Soil-Gas Surveying for Subsurface Gasoline Contamination Using Total Organic Vapor Detection Instruments
Part I. Theory and Laboratory Experimentation

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Abstract

Factors influencing the response of total organic vapor detection instruments used in soil-gas surveying for subsurface gasoline leakage were investigated through performing theoretical assessments and laboratory experiments. Theoretical assessments indicate that total organic vapor measurements will depend on response conditions and the relative concentration of constituents in soil gas, in addition to absolute constituent levels. Laboratory tests conducted using flame ionization, photoionization and explosimeter devices indicated that conditions influencing their responses included instrument flow rate and soil-air permeability when performing direct-probe sampling; the linear range of the instrument; the multicomponent nature of gasoline vapors; and levels of oxygen, nitrogen, carbon dioxide and relative humidity in soil air. If an instrument's response to these conditions is not taken into account, survey results may be misleading. To circumvent adverse instrument responses, a serial dilution technique is presented.

Introduction

Soil-gas surveying has become an effective means to screen for subsurface gasoline contamination. Most reported studies have described the use of gas chromatographs in conducting surveys (e.g., Spittler et al. 1985, Thompson and Marrin 1987, Marrin 1988, Kerfoot 1988). In contrast, relatively few published studies have described the use of total organic vapor detection instruments in conducting surveys, despite their common use. Although these instruments lack the specificity of gas chromatographs, they require less operator proficiency, provide more rapid results, are less costly, and have been shown to be effective in delineating subsurface contamination (Glaccum et al. 1983, Mehran et al. 1983, Goodwin and Burger 1989).

The objectives of this study were to evaluate how sampling and the composition of soil air might influence soil-gas measurements performed using total organic vapor detection instruments; to assess the reliability of using these instruments to detect and delineate subsurface contamination; and to develop techniques which circumvent instrument and site-related sampling problems. Instruments of interest include flame ionization detectors (FID), photoionization detectors (PID) and explosimeters (ED). In Part I, a theory is presented that describes how actual and measured concentrations may be related using response factors. These response factors incorporate the effects of soil-air composition on detecting organic vapors. Also, the theory underlying a serial

dilution method is presented. This theory provides a means to define response factors and to overcome soil-air compositional effects. Laboratory experiments are presented that were conducted to test the preceding theories and to quantify response factors. In Part II, field studies performed at a service station site are presented to illustrate instrument responses under actual field conditions and to demonstrate the use of the serial dilution technique.

Theory
Instrument Response

Consider the measurement of a single volatile constituent in air by a total organic vapor detector. The concentration measured may be equated to the actual concentration by

$$C_{mi} = R_i C_i, \tag{1}$$

where C_{mi} equals the measured vapor concentration for constituent i, C_i equals the actual vapor concentration, and R_i is a response factor for constituent i (Robbins et al. 1989). If R_i is constant, Equation 1 predicts that measured and actual concentrations among vapor samples will be linearly related.

The magnitude of the response factor depends on the specific instrument's sensitivity to constituent i relative to a calibration gas and a given set of calibration conditions. Instrument manuals often emphasize the

former and give little attention to the latter; yet, calibration conditions, such as column flow rate and carrier gas composition, have long been known to affect the response of flame ionization and photoionization detectors used in gas chromatography (McNair and Bonelli 1969, Ettre 1973, Freedman 1980). With respect to conducting soil-gas surveys using FID, PID, and ED instruments, a variety of conditions may affect their responses to organic vapors. Soil-air composition may be significantly different than the air composition of a calibration standard. For example, elevated carbon dioxide and methane levels in soil air have been reported at sites exhibiting subsurface gasoline leakage (Marrin 1985, Marrin 1987). Such conditions are likely due to biodegradation of gasoline constituents, and hence, depressed soil-air oxygen levels would also be expected. The relative humidity of soil air is expected to be close to 100 percent whereas calibration gases are generally in dry air. In addition to these factors, the concentration of organic vapors detected may exceed the linear range of an instrument.

Sampling factors may also affect the response of an instrument. For example, Robbins and Temple (1988) have found that a decrease in the operational flow rate of an FID in direct-probe sampling results in a decrease in instrument response. The degree to which this may occur depends on the soil's permeability to air and the instrument's pumping rate.

Variations in the preceding factors from sampling probe to probe could, in effect, vary R_i. This would introduce a non-linearity in the correlation between measured and actual concentrations.

Where the measurement of a single vapor constituent is being influenced by more than one soil-air compositional condition (e.g., high relative humidity and carbon dioxide level relative to that of a gas standard), the R_i value in Equation 1 becomes a composite response factor. With respect to the FID and PID, and the ED in its hot wire mode, measured concentration is proportional to an ion current reaching the detector. In effect, air compositional conditions can cause ion current reduction (Freedman 1980). The response factor describing the reduction in ion current brought about by a single air compositional condition may be taken as the ratio of the reduced ion current (I_1) to that of the ion current if the condition were absent (I_o). If a second compositional condition is active, it would reduce I_1 to an even lower ion current (I_2). The response factor describing the second condition would be equal to I_2/I_1. If further conditions were influencing the ion current, their individual response factors would be described by I_n/I_{n-1}, where n is the nth condition. In this manner the composite response factor, R_i, can be shown to be equal to the product of the individual response factors.

An important factor in sensing for gasoline is the multicomponent nature of its vapors. Wadden et al. (1986) reported that fresh gasoline vapors are dominated by five alkane constituents (butanes and pentanes constituting about 90 percent by weight). Upon leakage of gasoline into the subsurface, diffusion, biodegradation, air/water and air/soil constituent exchange can result in altering the relative abundances of vapor constituents from location to location (Silka 1988, Robbins 1987). For the multiconstituent case, the effects on instrument response may be examined by expanding Equation 1 to

$$C_{mT} = \sum_{i=1}^{n} C_{mi} = \sum_{i=1}^{n} (R_i C_i) = [\sum_{i=1}^{n} (R_i C_i / C_T)] C_T, \qquad (2)$$

where C_{mT} is the measured total concentration, C_T is the actual total concentration, and n is the total number of constituents (Robbins et al. 1989). As expressed in Equation 2, the measured total concentration of a mixture of gases is a weighted sum. The sum term in brackets in Equation 2 is an effective response factor for the mixture. Equation 2 predicts that the measured and actual total concentration will be linearly proportional only if the R_i values and the relative concentrations of all constituents remain constant from sample to sample.

