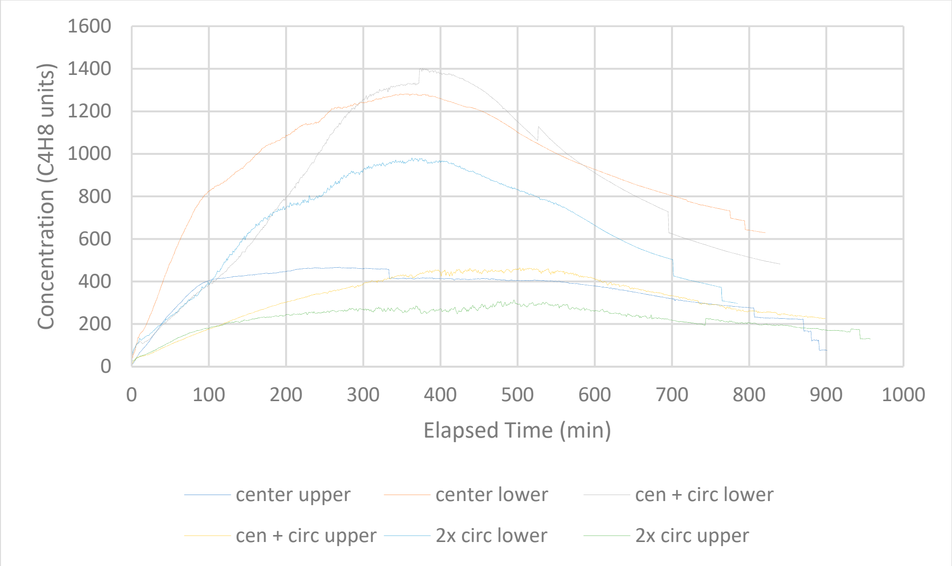

Figure 8. Arithmetic mean composite, all conditions. (The abrupt changes in concentration reflect artifacts created from use of data from a smaller number of curves in calculating average concentrations. The instruments did not always operate for the longest possible time due to limitation in performance of individual batteries.)

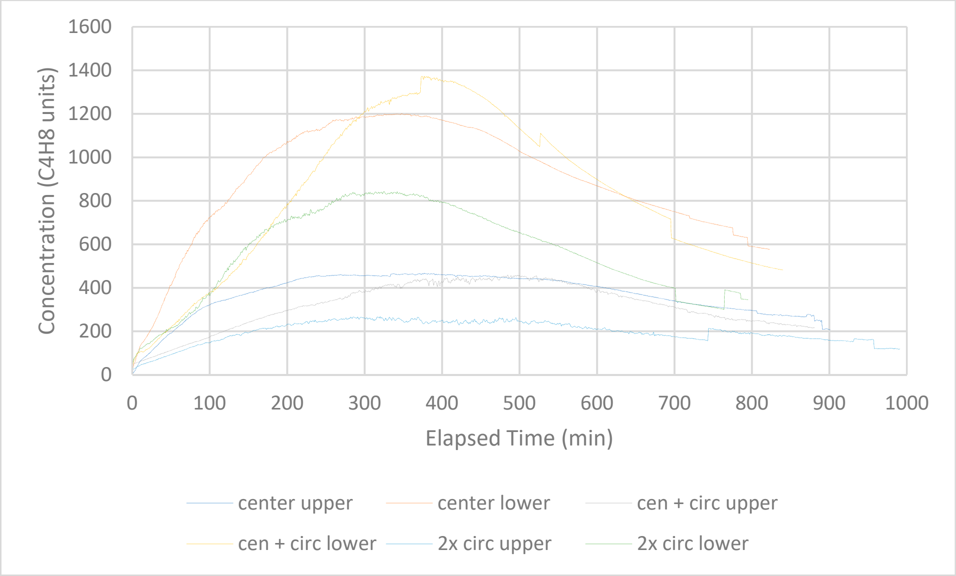

Figure 9. Logarithmic mean composite, all conditions. (The abrupt changes in concentration reflect artifacts created from use of data from a smaller number of curves in calculating average concentrations. The instruments did not always operate for the longest possible time due to limitation in performance of individual batteries.)

