D-025, in: H.V. Rectanus and P. Rodgers (Chairs). *Remediation of Chlorinated and Recalcitrant Compounds—2016.*
Tenth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Palm Springs, CA; May 2016).
ISBN 978-0-9964071-1-3, ©2016 Battelle Memorial Institute, Columbus, OH, **www.battelle.org/chlorcon**.

Soil Gas Sampling for Identification of CAHS Sources in Groundwater: A Case Study

Andrea Mastorgio, Laura Romele, Sabrina Saponaro (sabrina.saponaro@polimi.it)
and Elena Sezenna (Politecnico di Milano, Department of Civil and
Environmental Engineering, Milano, MI, Italy)
Giorgio Bressi and Stefano Micco (Tecnitalia Ingegneria, Milano, MI, Italy)

ABSTRACT: Groundwater contamination studies involving possible multiple sources of contaminants poses a considerable challenge. When the contaminants of interest are chlorinated aliphatic compounds (CAHs), soil gas sampling can be precious for focusing site investigations. Soil gas monitoring at a former industrial site in Milan in an area of diffuse groundwater contamination demonstrates the usefulness of soil gas data together with groundwater and soil data for the correct reconstruction of the conceptual site model. Repeated gas sampling at different locations and depths provided data on the spatial and vertical concentration gradients of contaminants, which were useful to distinguish between background and local sources. In all the soil gas monitoring wells, CAH concentrations increased with depth, clearly indicating groundwater as the source of vapors at the site. Moreover soil gas and groundwater concentrations showed a similar pattern, with the highest soil gas concentrations recorded in the probes located in the area overlying highly contaminated groundwater. The data suggested groundwater contamination at the site was to be traced to the diffuse plume, but a discernible plume of PCE appeared to originate from a local off-site cross gradient source, which was responsible for the high PCE concentrations in the eastern portions of the site.

INTRODUCTION

Chlorinated aliphatic compounds (CAHs), especially tetrachloroethene (perchloroethylene or PCE) and trichloroethylene (TCE), are among the most widespread volatile organic compounds (VOCs) detected in soil and groundwater (Pankow et al., 1996; National Research Council, 1994). At industrial or former industrial districts, as a consequence of the widespread use of degreasing and cleaning agents and possible multiple facilities using any of these compounds on the same area, CAHs often show complicated contamination patterns (Duffy and Brandes, 2001; Glaser et al., 2005; Squillace and Moran, 2007). Correct delineation of contamination plumes as well as source identification of chlorinated solvents poses a considerable challenge but is an essential procedure for the management and remediation of contaminated groundwater, and also for assigning appropriate remediation responsibilities (Morrison and Murphy, 2006).

Typically to address such problems a multiple-lines-of-evidence approach that includes evaluation of groundwater historical data and various techniques (geostatistics, inverse modeling, chemical fingerprinting, etc.), to recreate contamination scenarios are used (Atmadja and Bagtzoglou, 2001; Alimi et al., 2003). Also the knowledge of the groundwater flow conditions at the site and the correct placing of the monitoring points is crucial. In all these activities soil gas monitoring can be used to focus site investigations and define the conceptual site model (Rivett, 1985).

This work reports about the approach adopted at a contaminated site in Milan (Italy) overwhelmed by a CAH plume originating from external areas, where groundwater data alone were inconclusive as limited by several on-site and off-site structures and seasonal fluctuations.

MATERIALS & METHODS

Site Description. The field study site, approximately 24000 m^2, is a former industrial area recently redeveloped as a part of a more extended service-sector area of the city (Figure 1). The southern zone of the site is used as a parking area, whereas the northern zone has a recreational use; a building ("A" in Figure 1) is located and already used in the central zone of the site. Between the existing building and the parking area, another building ("B" in Figure 1) is under construction. A railway line runs alongside the eastern boundary of the site.