Because the composition of soil air and the relative abundance of detectable organic vapor constituents are likely to vary at a site, the relation between measured and actual total concentrations may be probe-specific and non-linear among probes. Importantly, these effects may not be recognized during the course of a survey using direct-probe or gas bag sampling and can lead to misinterpretations of survey data.

Serial Dilution

Robbins and Temple (1988) introduced a serial dilution technique to determine soil-gas concentrations when they exceeded the upper detection range of an FID, and to circumvent the extinguishing of the instrument's flame caused by low soil-air oxygen levels. This technique was used to examine how soil-air composition may influence measured vapor concentrations and to define response factors. As modified here, the technique entailed the following steps. An evacuated Tedlar bag was initially filled to a desired volume with a gas sample having a detectable constituent. A known volume of gas was then removed and transferred to another evacuated Tedlar bag and sampled directly. The initial bag was then refilled with a volume of clean air (i.e., air with no detectable constituents) equal to that which was first removed. These steps were then repeated keeping the volume of gas removed and clean air added equal and constant at each increment. In this manner, the initial volume of the gas bag is restored after each refilling increment.

Using the preceding procedure, if the response factor is assumed constant, the measured concentration of the detectable constituent in the sampling bag after each refilling increment may be described by the following mass and volume continuity expression

$$C_m(j) = (C_m(j-1)V_o - C_m(j-1)V_r)/V_o, \qquad (3)$$

where $C_m(j)$ equals the measured concentration in the sampling bag after the jth refilling increment, $C_m(j-1)$

equals the concentration in the sampling bag just prior to the jth refilling increment, V_o is the initial bag volume, and V_r is the volume of clean air added at each refilling increment. Expanding Equation 3 from $j = 1$ to N, where N is the number of refilling (i.e., dilution) increments, and factoring $(V_o\text{-}V_r)/V_o$ terms results in

$$C_m(N) = C_{mo}[(V_o - V_r)/V_o]_1[(V_o - V_r)/V_o]_2 \dots [(V_o - V_r)/V_o]_N, \tag{4}$$

which simplifies to

$$C_m(N) = C_{mo}[(V_o - V_r)/V_o]^N, \tag{5}$$

where C_{mo} equals the initial concentration in the gas sample. Taking the logarithm of both sides of Equation 5 results in

$$\text{Log}\{C_m(N)\} = \text{Log}\{C_{mo}\} + N\text{Log}[(V_o - V_r)/V_o]. \tag{6}$$

Equation 6 predicts a log-linear relation between $C_m(N)$ and N. The intercept of the equation is the initial bag concentration, C_{mo}. The slope of the log-linear curve is the logarithm of the volume terms. Thus, for log-linearity to hold, the volumes out and in (V_r) during each increment must remain constant and equal. It should be noted that volume terms in the equation may be replaced by the product of air flow rate and pumping time, and N by the total dilution time divided by the time for a dilution increment. Because the dilution increment is a constant, a plot of Cm(N) vs. total dilution time will also be log-linear.

The substitution of Equation 1 into 6 gives Equation 7,

$$\text{Log}\{R_i(N)C(N)\} = \text{Log}\{R_{io}C_o\} + N\text{Log}[(V_o - V_r)/V_o]. \tag{7}$$

This equation permits examining how R_i may influence a serial dilution curve. In Equation 7, $R_i(N)$ and C(N) are the response factor and actual concentration at the Nth dilution increment, respectively. Their product is the measured concentration. Likewise, R_{io} and C_o are the response factor and actual concentration in the initial gas bag, respectively. Their product would be the initial measured concentration, which is the intercept of a plot of $\text{Log}\{R_i(N)C(N)\}$ vs. N.

Figure 1 illustrates idealized dilution curves described by Equation 7. The shapes of the curves depend on how the response factor varies as the initial gas in the bag is serially diluted with clean air. Curve A represents the case where the response factor is constant over the serial dilution. Curve B illustrates the case where initially the response factor is low and then it increases to a constant value. In this case, the proportional increase in the response factor with dilution is less than the proportional decrease in concentration. The ratio of concentrations between curves B and A at any dilution increment equals the response factor for the gas conditions in the bag at that increment. To circumvent variable response factor conditions, the log-linear portion of curve B can be extrapolated to the
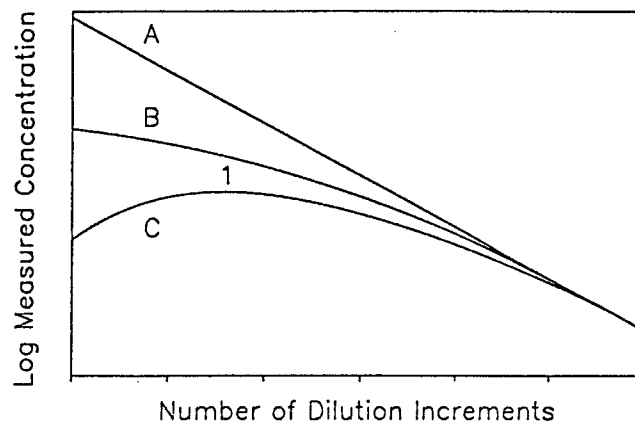

Figure 1. Idealized serial dilution curves. [(A) constant response factor; (B) response factor increases to a constant value at a rate less than concentration dilution; (C) response factor increases to a constant value but at an initial rate greater than concentration dilution (to the left of point 1) and then at a rate less than concentration dilution.]

concentration intercept. This concentration would equal the concentration measured in the sampling bag prior to dilution for the constant response factor condition of curve A. Curve C represents the case where the response factor was initially low. To the left of point 1, the proportional increase in the response factor with dilution is greater than the proportional decrease in concentration. To the right of point 1, the shape of the curve is due to the same conditions that govern curve B. Thus, by performing a serial dilution on a bag sample, theoretically, one can evaluate how soil-air conditions influence instrument response, determine response factors, and, through extrapolating the log-linear portion of serial dilution curves, circumvent variable response factor effects.

