NICOLE BRASIL
Latin America Network for Soil and Water Management

VAPOR INTRUSION IN THE INDOOR AIR ENVIRONMENT

Basic Concepts, Evaluation and Management at Brazilian Contaminated Sites

Ficha Catalográfica

Elaborada pela NICOLE Brasil – Latin America Network for Soil and Water Management

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Abstract

Brazil is a country blessed with an abundant natural resource base, burgeoning economy and population, and strategic positioning within a developing international region. But this position of relative privilege has come at a high environmental cost. Despite the country's well-developed environmental consciousness, with roots in a decades-long struggle to preserve its Amazon rainforests, much needs to be done in Brazil to rectify past environmental ills that afflict the entire country.

Of particular interest, and the subject of growing public awareness, are contaminated lands in the nation's major industrial areas (São Paulo, Rio de Janeiro, etc.), and increasingly, in less populated zones. Largely unchecked industrial growth and the reuse of contaminated areas by the country's expanding housing market have caused several highly publicized incidents of acute indoor air contamination. For example, a commercial supermarket built on a former unregulated landfill resulted in the vapor intrusion of methane and temporary closure of the establishment (CETESB, 2015). Incidents such as this can occur when stakeholders are ignorant of the potential for vapor intrusion and contaminated land is redeveloped for inappropriate uses.

Increasing public awareness and greater regulatory scrutiny have meant that indoor air quality is now of concern to Brazil's governmental agencies, as well as other stakeholders involved. Despite that, technical guidance on the issue almost exclusively hails from North America and Europe. While such expertise is certainly relevant on its technical merit alone, it cannot acknowledge or consider country-specific physical and contextual realities which may or may not be adequately represented; as such, a concerted technical response to the issue itself necessarily starts from a position of disadvantage.

The present document seeks to change that. NICOLE Brasil was founded in 2014 by a network of industrial and consulting companies with the intent of addressing complex contamination issues as a diverse, collaborative group. The organization follows in the model of NICOLE Europe, which has more than 20 years of history finding solutions to a variety of environmental challenges.

NICOLE Brasil (http://www.ekosbrasil.org.br/nicole.html) chose vapor intrusion as a focus area for the 2015 technical program and formed a Working Group to research the issue.

The Working Group has produced this White Paper in an effort to provide an authoritative and country-specific treatise on vapor intrusion for the benefit of all stakeholders in Brazil, whether they are academia, government, industry, consulting, or the interested public. Hopefully, this White Paper will also clarify the research needs in this area within Brazil. Special care has been taken to focus this technical analysis on the Brazilian reality. Where possible, expertise and sources from North America and Europe have been combined with Brazil-specific knowledge. The members of the Working Group gratefully acknowledge the assistance of our reviewers for their invaluable feedback:

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Yours Sincerely,

The NICOLE Brasil Vapor Intrusion Working Group (undersigned),

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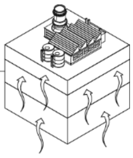