Over the period of time that the site operated, the soil became contaminated mostly with mono- and poly-aromatic hydrocarbons and total petroleum hydrocarbons. Few vadose soil samples, close to SG7 and SG15, exhibited also tetrachloroethylene (PCE) concentrations slightly exceeding the Italian regulatory limit for residential areas (up to 1.3 mg/kg). Groundwater contamination at the site included PCE, trichloroethylene (TCE), hexachlorobutadiene (HCB) and chloroform, with little to no evidence of degradation. Chlorinated aliphatic hydrocarbons (CAHs) were known also to affect groundwater at large scale in the urban setting, with values similar to those observed at the site.

Partial remedial activities for soil (excavation and off-site disposal) were carried out in 2005, while residual contamination was addressed with site-specific risk assessment (Mastorgio et al., 2015). For the management of the CAH plume, a groundwater, soil gas and air monitoring plan was also initiated to collect data to discriminate between possible local sources and the background values and excluding unacceptable risks.

The local geology of the site, assessed with more than 30 boreholes, at maximum depths between 4 and 25 m bgs. results in the following stratigraphy: (1) pavement, with an average thickness of about 0.5 m; (2) sandy silt with pebbles, down to a depth between 1.5 and 7.5 m bgs; (3) gravelly sand or sand with gravel (autochthonous materials), in the remaining investigated thickness.

Groundwater flows N/NNW-S/SSE (Figure 1), with hydraulic gradient in the range of 0.2% to 0.3%. The average water table elevation at the site, as a result of reduced groundwater use in the area, has increased from about 20 m bgs in 2004 to about 15 m bgs in 2013, with yearly fluctuations lower than 3 m.

Field Activities. Groundwater monitoring, limited to a few on-site monitoring wells, was initially carried out between 2004 and 2008. In 2011 new groundwater monitoring wells at the site and at the eastern boundary (EP1-EP10) were placed and existing piezometers in the neighborhoods were included in the monitoring activities (final setup: 22 piezometers, screened between 10 to 20 m bgs).Despite the pattern of groundwater contamination suggesting an external source to the CAH plume, groundwater data alone were inconclusive as limited by several on-site and off-site structures (e.g., buildings and the railway) and seasonal fluctuations. Since January 2009, soil gas investigations were carried out at the site; in 2011 the soil gas and groundwater monitoring networks were upgraded to their final configuration including 60 soil gas probes at four different depths from ground surface (15 at 1 m bgs, 17 at 4 m bgs, 14 at 10 m bgs and 14 at 15 m bgs). After that, seasonal soil gas and groundwater monitoring campaigns were performed until November 2013. These measurements allowed optimization of the placement of two further groundwater monitoring wells outside the area (EP11-EP12) to draw conclusions about groundwater contamination.

In order to collect further data for risk assessment and confirm the results of such a procedure, several indoor air (18 locations), outdoor air (7) and crawl-space (4) air samplings were carried out, including background monitoring locations in 2009-2013.