Laboratory Experiments

Instruments

FID, PID, and ED instruments used in testing were a Foxboro Century Systems Organic Vapor Analyzer 128 GC (in the total mode), an HNU Systems model ISPI 101, and a GasTech Natural Gas Indicator model NP-204, respectively. Relative humidity, carbon dioxide, and oxygen were measured using a Fischer Scientific fast response digital thermo-hygrometer, a GasTech portable carbon dioxide detector model RI-411, and a GC Industries oxygen gauge model GC 501, respectively. Serial dilutions and gas mixing experiments were performed using the system shown in Figure 2. The system components consisted of a stainless steel in-line particulate filter (Fisherbrand, Cat. No. 09-753-13A, Fisher Scientific, New York, New York), two flow gauges (0 to 3124 mL/min. Teflon® Flowmeter, and 0 to 333 mL/min. Teflon Flowmeter, respectively, Cole-Palmer Inc., Chicago, Illinois), a pressure gauge (0 to 15 inches of water, vacuum/pressure magnehelic gauge, Cat. No. 2330, Dwyer Inc., Michigan City, Indiana), a needle valve (Whitey, model SS-1RM4, Hartford Valve and Fitting Inc., Hartford, Connecticut), and a diaphragm
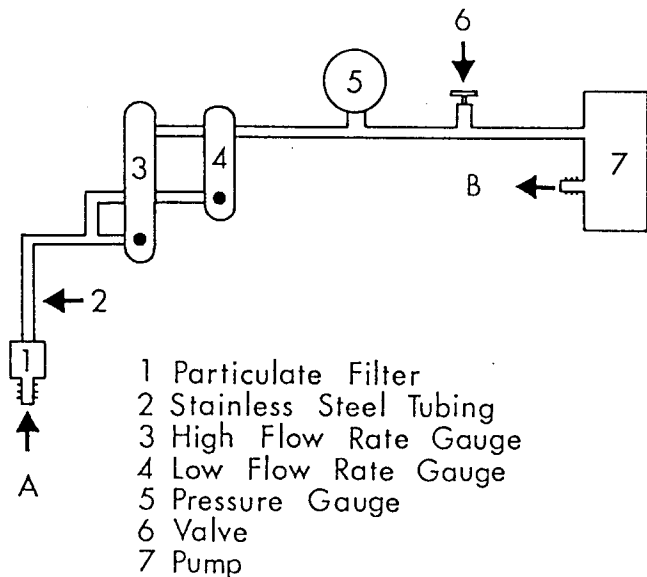
1 Particulate Filter
2 Stainless Steel Tubing
3 High Flow Rate Gauge
4 Low Flow Rate Gauge
5 Pressure Gauge
6 Valve
7 Pump

Figure 2. Flow control system for performing air and gas transfer, and conducting serial dilution tests.

pump (model TD-4N, Brailsford and Co. Inc., Rye, New York). Components were connected using 1/4-inch O.D. 1/8-inch I.D. stainless steel tubing and Swagelok fittings.

To perform a serial dilution a 3-liter Tedlar bag (equipped with septum and hose/valve fittings, SKC Inc., Eighty Four, Pennsylvania) filled with a gas sample was attached to point A of the sampling system (refer to Figure 2) and a volume of gas was extracted. The bag was then attached to point B and filled to its original volume with clean air. The bag was then reattached to point A and gas was extracted into a clean, evacuated Tedlar bag attached to point B. The gas concentration in this latter sampling bag was measured and the process repeated. Between gas and air transfers, the system was purged. By regulating the flow using the needle valve, transfer volumes were controlled. Transfer volumes were then calculated using flow gauge measurements and the duration of flow.

Flow Rate Restriction

The operational flow rates of the FID, PID, and ED are likely to be restricted in conducting direct sampling of soil-gas probes, owing to finite soil-air permeability. To examine instrumentation responses to flow rate restriction, sampling simulations were performed. The ED simulations entailed sampling of a standard within a Tedlar bag that was connected to a flow gauge and then to an instrument. The flow rate of the instrument was then controlled by a needle valve on the flow gauge. The PID's low operational flow rate and high sensitivity to flow restriction required an alternative method of testing. A needle valve was attached to a flow gauge and a vacuum pump, and the valve adjusted to achieve a desired percentage of the initial flow rate. The valve was then connected to a Tedlar bag containing a standard and then to the PID. The process was then repeated for different percent flow rates.

Linear Detection Range

The linear detection range of each instrument was tested by performing serial dilutions using commonly

employed standards and gases of interest. The ED was tested using methane. The FID was tested using methane, isobutylene, benzene, and unleaded gasoline. The PID was tested with the same constituents as the FID, except for methane which it cannot detect.

Air Composition

The PID and FID were tested to determine how concentration measurements of gas samples might be influenced by the level of oxygen, nitrogen, carbon dioxide, and relative humidity. Two types of experimental procedures were used. The first type entailed the mixing of commercially or laboratory prepared gas standards to obtain Tedlar bag samples possessing desired vapor concentrations and air compositions. The second method involved serially diluting a prepared gas sample contained within a Tedlar bag. Through performing serial dilutions using clean room air having ambient humidity or zero dry air, the gas concentration and air composition of the bag could be varied systematically.

Multicomponent Response

These serial dilution tests entailed evaluating the response of the PID to mixtures of methane and isobutylene, and butane and isobutylene. Because the PID is relatively insensitive to the alkanes, these experiments provided a means to evaluate whether the presence of alkanes in gasoline vapors might influence the response of the instruments to detectable constituents.