List of Abbreviations and Acronyms

ABNT	Brazilian Technical Standards Association (Associação Brasileira de Normas Técnicas)
AC	Contaminated Area
ACBR	Risk-based Corrective Actions (RBCA) Applied to Contaminated Sites with Hydrocarbon Derived from Oil and Other Liquid Fuels - Procedures
API	American Petroleum Institute
ALSs	Applicable Legal Standards
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
C	Commercial Receiver
C_6H_6	Benzene
$C_6H_5CH_3$	Toluene
$C_6H_5C_2H_5$	Ethylbenzene
$C_6H_4(CH_3)_2$	Xylene
CETESB	São Paulo State Environmental Agency (Companhia Ambiental do Estado de São Paulo)
CD Ssup	Dermal Contact with the surface soil
CMA	Maximum Acceptable Concentration at the Exposure Point
CMA-HS	Maximum Acceptable Concentration at the Hot Spot
CMA – POE	Maximum Acceptable Concentration at the Exposure Point
CPTU	Cone Penetration Test (Ensaio de Piezocone)
COC	Chemical Compounds of Concern
OWS	Oil-Water Separator Tank
DD nº 263/2009/ P	Decision of Board No. 263/2009, published in Diário Oficial do Estado de São Paulo on October 20, 2009 (CETESB, 2009)
DNA	Deoxyribonucleic acid
E-20	Mix of 80% gasoline and 20% ethanol
EW	Extraction Well
HS	Hot Spot
IGSsup	Particle intake from surface soil
IP Ssup	Particle inhalation from surface soil
ISCO	In situ chemical oxidation
ITRC	The Interstate Technology & Regulatory Council
IVIG	Indoor vapor inhalation from groundwater
IVI Ssup	Indoor vapor inhalation from surface soil
LNAPL	Light Non-Aqueous Phase Liquid
MPE	Multiphase Extraction
MR	Remediation Control Action
MTBE	Methyl *Tert*-Butyl Ether
NAPL	Non-Aqueous Phase Liquid
MW	Monitoring Well
ND	Not detected

NW	Northwest
O_2	Oxygen
OSWER	Office of Solid Waste and Emergency Response
OVIG	Outdoor vapor inhalation from groundwater
OVI Ssup	Outdoor vapor inhalation from surface soil
pH	Hydrogen ionic Potential
PVI	Petroleum Vapor Intrusion
QL	Quantification Limit
R	Residential Receiver
RAIS	The Risk Assessment Information System
SSTL	Site Specific Target Level
TO 14	Methods for the determination of toxic organic compounds in ambient air - determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography
TO 15	Methods for the determination of toxic organic compounds in ambient air - determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chro matography/ mass spectrometry (GC/MS)
TO 17	Methods for the determination of toxic organic compounds in ambient air - determination of volatile organic compounds in ambient air using active sampling on to sorbent tubes
TNT	Trinitrotoluene
TPH	Total Petroleum Hydrocarbons
USEPA	United States Environmental Protection Agency
VI	Intervention Values for underground Water on Estado de São Paulo - CETESB, Board decision n. 195-2005 from 23/11/2005
VI Ssup	Vapor inhalation from surface soil
VOC	Volatile Organic Compounds

List of Symbols

α	:	Attenuation Factor	[-]
K_{oc}	:	Coefficient of organic carbon-water partition	[mL/g]
K_{ow}	:	Coefficient of Octanol-water partition	[mL/g]
J	:	Diffusive flow	
D	:	Diffusion coefficient	[cm^2/s]
C	:	Concentration of solute	[g/cm^3]
x	:	Relative position	
t	:	Time	[s]
dC/dx	:	Concentration Gradient	[$g/cm^3/cm$]
$D*$	:	Coefficient of effective diffusion	[cm^2/s]
ω	:	Coefficient of tortuosity	
D_o	:	Diffusion coefficient in a free solution	
V_x	:	Percolation rate	[cm/s]
K	:	Permeability Coefficient	[cm/s]
n	:	Porosity	[cm^3-void/cm^3-soil]
i	:	Hydraulic Gradient	[%]
A_B	:	Building surface area in contact with the soil	[m^2]
$D^{eff}{}_{crack}$	:	Overall coefficient of effective diffusion of vapor through cracks in the walls and foundation	[$m_{crackeff}{}^2/d$]
$D^{eff}{}_{T}$	:	Overall coefficient of effective diffusion of vapor in the soil column between the foundation and the source	[m^2/d]
L_{crack}	:	Floor slab thickness	[m]
L_T	:	Distance (Depth) to the vapor source, as measured from the slab	[m]
Q_B	:	Volumetric air flow	[m^3/d]
η	:	Fraction of cracks in the foundation	[m^2/m^2]