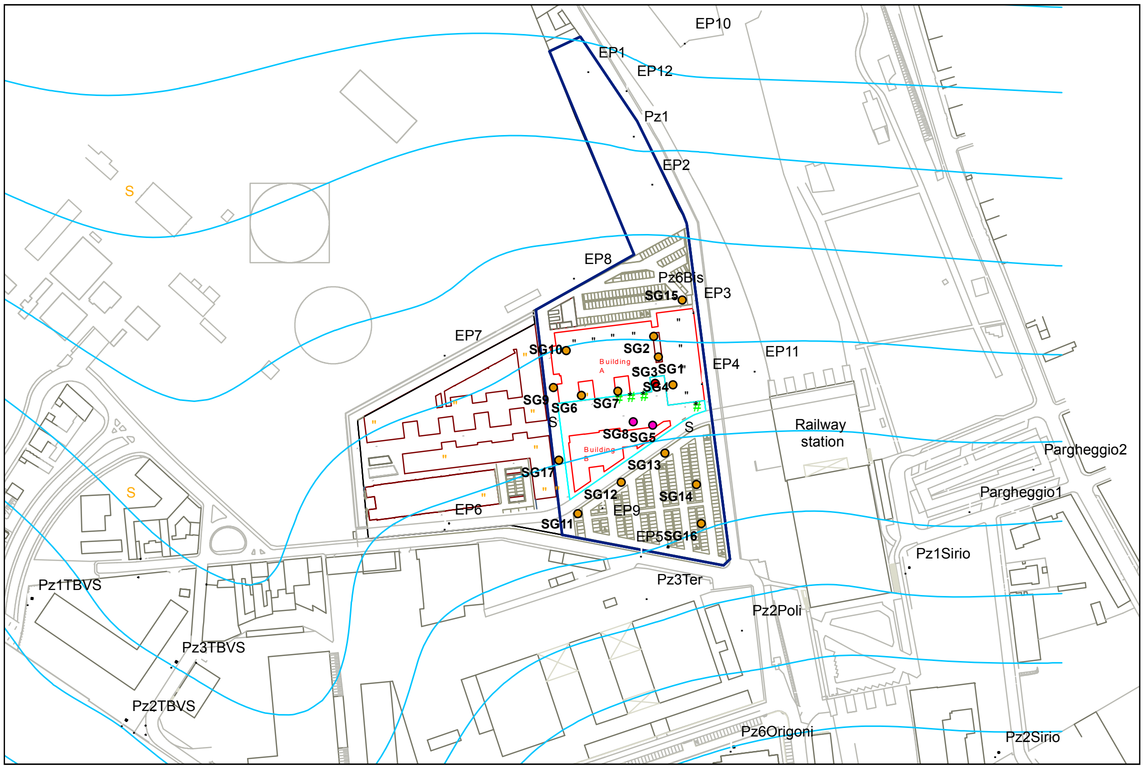

FIGURE 1. Site map. —: site boundary; ●: soil gas probes at 1, 4, 10 and 15 m bgs; ●: soil gas probes at 1 and 4 m bgs; ●: soil gas probes at 4 m bgs; ⊙:groundwater monitoring wells; —: contour mapping of the water table elevation (spacing 0.2 m) ■: indoor monitoring locations at the site; ☒: outdoor monitoring locations at the site; ▲: crawl-space monitoring locations; ■: indoor background monitoring locations; ☒: outdoor background monitoring locations.

All samples (groundwater, air, and soil gas) were analyzed for selected CAHs, principally PCE, TCE, HCB, TCM, and possible metabolites based on detections reported during historical site sampling activities.

Groundwater samples were collected according to low-flow purging and sampling methods (USEPA, 1996). Depth to groundwater and indicator field parameters (pH, temperature, dissolved oxygen, conductivity and oxidation-reduction potential) were registered during purging. All groundwater samples were collected in 40 mL amber glass vials with Teflon®-lined septa and no headspace and samples were shipped on ice to the laboratory and analyzed for selected CAHs using USEPA Method SW8260.

Active sampling of the vapor phase was performed at the flow rate of 1 L/min for 4 to 7 h. Activated carbon sorbent tubes (ORBO 32, 400/200 mg, Sigma Aldrich) were used to capture VOCs. A PTFE filter (37 mm diameter, 0.5 µm pore size) was placed in the sampling line to remove aqueous vapor. VOCs were extracted from the sorbent cartridges with 2 mL carbon disulfide, separated chromatographically with a Petrocol DH column (50 m x 0.2 mm i.d., 1.5 µm film thickness) and quantified by gas chromatography-mass spectrometry - GC/MS (Trace DSQ, Thermo Corporation) operating in selected ion monitoring mode with the following instrumental conditions: 220°C split injector temperature, 35°C initial oven temperature (held for 5 min), 220°C final oven temperature (held for 15 min), oven temperature ramp 8 °C/min.