Results and Discussion

Figure 3 shows the results of the flow rate restriction tests. Initial flow rates were 1425, 234, and 260 mL/min. for the FID, PID, and ED, respectively. Standards used were 100 Vppm methane in dry air and 100 Vppm isobutylene in dry air for the FID and PID, respectively. The ED was connected to its external sampling pump and tested in two operational modes. In the low scale mode, the instrument reads 0 to 5 percent combustible gas (all cited percent concentrations are on a volume basis) and operates using a heated catalytic platinum filament. In the high scale mode, the instrument reads 0 to 100 percent combustible gas and operates using a thermal conductivity filament. The ED low and high scale standards
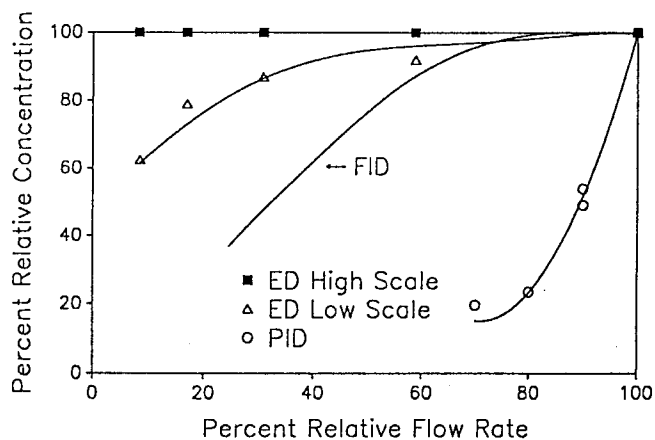

Figure 3. Decreased relative concentration readings of PID, FID, and ED instruments in response to flow rate curtailment [FID after Robbins and Temple (1988)].

were 2.5 and 30 percent methane in air, respectively. As shown on Figure 3, the responses of all three instruments were affected by flow rate curtailment, with the exception of the ED in its high scale mode.

The observed PID, FID, and ED responses to flow rate restriction would suggest that a concentration reading obtained by attaching these instruments directly to a soil-gas probe may reflect the soil-air permeability at the probe location. Spatial variations in soil-air permeability at a site due to changes in soil lithology, texture, and moisture content could introduce variations in soil-gas readings and would complicate interpreting survey results. The tests would also suggest that avoidance of the problem can be achieved by pumping soil air into collapsible bags for concentration measurement.

The PID response was found to be sensitive even to the slight vacuum induced in sampling Tedlar bags. This problem was readily overcome by the addition of a weight onto a bag during sampling. The weight induced a slight positive pressure in the bag, reduced the level of flow rate restriction, and resulted in increased consistency in PID readings.

Figure 4 illustrates log-linear serial dilution results using the FID for single constituents and unleaded gasoline vapors. The log-linear nature of the curves provides verification of the serial dilution theory. The curves also demonstrate that the response factors were constant over the dilution (constant slopes) and indicate the instrument exhibited linear response over its detection range up to 1000 Vppm.

Figure 5 demonstrates that the ED also exhibits linear response in its two modes of operation. The displacement between the high and low scale ED curves is likely due to calibration errors related to internal potentiometer settings and the accuracy of the meter scale. The low scale curve also illustrates the use of the serial dilution method for extrapolating beyond an instrument's upper detection limit. The intercept concentration, based on log-linear regression, is 27 percent, which is comparable to the initial bag concentration of 20 percent, as measured with the ED in the high scale mode. Also shown on the figure is the serial dilution curve for the FID. In this case the FID was calibrated using a 77 Vppm methane in dry air standard. The slope of the FID curve is essentially the same as that of the ED curves indicating that the serial dilution technique is well controlled even over many dilution increments. The displacement between the curves is likely a result of the previously cited sources of error. Extrapolating the FID curve beyond its upper detection limit through two orders of magnitude results in an intercept concentration that differs from those of the ED curves by about a factor of 2 to 3. This difference is well within the error range of ED meter readings (about 20,000 Vppm on the high scale and 1000 Vppm on the low scale).

Figure 6A illustrates serial dilution data for the FID and PID using benzene. The FID was initially calibrated to a methane in dry air standard. It was then used to determine the concentration of a benzene sample to which the PID was then calibrated. The FID data in
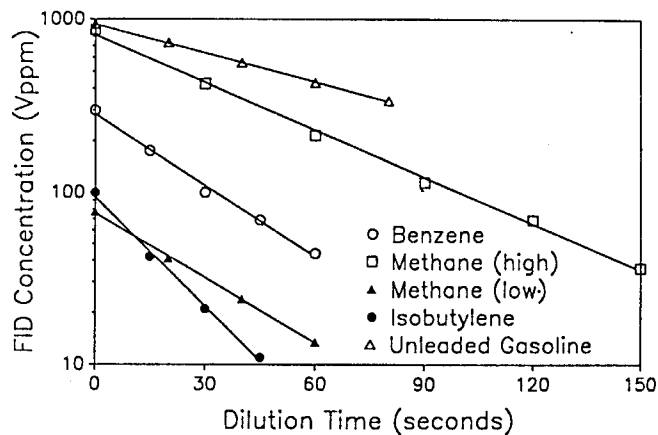

Figure 4. FID serial dilution curves for different organic vapors, which illustrate constant response factor conditions and verify the serial dilution method.
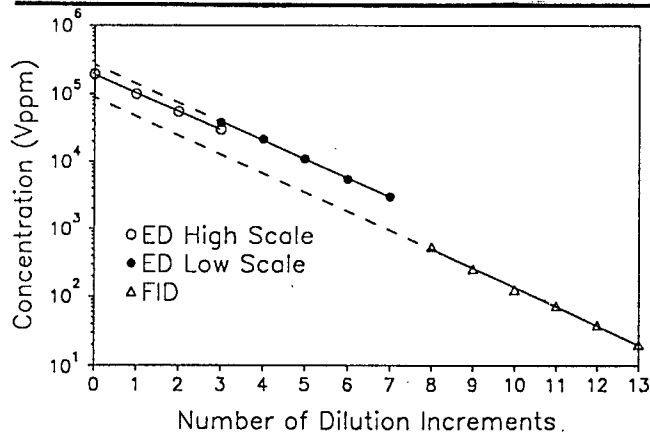