Q_{soil}	:	Underground gas flow directed by pressure to the indoor environment	[m^{3}/d]
C_{indoor}	:	Indoor air concentration	[μg/m^{3}]
C_{source}	:	Source concentration	[μg/L]
ϑ Tsoil	:	Soil porosity	[cm^{3}-void/cm^{3}-soil]
ϑ w-soil	:	Humidity in the unsaturated zone	[cm^{3}-water/cm^{3}-soil]
foc	:	Fraction of organic carbon in soil	[%]
ρS	:	Soil Density (total)	[g-soil/cm^{3}-soil]
T	:	Temperature	[ºC]
ϑw	:	Water Content in Soil	[%]
$\vartheta w,cap$	:	Humidity in the capillary fringe	[%]
CZh	:	Height of the capillary fringe	[cm]
EB	:	Ratio of air exchange	[h^{-1}]
HB	:	Mixing zone height inside the building	[m]
FB	:	Building Area	[m^{2}]
EDnc	:	Duration of exposure to non-carcinogenic compounds	[years]
EFc	:	Frequency of exposure to carcinogenic compounds	[days/year]
ATc	:	Average duration of exposure to carcinogenic compounds	[years]
EFnc	:	Frequency of exposure to non-carcinogenic compounds	[days/year]
ATnc	:	Average time for non-carcinogenic compounds	[days/year]
THQ	:	Target level of individual risk quotient	[-]
L_{mix}	:	Air mixing height of indoor environmental	[cm]
ER	:	Air Exchange rate	[1/day]
ϑ Tcrack	:	Total Porosity	[cm^{3}-void/cm^{3}-soil]
ϑ w-crack	:	Porosity filled with water	[cm^{3}-void/cm^{3}-soil]
Q_{s}	:	Air flow through foundation	[cm^{3}-air/sec]

TR (-)	:	Risk index (carcinogenic)	[-]
ATHC	:	Average time of exposure	[yrs]
BW	:	Average body weight	[Kg]
ED	:	Exposure duration	[yrs]
EF	:	Exposure Frequency	[days/yrs]
CF (-)	:	Adjustment factor for indoor inhalation	[-]
<	:	Concentration lower than the quantification limit of the method used by the laboratory	
EDc	:	Duration of exposure to carcinogenic compounds	[years]
αSG	:	Attenuation factor for soil vapors	[-]
αGW	:	Johnson & Ettinger Attenuation factor for groundwater	[-]

1 - INTRODUCTION

The process of migration of volatile chemical compounds, in vapor phase, from a subsurface source to the interior of buildings on the surface is known as vapor intrusion. The volatile chemical compounds in soil and contaminated groundwater can vent vapors with the potential to migrate through the layer of soil subsurface and through cracks, fractures, and discontinuities that may exist on the foundations, reach indoor environments, and affect air quality on the site.

In extreme cases, the accumulated vapors inside buildings may pose an imminent risk, such as an explosion. However, in most cases, only low concentrations of the chemicals of interest are observed. Over a long exposure duration, these low concentrations can increase the risk of chronic health effects on receptors in these spaces (USEPA, 2002).

Indoor intrusion of vapors from soil and / or groundwater is the result of a complex series of physical and chemical processes that occur in landfills, industrial plants, fuel distribution and storage points and other places where products containing organic volatile compounds are stored, handled or transported.

Several environmental regulatory agencies around the world have recognized the importance of this route of exposure and require its consideration when analyzing risks to human health in areas potentially contaminated by the presence of volatile organic compounds.

Currently in Brazil, the need of intervention methods is verified through comparative tables between the concentrations detected in soil samples and groundwater, the maximum acceptable concentrations according to the distance to the receptor, and applicable legal standards. These comparisons are used to elaborate risk maps that identify sites that pose an unacceptable risk and require intervention.

This analysis method can be considered conservative as important variables associated with attenuation processes that occur during transport of the contaminants from the vapor source to the environments in study, such as biodegradation, are not included in this approach or are treated in a generic way. However, improving site-specific, quantifiable information about these processes could be quite costly and in some cases technically impossible, particularly when there is large spatial and temporal variability.