RESULTS AND DISCUSSION

Summary of Field Data. Table 1 summarizes the concentrations of selected CAHs detected during the different monitoring campaigns in 2009-2013 for each sample medium. Other chemicals, were sporadically detected in a single medium during the various sampling events (data not shown). For groundwater and soil gas data only the range is reported, whereas for air the mean values and standard deviation are reported. PCE and TCE were the constituents most often detected across all media. HCB was detected only in groundwater and deep soil gas samples, whereas in shallow soil gas and air samples the values were always below the detection limit.

TABLE 1. Ranges of CAH$_{S}$ concentrations measured at the site in groundwater, in soil gas, and air (2009-2013).

Media	Sample	PCE	TCE	TCM	HCB
Groundwater (μg/l)	Extended monitoring network (n=172)	0.5 – 550	0.3 - 81.2	<0.1 – 28.5	<0.1 - 18.5
	On site monitoring wells (in the area of soil gas monitoring) (n=92)	1.8 - 124	0.3 - 11.2	1 - 24.9	<0.1 - 10.5
Soil gas (μg/m^3)	1 m (n = 128)	<1- 1900	<1 - 320	<0.3-127	<0.3
	4 m (n = 155)	<1 - 1100	<1 - 462	<0.3 - 91	<0.3
	10 -15 m (depending on water table level bgs) (n = 98)	10.5 - 8100	<1 - 740	<0.3 - 200	<0.3 - 2.4
Air (μg/m^3)	crawl-space (n= 48)	4.05 ± 5.8 (<1 – 86)	1.05 ± 0.13 (<1 – 3)	0.47 ± 0.17 (<0.3 – 0.8)	<0.3
	indoor (n = 148)	2.0 ± 1.6 (<1- 5.9)	1.1 ± 0.24 <1 - 7	0.68 ± 0.42 (<0.3 – 3.1)	<0.3
	background indoor (n = 99)	1.8 ± 0.9 (<1 – 6.9)	<1 - 1	0.41 ± 0.25 (<0.3 – 0.71)	<0.3
	outdoor (n = 42)	1.9 ± 1.2 <1 – 5.3	1.0 ± 0.01 <1 – 1.1	0.33 ± 0.1 (<0.3 – 0.64)	<0.3
	background outdoor (n=61)	1.7 ± 0.9 <1 – 5.6	<1	0.35 ± 0.11 <0.3 – 0.68	<0.3
	95th percentile background range range (USEPA, 2011)	4.1-9.5	0.56-3.3	4.1 – 7.5	-
	Indoor Air Target (USEPA 2015)	47	3	0.53	3

Note: groundwater and soil gas data: range of values;
air average ± standard deviation of the dataset; range of values in brackets.

The average outdoor and indoor concentrations at the site were fully aligned to the outdoor background and the indoor background respectively. The indoor values are within the typical ranges of indoor background values reported in USEPA (2011) and the mean values also below the air screening levels (USEPA, 2015) for long-term exposure at commercial sites.

In the monitoring period, the site experienced a high PCE pulse from undefined upstream areas, with a sporadic rise of PCE levels in groundwater (up to 500 µg/L in the upgradient well Pz1 in March 2011) and in the deep soil gas monitoring probes (up to about 4 mg/m^3 in March and July 2011 in the downgradient area SG1 – SG15). Excluding that, the comparison between the different groundwater data showed CAH concentrations in the monitoring wells varying up to one order of magnitude without a systematic seasonal effect. For the soil gas monitoring campaigns, the concentrations in the deep probes (10-15 m) generally differed by up to one order of magnitude, whereas higher variations, up to about two orders of magnitude, were registered for the 1 m and 4 m probes.

Spatially, PCE concentrations in soil gas and groundwater showed a similar pattern, with the highest soil gas concentrations recorded in the probes in the eastern part of the site overlying high dissolved PCE area (Figure 2, showing, as an example, the situation in October 2012).