Figure 5. ED and FID serial dilution curves illustrating constant response factor conditions and concentration extrapolation beyond upper detection limits.
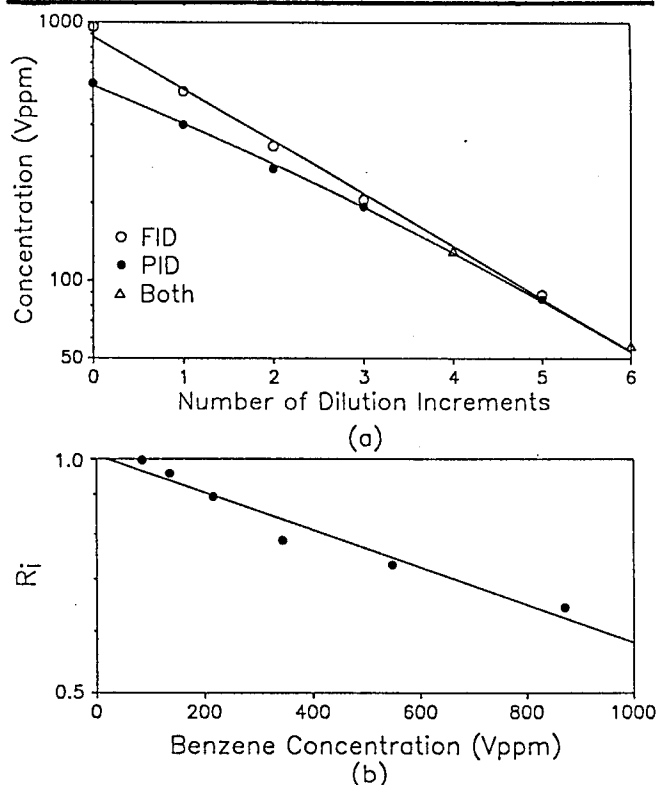

Figure 6. FID and PID responses to benzene vapor concentration. (A) serial dilution curves showing constant FID response and variable PID response; (B) relation of PID response factor to benzene concentration [$\log(R_i) = -2.6 \times 10^{-4}C_{be} + 0.013$; $r = -0.974$].

Figure 6A are log-linear and reflect a constant response factor. The PID data exhibit a non-linear response pattern above 125 Vppm, similiar to curve B in Figure 1. Below several hundred Vppm, the PID and FID data define the same log-linear curve whose intercept closely approximates the initial sample concentration of 960 Vppm. This demonstrates that by serially diluting a sample whose concentration is initially above the PID's linear range to achieve readings within its linear range, and by extrapolating the linear portion of the curve to the concentration intercept, the effect of non-linearity can be circumvented.

Figure 6B is a plot of computed PID response factors vs. benzene concentration. The relation of the response factor to benzene concentration was found to be approximated by a log-linear function.

Figure 7A illustrates serial dilution curves for the PID and FID for unleaded gasoline vapors. The FID was calibrated using a methane in dry air standard and the PID was calibrated using an isobutylene in dry air standard. Because the instruments were calibrated to different standards, their concentration readings would not be expected to be equivalent. Also, the instruments are sensitive to different components in the gasoline vapors. Due to these conditions, the serial dilution data for both instruments should ideally define two parallel log-linear curves, if linear response is maintained. Above an FID concentration of 250 Vppm or a PID reading of about 125 Vppm, the PID response was found to be non-linear. The non-linear concentration-related responses of the PID for gasoline and benzene would imply that the instrument in field surveying may underestimate soil-gas concentrations when areas of elevated contamination are probed. It would also suggest a decreased ability to delineate relative variations in subsurface vapors in these areas.

The PID data were extrapolated to lower concentrations until the slope of the curve matched that of a regression of the FID data. This resulted in the dashed curve shown on Figure 7A. The dashed curve was used to estimate the response factors in Figure 7B. The relation between the PID response factor and gasoline vapor concentration was found to be approximated by a log-linear function, having an apparent threshold at about 120 Vppm. If measurements had been performed at lower concentrations, the dashed curve, as in the case for benzene, would represent a constant response factor serial dilution curve that would permit circumventing the non-linear PID response to gasoline vapors.

Because gasoline vapors are dominated by alkanes, experiments were performed to evaluate whether their presence would influence the PID's sensitivity to detectable compounds. It should be noted that the PID has relatively negligible sensitivity to the alkanes that dominate gasoline vapors. In the first experiment, a serial dilution was performed on a Tedlar bag sample containing 23 Vppm isobutylene and 1.2 percent methane in dry air. In the second experiment, a serial dilution was performed on a Tedlar bag sample containing 28 Vppm isobutylene and 2680 Vppm butane in dry air.
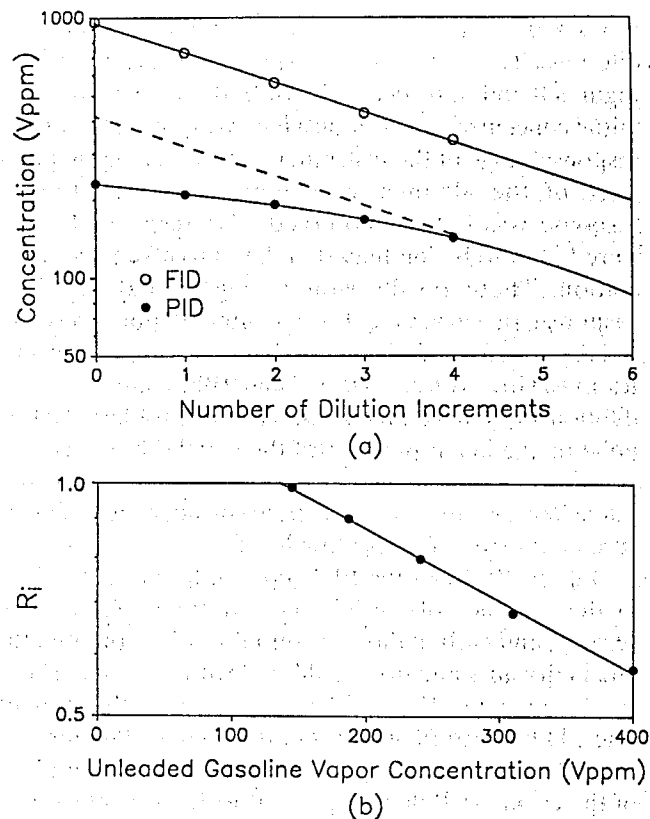