Table 1 summarizes characteristics of the composite curves.

Table 1. Summary of data from composite fitted curves.

Characteristic	**Arithmetic Mean of Data Points**		**Antilog of Logarithmic Mean of Data Points**	
	Upper Position	**Lower Position**	**Upper Position**	**Lower Position**
Single opening				
Time of peak (min)	273	381	379	350
Peak height	467	1280	466	1200
Peak height ratio	2.74		2.58	
Composite equation *	$x^3 = 0.0001$ $x^2 = -0.0359$ $x^1 = 6.4911$ $x^0 = 0$	$x^3 = 0.0002$ $x^2 = -0.0654$ $x^1 = 12.285$ $x^0 = 0$	$x^3 = 6 \times 10^{-5}$ $x^2 = -0.0227$ $x^1 = 4.6924$ $x^0 = 27.56$	$x^3 = 7 \times 10^{-5}$ $x^2 = -0.0291$ $x^1 = 9.2505$ $x^0 = 0$
R^2 value	0.98	0.9965	0.9947	0.9984
Two openings, center + circumference				
Time of peak (min)	445	379	517	379
Peak height	454	1402	457	1372
Peak height ratio	3.09		3.00	
Composite equation *	$x^3 = 3 \times 10^{-5}$ $x^2 = -0.0091$ $x^1 = 2.4615$ $x^0 = 0$	$x^3 = 0.0001$ $x^2 = -0.01$ $x^1 = 3.8647$ $x^0 = 0$	$x^3 = 3 \times 10^{-5}$ $x^2 = -0.0077$ $x^1 = 2.1149$ $x^0 = 0$	$x^3 = 0.0001$ $x^2 = -0.0112$ $x^1 = 3.9084$ $x^0 = 0$
R^2 value	0.9969	0.9926	0.9957	0.9938

Table 1. *Cont.*

Characteristic	**Arithmetic Mean of Data Points**		**Antilog of Logarithmic Mean of Data Points**	
	Upper Position	**Lower Position**	**Upper Position**	**Lower Position**
Two circumferential openings opposite each other				
Time of peak (min)	498	365	298	316
Peak height	310	980	265	841
Peak height ratio	3.16		3.17	
Composite equation *	$x^3 = 6 \times 10^{-5}$ $x^2 = -0.0189$ $x^1 = 3.2844$ $x^0 = -8.2518$	$x^3 = 2 \times 10^{-5}$ $x^2 = -0.007$ $x^1 = 4.6545$ $x^0 = 0$	$x^3 = 2 \times 10^{-5}$ $x^2 = -0.0084$ $x^1 = 2.2235$ $x^0 = 0$	$x^3 = -1 \times 10^{-4}$ $x^2 = 0.014$ $x^1 = 3.3085$ $x^0 = 0$
R^2 value	0.9705	0.9943	0.9613	0.9904

* Notes: Excel treats these equations with contributions to x^6 terms. Terms higher than x^3 make negligible contributions. In these equations, the y-value corresponds to concentration and the x-value to elapsed time (min).

Microsoft Excel provides best fit of the data points as a sixth order polynomial. Terms higher than x^3 make negligible contributions and can be neglected from further consideration. The y-term is the arithmetic mean (or the antilogarithm of the logarithmic mean) concentration in isobutylene units and the x-term is the time that has elapsed since the start of measurement. The logarithmic mean and the antilogarithm of the logarithmic mean concentration were calculated because of the variability in the curves observable from visual inspection of the composite plots (Figure 2 to Figure 7). Inspection of the values from the composite fitted curves (Table 1) indicates that the R^2 values are almost the same in most cases. There appears to be no clear benefit offered by one method of calculation over the other.

Figure 10 shows the relationship of the difference in concentration between the lower and upper levels inside the chamber for the arithmetic mean composite curves (Figure 8). The curves in Figure 10 reflect the shape of the lower level curves contained in Figure 8. This occurred because of the flatness intrinsic in the upper level curves. The difference is calculated by subtraction of essentially a constant value through most of the duration of the process. A non-zero value existed at all times during these studies as shown in Figure 2, Figure 4, and Figure 6, which was confirmed on examination of the raw data. This confirms that evaporation was sufficient at the beginning of all tests to be detectable by the instruments regardless of the level of residual toluene in the air detectable by nose as an odor following purging of the airspace of the structure after removal of the instrument stand containing the source of lacquer thinner.