Considering these challenges, data obtained directly from sampling vapors in the subsurface near the exposure point can provide a more accurate estimate of subsurface concentrations that have real potential to reach the receptors present indoors.

However, for this process to be consistent and more accurately represent risk to human health, the results and concentrations quantified directly in vapor phase should be compared to appropriate standards, determined using the physical parameters of the place and specific characteristics of receptors and buildings that exist in the affected areas.

In this context, this study presents a proposal for addressing this potential route of exposure, based on performing systematic evaluations, considering that various parameters of the physical environment of the evaluated sites can significantly influence this process, including geotechnical and geological characteristics, nature of the contamination, location of the vapor sources and characteristics of buildings on the surface.

2 – TECHNOLOGIES AND APPLICATION

The importance of vapor intrusion has been the subject of debate between the scientific and regulatory communities for over two decades. Initially, the focus of the research was limited to the migration of radon naturally present in soils and gases from landfills to closed environments (MCHUGH & NICKELS, 2008).

In the early 90s, the indoor vapor intrusion process attracted the interest of North American environmental agencies during the implementation of a new approach to corrective action (Risk Based Corrective Action) that focused on addressing risks to human health. In 1991, Johnson and Ettinger (1991) published a model that built on radon intrusion models to assess diffusive and advective flows from a much wider category of subsurface contamination. The results of this model provide an attenuation factor (α), considering the depth of the source of vapors and specific geotechnical characteristics of the evaluated areas. With the use of specific mitigating factors, the vapor concentrations expected in indoor air are estimated, allowing an evaluation of exposure to these concentrations in terms of risk to human health.

During the second half of the 1990s, various North American State environmental agencies and the USEPA (USEPA, 2002) used the Johnson and Ettinger (1991) model, associated with some conservative assumptions, to calculate risk-based target levels for groundwater, to predict the degree of exposure to indoor air receptors impacted by the presence of volatile organic compounds in the subsurface.

In the late 1990s, the intrusion of vapors attracted public attention in the United States when two areas in Colorado located above a chlorinated solvent groundwater plume were found to have indoor air concentrations that exceeded the established target levels. To support a response action in these cases, the division of corrective actions of the USEPA’s Office of Solid Waste and Emergency Response (OSWER) developed and released a supplemental guide in 2001 to facilitate the evaluation of the intrusion of vapors (MCHUGH & NICKELS, 2008).

In 2002, the USEPA began to limit the use of modeling to assess the relevance of the route of exposure related to vapor intrusion indoors, recommending instead the use of data obtained in the field, during evaluations focused on quantifying concentrations of vapor.

The US EPA encourages the use many lines of evidence, which include modeling, empirical data and other assessment methods to verify that the intrusion of vapors actually occurs in the area evaluated. Currently, several North American States, (California, Oregon, Washington, Idaho, Montana, Wyoming, Colorado, South Dakota, Nebraska, Kansas, Missouri, Minnesota, Louisiana, Alabama, Wisconsin, Michigan, Indiana, Ohio, Pennsylvania, New York, Maine, New Hampshire, Massachusetts, Rhode Island, Connecticut, New Jersey, Delaware, Maryland, Virginia, North Carolina and others) have their own methods for assessing vapor intrusion, similar to the approach recommended by the USEPA (NEW JERSEY, 2005).

Although the USEPA (USEPA, 2002), has limited the use of predictive models, the Johnson and Ettinger model (1991) is still widely used for evaluating the indoor intrusion of vapors from subsurface sources (MCHUGH; NICKELS, 2008). The API BioVapor model has also been widely used for petroleum sites. It can be found in the American Petroleum Institute (API) website.

The State of São Paulo has its own guideline for evaluating this route of exposure that incorporates the Johnson and Ettinger model (1991). On October 20th, 2009 the State of São Paulo Environment Agency, CETESB, published guidance for fuel retailers on site investigation and intervention plans, and included in that guidance procedures for assessing vapor intrusion (CETESB 2009).