Figure 7. FID and PID responses to unleaded gasoline vapors. (A) serial dilution curves showing constant FID response and variable PID response; (B) relation of PID response factor to unleaded gasoline vapor concentration [log(R_i) = -9.3 x $10^{-4}C_{gs}$ + 0.13; r = -0.999].
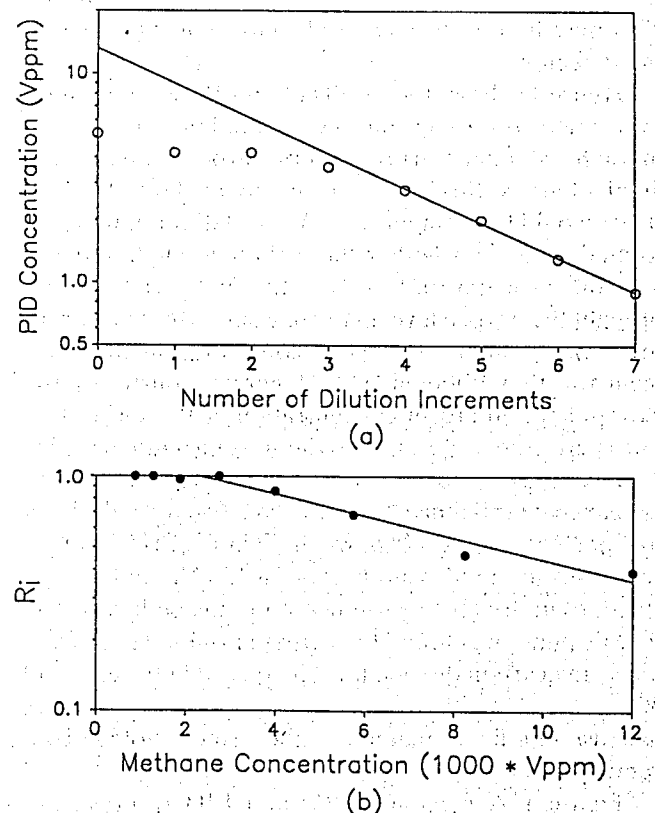

Figure 8. PID serial dilution of isobutylene in the presence of methane. (A) serial dilution curve illustrating decreasesd PID response; (B) relation of PID response factor to methane concentration [log(R_i) = -4.6 x $10^{-5}C_{me}$ + 0.11; r = -0.976].

In both experiments dry air was used in performing the dilutions. The results of the experiments are shown on Figures 8 and 9, respectively. In both experiments, the initial concentration of isobutylene was within the linear response range of the instrument. However, in the presence of the alkanes, non-linearity in instrument response was initially observed. The response factors were found to be log-linearly related to alkane concentration. These results would suggest that the PID response in surveying for gasoline vapors may be reduced, even at relatively low detectable vapor concentrations. However, as Figures 8 and 9 illustrate, the serial dilution technique can circumvent this problem. Extrapolating the linear portions of the serial dilution curves results in intercept concentrations that are close to the initial bag concentration values, in consideration of measurement errors at these low levels.

Figure 10 shows the FID reponse to a test standard in the presence of varied concentrations of nitrogen, oxygen, and carbon dioxide. Initially, a 77 Vppm methane in dry air standard was diluted with clean air. These results appear in Figure 10 as the points on the straight line. The dilution was repeated using 100 percent nitrogen and then 100 percent carbon dioxide in place of the clean air. Below 10 percent to 13 percent oxygen the instrument flame was extinguished. Hence, if low oxygen levels in soil gas are encountered during surveying, the instrument's flame will go out and may preclude gasoline vapor detection. Prior to flame out, increased levels of nitrogen and carbon dioxide (or decreased levels in oxygen) tended to cause increased sensitivity to methane relative to methane measurements in air. This may be due to increased ionization efficiency in the detector.

Figure 11 shows the results of an FID serial dilution experiment on a bag initially containing a 435 Vppm methane standard, 41.8 percent carbon dioxide and ambient air. At this initial carbon dioxide level, the FID flame would be extinguished. A serial dilution was performed to assess whether the technique might circumvent this problem. In this case, the first serial dilution brought the oxygen level in the bag above that necessary to support combustion and a concentration measurement was then obtainable. As Figure 11 illustrates, the extrapolated intercept concentration of the serial dilution curve agreed closely with the starting methane level.

PID vapor concentration measurements did not appear to be influenced by reduced oxygen levels down to 4 percent. Figure 12 shows the relative PID and FID responses in the measurement of a 125 Vppm benzene standard in dry air to varied carbon dioxide levels. The PID response was found to decrease in a log-linear fashion as the carbon dioxide level increased between 5 and 30 percent. The FID relative response tended to slightly increase in a linear manner as the carbon dioxide concentration rose.

Figure 13A compares PID and FID responses to varying relative humidity. Known volumes of a benzene standard in dry air were mixed with known volumes of clean air at 95 percent relative humidity. The line on Figure 13A shows how the benzene concentration would
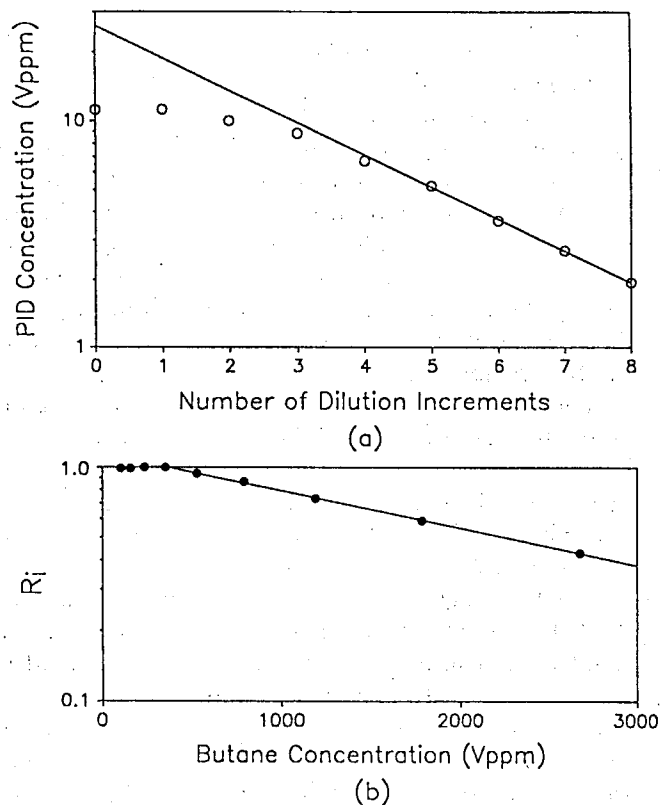
(a)