Figure 11 shows the ratios of the lower level values to the upper level values for the arithmetic mean composite curves (Figure 8). The highest lower-to upper ratios, meaning difference in concentration between the lower and upper level devices, occurred when two circumferential openings were present in the manhole cover. This curve exhibits choppiness throughout the duration but more so during higher lower-to-upper ratios. One opening in the center of the manhole cover produced a curve of similar shape in which the ratio was consistently less than that for the two openings in the circumference. This curve contains no choppiness. Two openings (center and circumference) produced a curve with features of the other types. These included a higher ratio than that of the center opening during the first half of the process and a lower ratio during the second. This curve contains choppiness throughout the duration but more so at higher lower-to-upper ratios.

Difference in concentration between lower and upper level (Figure 10) and the ratio of these values (Figure 11) relate to the potential for evaporation of solvent, dispersion into the airspace and ventilation of the structure induced by natural forces [10,11]. Peak values (tabulated in Table 1) provide an indication of the quantity of hydrocarbon vapor in the air at any point during the process observable within the limitation of the batteries in the instruments. The highest concentration at the upper level curves is very difficult to estimate since this remained almost constant once the broad plateau formed.

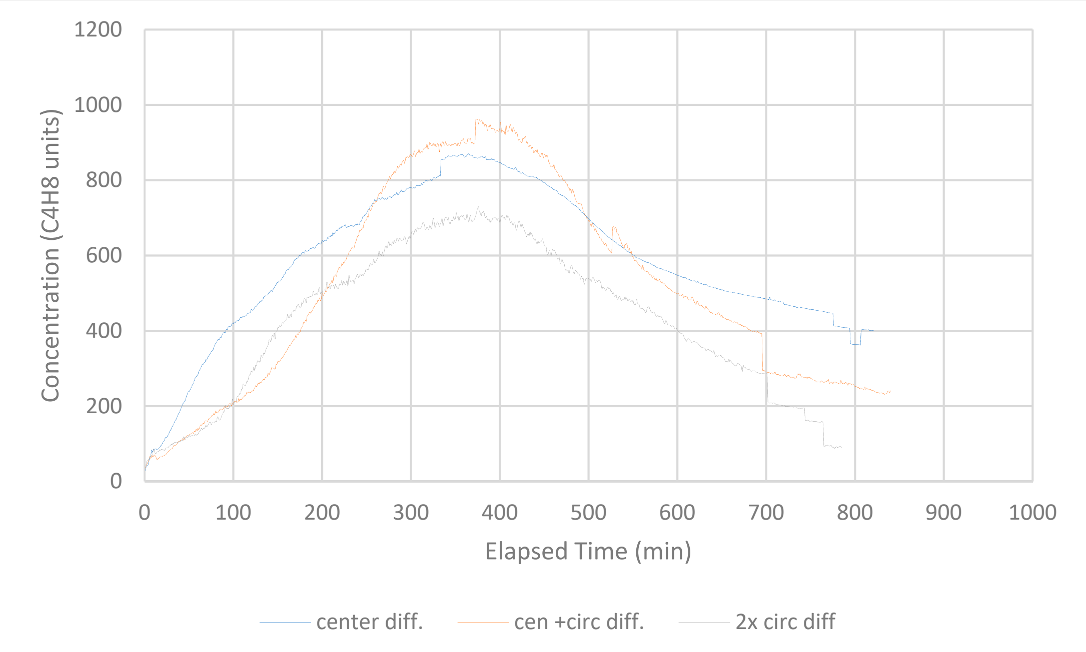

Figure 10. Difference in concentration between the lower and upper level in the chamber. (The abrupt changes in concentration reflect artifacts created from use of data from a smaller number of curves in calculating average concentrations. The instruments did not always operate for the longest possible time due to limitation in performance of individual batteries.)