According to the guidance, when the spatial distribution of contamination plumes is mapped during the detailed investigation stage, risk maps are drawn that show iso-concentration curves corresponding to CMAs (maximum acceptable concentrations) that were exceeded. On the vapor intrusion risk maps, the limits of iso-concentration curve of the CMA are increased by 10 meters, thus defining a constraint area for the presence of receptors subjected to this exposure. If there are buildings and receptors occupying spaces within the mapped risk area, intervention measures should be adopted to reduce concentrations in source areas or at exposure points until they reach acceptable levels established by the risk assessment worksheet of CETESB (risk increase of 10^{-5} for carcinogenic compounds and 1.00 risk ratio to toxic effects).

Currently, regardless of the specific parameters of the area, the CMA for dissolved benzene for a residential occupancy scenario (assuming a typical adult) is 272 µg/L; for a commercial occupancy scenario, the CMA is 892 µg/L. If there is any building occupied by any of these types of receptors within the limits of the risk map corresponding to the CMA, an intervention plan is required.

However, in this method, variables associated with attenuation processes that occur during the transport of contaminants between the vapor source and target environments of study are not included or are treated in a generic way (aerobic biodegradation, deep in the water level, organic carbon fraction in the soil, porosity, etc.).

3 – CONCEPT REVIEW

The process of migration of volatile compounds from a source on the subsurface to the interior of existing buildings is known as vapor intrusion. Volatile compounds present in soil and groundwater may be liberated into vapor phase, with potential to migrate through layers of unsaturated soil and fractures or cracks on the buildings' base, eventually reaching indoor environments and altering air quality. **Figure 01** shows the conceptual basis of the process and the relationship between the main parameters involved in the vapor intrusion process.