(b)

Figure 9. PID serial dilution of isobutylene in the presence of butane. (A) serial dilution curve illustrating decreased PID response; (B) relation of PID response factor to butane concentration. $[\log(R_i) = -1.6 \times 10^{-4} C_{bu} + 0.055; r = -0.999]$.
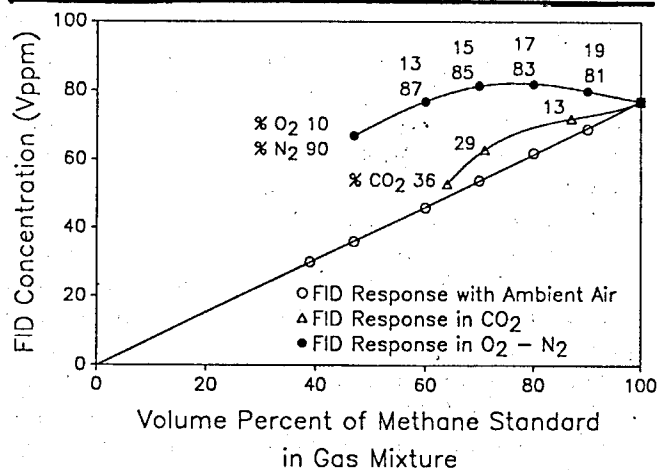

Figure 10. Increased FID sensitivity to methane in the presence of elevated levels of nitrogen and carbon dioxide.
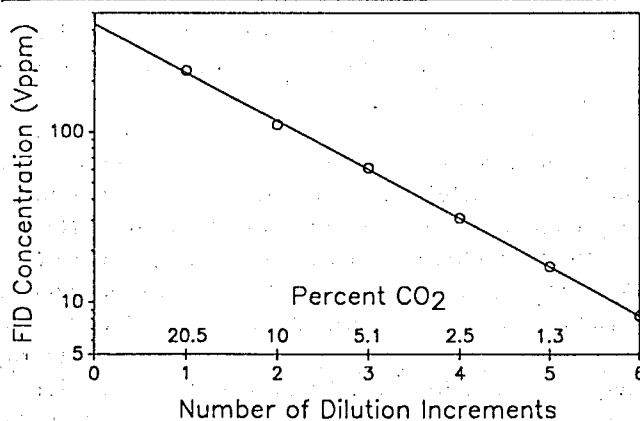

Figure 11. FID serial dilution of a methane standard illustrating the circumvention of flame out conditions due to a high carbon dioxide background level.
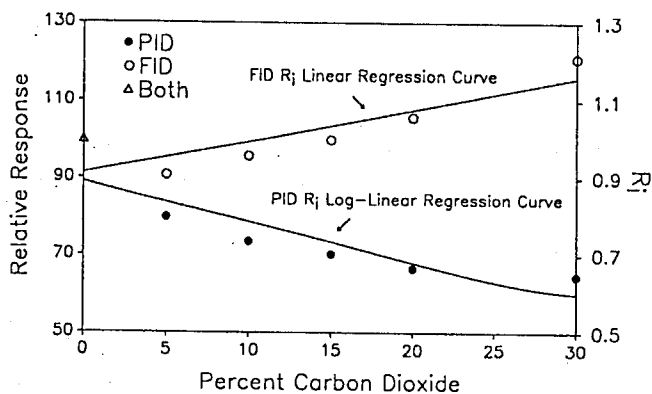
Figure 12. Relative FID and PID responses to benzene in the presence of carbon dioxide. [PID curve: $\log(R_i) = -5.7 \times 10^{-3}\%CO_2 - 0.049$, $r = -0.888$; FID curve: $R_i = 8.2 \times 10^{-3}\%CO_2 + 0.91$, $r = 0.846$].

vary due to dilution for the different air mixtures, if relative humidity did not affect instrument response. The correspondence of the FID data and the dilution curve indicates no discernible influence of relative humidity on the FID response. In contrast, the PID exhibited a marked decrease in response with increasing relative humidity. As shown on Figure 13B, the PID response factor may be related to relative humidity by a log-linear curve. This would imply that PID soil-gas surveys may underestimate vapor levels, owing to high soil air relative humidity.

In the course of preparing benzene in dry and moist air standards in Tedlar bags, temporal changes in PID measurements that suggest water vapor leakage into and out of the bags was observed. For example, over a several-hour period, a decrease in the PID concentration reading of a dry air standard and an increase in the PID reading of a moist air standard was observed. Concentration measurements performed during this period with the FID showed no discernible change, indicating that the PID readings were not due to benzene leakage or adsorption. Further, the PID readings tended to converge on values estimated based on the PID response to relative humidity and laboratory's relative humidity. These observations, although not quantified, would suggest the need to perform expeditious measurements of soil-gas samples collected in Tedlar bags when using a PID. Also, they would imply the need for frequent preparation of calibration standards if standards are prepared in Tedlar bags. The cause of negative readings observed in using digital PID meters seen in sampling soil-gas bags and when recalibrating instruments to zero air standards that were prepared in Tedlar bags may also be explained by the preceding observations and PID sensitivity to relative humidity.