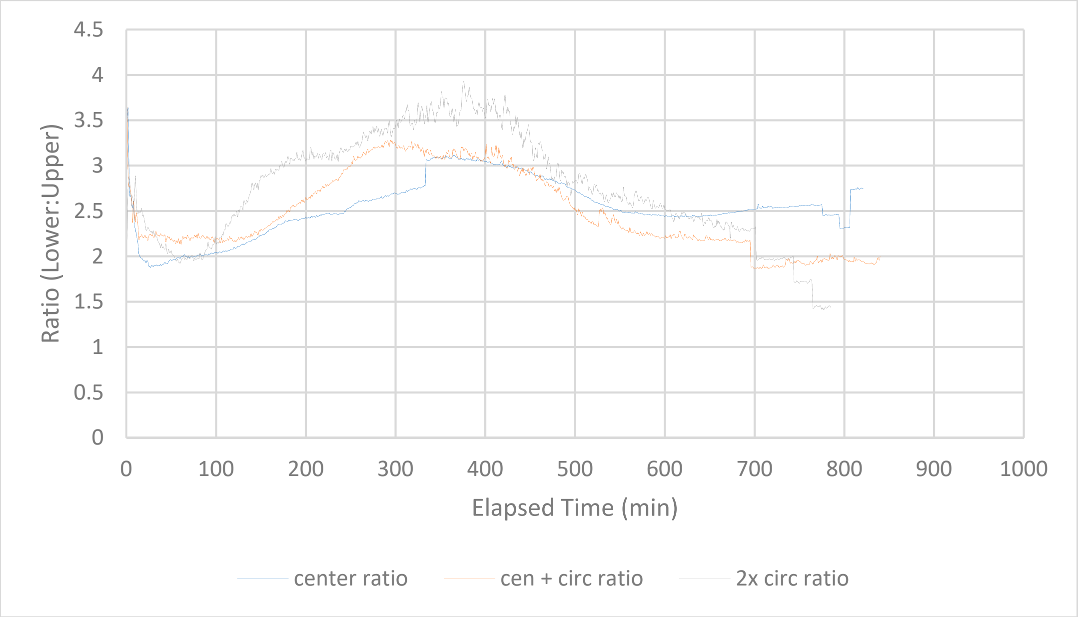

Figure 11. Lower-to-upper ratio of concentrations. (The abrupt changes in concentration reflect artifacts created from use of data from a smaller number of curves in calculating average concentrations. The instruments did not always operate for the longest possible time due to limitation in performance of individual batteries.)

4. Discussion

Ventilation induced by natural forces is an important contributor to minimization of contamination of airspaces contained within isolated subsurface structures [9–11]. Removal of contamination (vapor) from the airspace by ventilation induced by natural forces is essential in order to minimize risk of exposure of workers when opening the manhole cover to prepare the space for entry and to minimize risk of fire and explosion posed to bystanders and workers when walking along surfaces containing manhole and other access covers.

The rapid appearance of vapor at the upper level in Figure 2, Figure 4, and Figure 6 at a level detectable by the instruments when the odor of residual vapor in the airspace was not present at the start of the test suggests that exchange of the atmosphere in the airspace with the outdoor atmosphere commenced within the first minute after installing the instrument stand into the structure. The rapid appearance of vapor at the lower level in Figure 3, Figure 5, and Figure 7 suggests that circulation of air in the airspace was detectable within the first minute after installing the instrument stand into the structure. Response of the instruments at different levels within the structure in this manner suggests the existence of some type of air circulation or mixing process involving the entire volume of air [10,11].

Visually, there appear to be two or even three groups of curves in the composite for the single opening in the manhole cover. To the extent possible given the outdoor location, the conditions were replicated from test to test subject to the vagaries of the weather. Tests of the single opening in the manhole cover occurred sequentially one after the other. Tests involving two openings in the manhole cover (center and circumference versus two circumferential openings opposite each other) alternated.

Previous work examined removal of CO from the airspace through the process of exchange with the external atmosphere [10,11]. The present work adds the complication of evaporation from liquid to vapor to exchange. Previous work occurred throughout most of the year (2015) and reported on the concentration of CO at different heights in the structure. Typically, the concentration decreased in orderly fashion in a band such that readings from individual instruments were almost identical for any moment in time. Concentrations shown by the uppermost instrument, sometimes the second instrument from the top and rarely the third instrument decreased abnormally fast and showed considerable "vertical jaggedness" in several tests during June, July, and early August. This abnormality occurred unpredictably. Concentration reported by the lowermost instrument decreased in the orderly fashion reported above. The lowermost instrument in the study of CO occupied the same position as the lower instrument in evaporation of solvent.