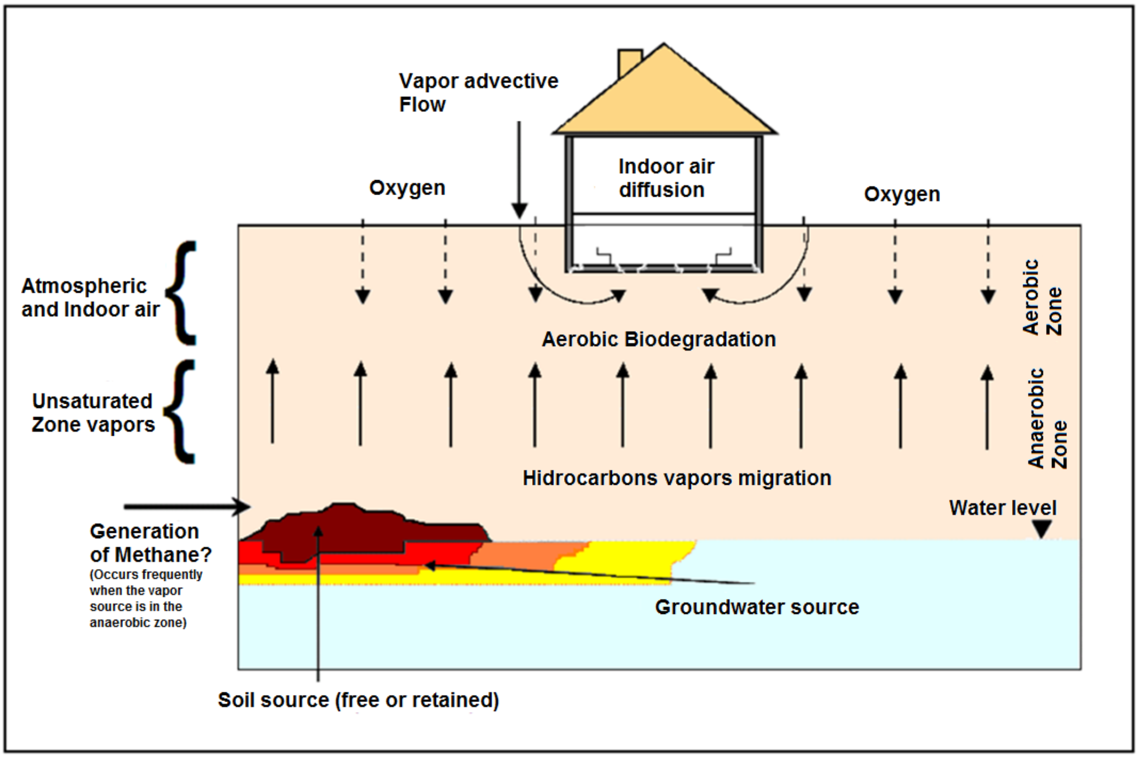


Figure 02 – Conceptual basis of the migration process for subsurface vapors to indoor environments and the relationship between the main parameters involved

Source: Modified from API 2005

In extreme cases, the accumulated vapor in the environment may represent imminent risk, for example, explosion or acute toxicity (**Photograph 01**). However, in most cases, only low concentrations of the chemicals of interest are observed, which can increase the risk of occurrence of chronic health effects on the receptors that occupy these spaces over a long exposure time (USEPA, 2002).

In this chapter, variables of the physical environment that can influence the process and vapor attenuation mechanisms that occur in the unsaturated zone will be discussed. Additionally, currently available methods for investigating the occurrence of vapor associated with subsurface volatile organic compounds are presented.

Photograph 01 – Combustion of gases and vapors from a subsurface source

Source: Tomlinson (2008)

3.1 - Vapor Sources

In any vapor intrusion scenario, the initial condition is the existence of a source area. In general, the vapor source may be characterized by the presence of volatile chemical substances or mass concentrations sufficient to represent a potential risk for migration indoors. This includes the presence of volatile compounds in free phase, dissolved in groundwater phase, residual phase or adsorbed to soil particles, in intra and intergranular spaces, fractures, discontinuities, planar structures (i.e., contact between distinct lithological layers, mirror of flaws, geological contacts) and other discontinuities in the soil or in the existing rocks in the study area.

The sources of vapors may be related to the presence of landfills, industrial plants, distribution depots and fuel storage (focus of evaluation in this study) and other places where products containing volatile organic compounds are stored, handled or transported. For petroleum products, the vapors formed, being heavier than air, will spread over the affected surface and may accumulate in concentrations that provide short-term risks (i.e. explosions or acute effects on human health) or nuisances due to the generation of odors (Johnson, 2002).

3.2 – Physical Environment Variables

3.2.1 Soil Profile

Site geology can affect the mobility of vapors and needs to be properly characterized and mapped to evaluate and detail the presence of geological barriers (fine-textured layers with high moisture content), preferential paths (vertical fractures with significant gaps, lithological diversity), or materials with potential to increase or retard the transport of vapors. Typically these data are obtained from geological surveys, visual inspection and laboratory analysis of geotechnical properties such as porosity, moisture, organic matter fraction and particle size distribution (New Jersey, 2005).

When evaluating the relevance of different indoor intrusion routes of subsurface vapor, the following parameters related to the local soil profile are typically considered:

- porosity (total and effective);
- volumetric content of water present in the soil;
- fraction of organic carbon in the soil;
- Total density of the soil; and,
- hydraulic conductivity of the porous medium.

In Brazil, the incorporation of geotechnical techniques for undisturbed soil sampling at depth (thin-walled samplers type Shelby, block sampling, etc.) and field tests for geotechnical soil classification and groundwater depth (CPTU test), has improved the quality of such data (IGNATIUS, 1999).

3.2.2 Physical characteristics of Brazilian soil

Soil forming processes, such as weathering and pedogenesis, can significantly influence geotechnical properties taken in consideration when evaluating vapor intrusion processes.