Figure 14 shows the FID and PID results for a serial dilution test for a benzene in air sample where the initial relative humidity was 91 percent. In this test, both instruments were calibrated to an isobutylene in dry air standard, and the serial dilution was performed using room air having a relative humdity of 42 percent. The FID log-linear serial dilution curve implies a constant
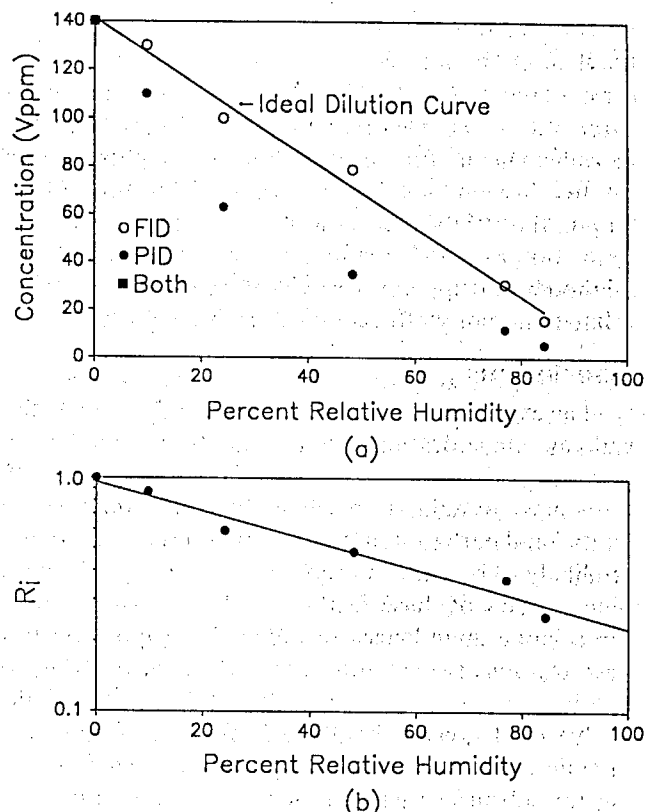

(a)

(b)

Figure 13. Effect of relative humidity on FID and PID responses to benzene. (A) illustrates no discernible FID response and decrease in PID response with increase in relative humidity; (B) relation of PID response factor to relative humidity [$\log(R_i) = -6.3 \times 10^{-3}\%RH - 0.017$; $r = -0.979$].
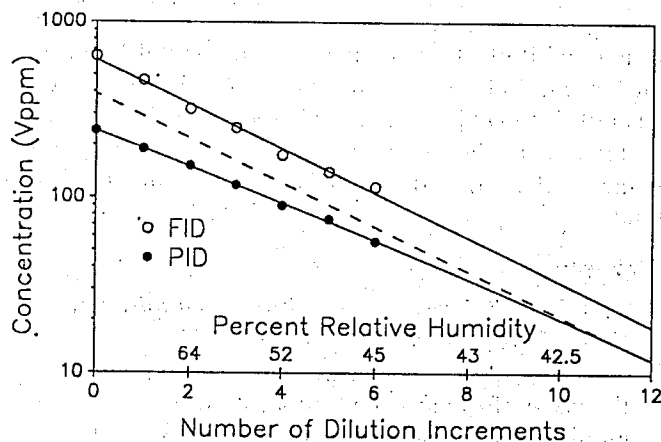

Figure 14. PID and FID serial dilution curves examining the effect of relative humidity on benzene vapor concentration measurements. [FID curve exhibits no discernible effect; PID curve exhibits decreasing response suppression with decreasing relative humidity, converging on constant response condition represented by the dashed line.]

response factor and a lack of sensitivity to relative humidity. The PID exhibited a variable response factor curve influenced by relative humidity. The PID curve converges at the room's relative humidity on a log-linear curve, which parallels that of the FID curve (the dashed curve in Figure 14). This log-linear curve extrapolates to an initial bag concentration of 389 Vppm. The difference between this value and the initial FID value reflects the different sensitivity of the instruments to benzene. As verification of this, the relative sensitivity of both

instruments was determined by calibrating them to iso-butylene in dry air and conducting measurements on a series of benzene in dry air samples. Concentration measurements are shown on Figure 15. The regressed curve provides a means for correlating measurements between the two instruments. For an FID concentration of 640 Vppm, the PID should read 412 Vppm, which is close to the observed PID reading. Hence, the serial dilution method would appear to provide a means of overcoming relative humidity effects on the PID response.

Conclusions

The experiments described in this study indicate that soil-gas concentration measurements obtained using total organic vapor detection instruments can be influenced by soil-air permeability and composition. Spatial and perhaps temporal variations in these factors are likely to be encountered during a survey. The combined effects of these factors, along with variations in the relative abundances of detectable vapor constituents, can make correlating vapor data with subsurface gasoline contamination complex. The results of this study would indicate that the effectiveness of using total organic vapor detection instruments in soil-gas surveying for subsurface gasoline leakage may be improved by collecting soil-gas samples in sample bags and by performing serial dilutions.

Notice

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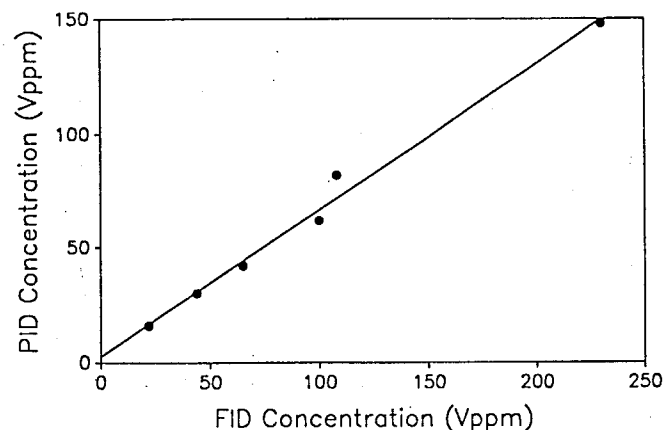
Figure 15. Correlation of FID and PID benzene concentration measurements when both instruments were calibrated to an isobutylene in dry air standard [$C_{PID} = 0.64C_{FID} + 2.56$; r = 0.993].

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