This effect may be affecting results obtained in the tests reported here for work performed in June, July, and August of 2016 using the same chamber. The occurrence of the two anomalies may be related since other parts of these studies indicated the occurrence of annually repeating patterns. If so, they affect the combination of evaporation and exchange differently from exchange only. Ventilation in an outdoor location reflects influences potentially including difference in temperature between different levels in the chamber and the external surroundings and air movement above the ground. Day-to-day weather is an additional uncontrollable influence.

Temperatures at different levels in the chamber and externally indicated that they follow annual patterns [10]. As well, superimposition of external temperature measured just above the ground with the temperatures recorded at two heights in the chamber indicates that the patterns do not superimpose in a repeatable pattern day by day. One of the articles in this series indicates that air moves across the surface of the ground [20]. Velocity fluctuates unpredictably and rapidly as shown in measurements obtained once per second. Velocity fluctuations follow annual patterns.

The curves shown in Figure 2 to Figure 11 provide no obvious indicator about the end of evaporation of the solvent and the period of purging to remove the remaining contamination. The raw data and confirmed in Figures 8 and 9 indicated that there were no zero readings on the dataloggers. Evaporation was immediately detectable by nose as an aromatic odor likely due to the presence of toluene [21,32].

Figure 10 shows that detection of solvent vapor by the lower instrument occurred immediately. The lag time between pouring the solvent onto the paper towel following activation of the instruments, lowering the instrument stand into the chamber and reclosing the manhole cover was about 1 min. In providing the difference in concentration between the lower and upper level, Figure 10 provides an indication of the effectiveness of mass transfer between the evaporating surface and the external atmosphere. The large difference in concentration when center and circumferential openings were studied compared to other configurations could indicate effectiveness of ventilation induced by natural forces. That is, a large difference in concentration could indicate depletion of vapor in the upper level compared to production of vapor at the lower level. The smaller difference in concentration for the single opening and the two circumferential openings indicates more similar concentrations between the lower and upper level. This could indicate less effective air exchange between the upper level atmosphere and the external atmosphere. Since the difference curves for the three conditions were similar in shape and that other factors remained constant except for the number and location of openings in the manhole cover, this seems to be a reasonable conjecture.

The curve for the single opening remained consistently above the curve for the two circumferential openings. The curve for the center and circumferential opening followed a different, unpredictable pattern compared to the other two conditions. Study of center and circumferential openings and two circumferential openings occurred on alternate days. Hence, these studies experienced similar weather conditions and other constant conditions. This would suggest that evaporation of liquid and dispersion and exchange of vapor in these two cases reflected ventilation of the space induced by natural forces under these conditions. This could apply to the curve produced for the single opening although with less confidence because this work occurred at the beginning of the period of study but involved a large number of tests. The decrease in difference between the lower and upper level occurring after 400 minutes affected all conditions almost equally. This likely shows the impact of decreasing quantity of solvent available for evaporation and decreasing concentration of vapor at the upper level available for exchange with the external atmosphere.

Figure 11 shows the ratio of lower-to-upper concentration. The curves for the three conditions show immediate high ratios followed by rapid decrease and subsequent recovery and final decrease. Ratios indicate relative relationships between numbers. The initial high ratios reflect the imbalance between production of vapor on the surface of the liquid and detection by the instrument close by (about 15 cm) and dilution and transfer to the upper level in the airspace where exchange with the external atmosphere occurs. Almost always during the process, the concentration at the level of the lower instrument was at least a factor of 2 greater than the concentration at the upper instrument even though the absolute level changed with time. By contrast, during ventilation of a mixture of CO introduced into the same space at time 0 with no further addition (Generation Rate = 0), concentrations measured by instruments at four levels remained almost equal for any moment in time [10,11]. The situation during this study (Generation Rate = decreasing value) shows a different pattern. The pattern observed in this study is consistent with ongoing production of vapor during the total time of operation of the instruments. A ratio of 1.0 would be consistent with equal concentrations observable at lower and upper levels. This result suggests that evaporation of solvent continued beyond the time observable during the tests because of limitations of the batteries in the instruments.