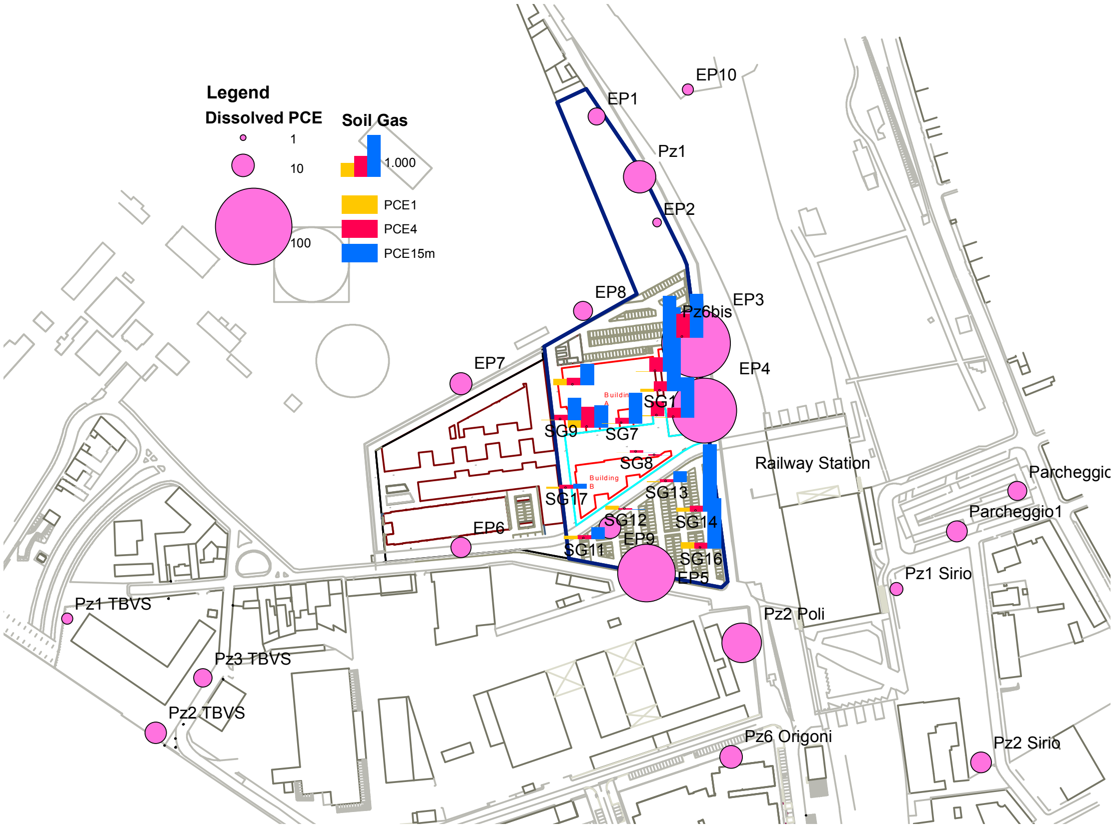

FIGURE 2. PCE concentrations in groundwater and soil gas at different locations and depths (October 2012).

In Figure 3 the average concentrations of PCE, TCE and HBC in monitoring wells in the different areas are reported. For PCE, despite the concentrations all ranging from 10 to 100 µg/L, it is evident a higher PCE area resides at the eastern boundary of the site. In the case of TCE and TCM (data not shown), in the different wells the average concentrations were similar with no high concentration area or significant difference in upgradient and downgradient locations. HBC was correlated to high PCE values, being

HBC quantified only in the high PCE wells (with the exception of a single detection in PZ1TBVS).