Evaporation of a solvent depends on temperature [33]. The minimum temperature to which the liquid in the isolated structure was exposed during late spring was around 13 °C. Development of a hazardous atmosphere in the airspace depends on rate of evaporation of liquid and rate of dispersion of vapor into the airspace of the structure and rate of exchange of the atmosphere in the structure with outdoor air. Rate of dispersion of the atmosphere in the airspace of the structure and rate of exchange of the atmosphere in the airspace depend on the number of openings in the manhole cover and the space between them, as well as other factors such as difference in temperature between the upper airspace and the exterior, air movement across the surface of the ground, diameter, shape, spacing, and angle of inclination of the opening(s) [10,11,20].

Readings provided by instruments and odor detectable by nose showed that the vapor produced from evaporation of a small quantity (10 mL) of lacquer thinner can persist in an isolated subsurface airspace for a considerable period and can require more than 48 hours for complete removal after the start of evaporation. Removal of vapor from a larger quantity of liquid could require considerably more time.

Observations presented in this report argue for preferential early evaporation of more volatile constituents in the lacquer thinner and long-term evaporation by toluene. Using the relative response factor for toluene of 0.53 [29] and data provided in the MSDS (21), the concentration reached a maximum of 600 ppm near the source of vapor and 233 ppm in the in the upper airspace during this study. These concentrations are considerably greater than the current Threshold Limit Value—Time-Weighted Average (TLV-TWA) of 20 ppm used by many regulators as a regulatory Exposure Limit [34]. Workers opening the manhole cover or hatch on the top of structures containing only a small quantity of residual volatile solvent could receive a substantial overexposure to vapor emitted rapidly from the opening [9]. The observations made during testing confirm the wisdom of regulatory requirements for work involving confined spaces in the jurisdiction (province of British Columbia) in which this work occurred [35]. WorkSafeBC, the regulator, requires a formal hazard assessment and written entry and work procedure prepared by a technically knowledgeable individual (Qualified Person) and testing and ventilating during the work. Evaporation of liquid, dispersion of vapor in the airspace, and exchange with the external atmosphere require considerably more time than simply exchange of an introduced gas or vapor [10,11]. Evaporation of spilled liquid must occur completely before return of the atmosphere to the uncontaminated state can occur. Work involving opening and entry into spaces containing liquid contents or residual liquid on surfaces demands considerably greater caution than it is currently receiving.

Results obtained during this work support recommendations in another article in this series that argued for application of concepts advocated by the National Institute for Occupational Safety and Health (NIOSH) in the Prevention through Design initiative to optimization of ventilation induced by natural forces in isolated subsurface structures [14]. The work of McManus [10] and McManus and Haddad [11] investigators at the Bureau of Mines [15–18] showed that such ventilation offers the potential for optimization through redesign of manhole covers.

5. Conclusions

This study shows that evaporation of a solvent introduced into an isolated subsurface structure (a type of confined space) and removal of vapor from the airspace by ventilation induced by natural forces are time-consuming processes even for small volumes of liquid. Small volumes of volatile solvent can create serious risk of overexposure, fire, and explosion. The number of openings in a manhole cover and their geometric relationship influence evaporation and exchange of the atmosphere in the airspace with the external atmosphere. This process demands more study because of the opportunity to influence and optimize ventilation induced by natural forces in these structures. Work involving volatile liquids having the potential to form ignitable mixtures in confined airspaces requires considerable caution and can occur with a minor level of risk provided that planning occurs and that precautionary measures are taken. The observations obtained in this study support current requirements of some regulators for involvement of individuals knowledgeable by education, experience, and training in the anticipation, recognition, evaluation, and control of workplace hazards involving confined spaces. These observations support further effort to optimize ventilation induced by natural forces in these structures with the intent to reduce atmospheric contamination to below levels of concern as fast as possible. This work argues for extensive public education to discourage casual, surreptitious disposal of waste or surplus solvent into these structures.

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