Figure 4 shows the average soil gas concentrations for PCE and TCE at the different soil gas probes in 2009-2013. HBC is not reported as always below the detection limit (0.3 μg/m^3). TCE concentrations in the soil gas were typically below 100 μg/m^3, except for the parking area (SG13, SG14, and SG16), where traces of CAHs were found in soil. In all the soil gas monitoring wells, PCE concentration increased with depth, suggesting groundwater as the sole source of vapors at the site. Similarly to groundwater data, PCE in the deep probes (10-15 m bgs) at the eastern portion of the site was on average above 1000 μg/m^3, three to 10 times higher than in the remaining parts of the site.

This was probably caused by an off-site cross gradient source located somewhere in the railway area, as confirmed by PCE concentrations constantly above 150 μg/L registered at EP11 in 2014-2015.

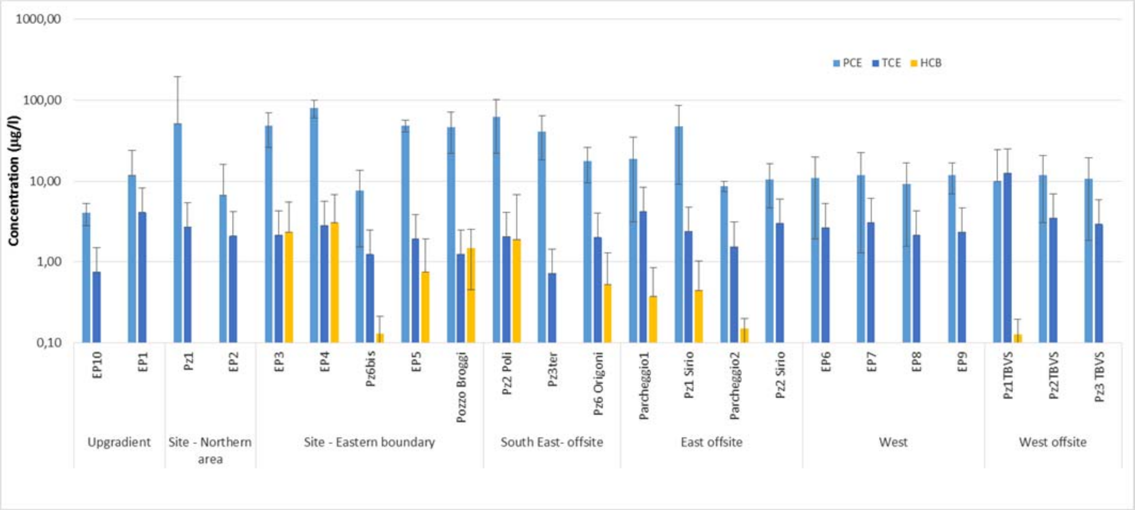

FIGURE 3. Average groundwater concentrations for PCE, TCE and HCB at monitoring wells in 2009-2013. The error bars show the standard deviation of data.

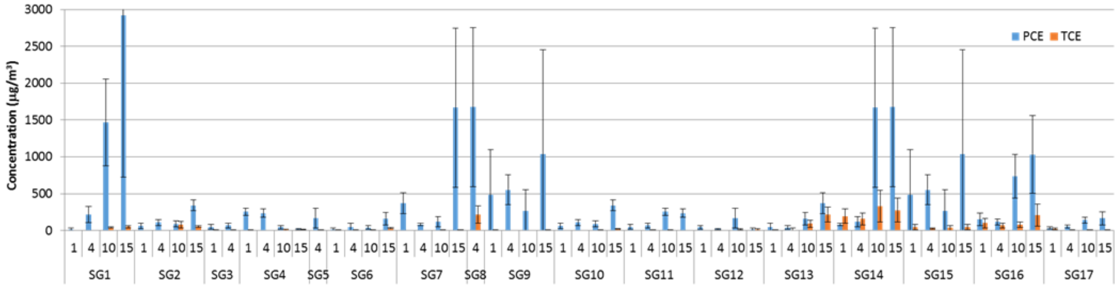

FIGURE 4. Mean soil gas concentrations of PCE and TCE in the different probes and depths (period 2009-2013). The error bars show the standard deviation of data.

CONCLUSIONS

Repeated soil gas sampling at different locations and depths provided data about the contaminant concentration gradient, which was useful to distinguish between background and point sources. In all soil gas monitoring wells, CAH concentrations increased with depth, indicating groundwater as the sole source of vapors at the site. Moreover soil gas and groundwater concentrations showed a similar pattern, with the highest soil gas concentrations recorded in the probes overlying highly contaminated groundwater. Soil gas data were thus useful in corroborating groundwater data and focus site investigations. The data suggested groundwater contamination at the site was to be traced to the diffuse plume (background PCE values about 15 μg/L), even if a local discernible plume of PCE from an off-site cross gradient source in the railway area was recognized as responsible for the higher PCE concentrations (45-80 μg/L) in the eastern part of the site.

ACKNOWLEDGMENTS

The authors thank Euromilano SpA and Politecnico di Milano for covering the costs of the monitoring campaigns.

REFERENCES

Alimi, H., Ertel, T., and Schug, B., (2003), Fingerprinting of hydrocarbon fuel contaminants: Literature review. Environmental Forensics, 4, 25−38.

Atmadja, J. and Bagtzoglou, A.C., (2001), State of the art report on mathematical methods for groundwater pollution source identification. Environmental Forensics, 2, 205−214.

Glaser, B., Dreyer, A., Bock, M., Fiedler, S., Mehring, M., and Heitmann, T., (2005), Source apportionment of organic pollutants of a highway-traffic-influenced urban area in Bayreuth (Germany) using biomarker and stable carbon isotope signatures. Environmental Science and Technology, 39, 3911−3917.

Mastorgio A., Romele L., Saponaro S., Sezenna E., Bressi G., Micco S. (2015) Five-Year Vapor Monitoring for Risk Management at a Hydrocarbon-Polluted Site pp.1-8. In Bioremediation and Sustainable Environmental Technologies - Proc. Third International Symposium on Bioremediation and Sustainable Environmental Technologies, Miami (FL), 18-21 May 2015 ISBN:978-0-9964071-0-6, Eds. R. Darlington and A.C. Barton, Battelle Memorial Institute, Columbus, OH.

National Research Council (1994). Alternatives for Ground Water Cleanup. Washington, D.C.: National Academy Press.

Morrison, R.D and Murphy, B.L. (2006) Environmental Forensics Contaminant Specific Guide, Edited by: Ph.D. Robert D. Morrison and Brian L. Murphy ISBN: 978-0-12-507751-4

Pankow, J.F., S. Feenstra, J.A. Cherry, and M.C. Ryan (1996), Dense chlorinated solvents in groundwater: Background and history of the problem [Chapter 1]. In Dense Chlorinated Solvents and Other DNAPLs in Groundwater, ed. J.F.Pankow and J.A.Cherry. Portland, Oregon: Waterloo Pres

Rivett, M. O. (1995), Soil-Gas Signatures from Volatile Chlorinated Solvents: Borden Field Experiments. Ground Water, 33: 84–98.

Squillace, P.J. and Moran, M.J. (2007), Factors associated with sources, transport, and fate of volatile organic compounds and their mixtures in aquifers of the United States. Environmental Science and Technology, 41, 2123−2130.

U.S. Environmental Protection Agency (1996) EPA540/S-95/504 Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. 1996. Office of Research and Development & Office of Solid Waste and Emergency Response.

U.S. Environmental Protection Agency (2011) Background indoor air concentrations of volatile organic compounds in North America residences (1990-2005): a compilation of statistics for assessing vapor intrusion.

U.S. Environmental Protection Agency (2015) Vapor intrusion screening level (VISL). Calculator (version 3.4)