This consideration is particularly important in the Brazilian context, since the predominant weathering processes in tropical and subtropical regions can affect the thickness of the soil profile (potential field for migration of organic vapors and water), dissolution and precipitation of mineral species, diagenetic processes related to the formation of clay minerals, etc. In the Serra do Mar region, for example, the soil profile can be as much as 100 meters thick (MELFI; MONTES, 2008).

Oxisol is a dominant soil type in Brazil. The soil particle size in these soils is predominantly clay mainly composed of kaolinite (clay 1:1), which has a lower vapor retention trend and humidity than the clay smectite type (2:1) (MELFI; MONTES, 2008). The iron, manganese and aluminum oxides, common in oxisols, form lateritic crusts, which constitute natural barriers to migration of vapors. The distribution of lateritic crusts is constrained by the topography of the land.

CETESB (CETESB, 2001) conducted soil characterization work in São Paulo to determine the regional background of naturally occurring substances in the soil, especially metals, and establish the guiding values for reference.

The methodology consisted of sampling the main types of soils across the state, concluding that oxisol is the predominant soil type, followed by podsol. The sampling interval was from ground surface (0 to 20 cm) and subsurface (80 to 100 cm). Results were considered statistically comparable, so that only one value has been adopted for the whole interval, maximum quartile of 75%.

Specific studies using column testing to simulate the behavior of the migration of vapors in relation to the intrinsic geotechnical properties of the soil are fundamental to establish national values related to vapor transport and migration phenomena. Currently, a research project being developed by PRIME (PRIME 2015) in the POLI-USP and IPT laboratories tests soil columns (Oxisols) and sand.

3.2.3 Weather Conditions

The influence of climatic conditions on the vapor transport process in the subsurface is very complex and difficult to predict. However, in some situations, they may significantly modify the process.

Air pressure and temperature directly influence how volatiles partition to the vapor phase (as defined by Henry's and Raoult's Laws), with an expected relationship (proportional, in the case of temperature and inversely, in the case of pressure) between the variation of these parameters and the magnitude of the process. That is, higher migration rates can be expected during the warmer periods of the year and lower rates during periods of higher atmospheric pressures.

Similarly, higher depressurization rates in buildings and consequent migration of vapors through unsaturated soil layers would be expected during warmer periods due to the ‘stack effect’.

The moisture content in the soil profile also has significant influence, since the saturation of the porous environment (i.e. unconfined aquifer) may represent a barrier to the migration of vapors. Thus, higher migration rates would be expected during drier periods of the year.

However, there is no simple relationship between these factors, so it can be difficult to predict the level of influence these variables have on vapor formation and migration.

This can be best illustrated when observing the climatic conditions prevailing in the Brazilian tropics. The hottest periods are also rainy, with the soil profile more saturated in humidity, which decreases the formation and migration of vapors. So in this scenario, the vapor transport rate could actually be reduced. However, during rainy periods the groundwater recharge fronts can induce advective flow of vapors.

Weather can also have an effect on biodegradation processes. The high moisture content can reduce the flow of oxygen from the atmosphere into the subsurface, thereby reducing the process of aerobic biodegradation of hydrocarbons in the unsaturated zone (NEW JERSEY, 2005).

The influence of seasonal factors over the ventilation inside the constructions is also hard to predict. For example, during the coldest periods of the year, natural ventilation through windows or doors can be reduced, decreasing the dilution of vapors that may come from subsurface. Daily temperature variations can be important when considering this seasonal factor.

It is worth noting that the extent of seasonal variations, especially temperature, decreases with increasing depth. In some situations where the average water level of the free local aquifer is deep, seasonal impact may be insignificant or nonexistent (NEW JERSEY, 2005).

3.2.4 Construction characteristics of the buildings

Conceptually, buildings with different types of structures in contact with the ground can lead to different processes of vapor intrusion. For example, for homes with basements, higher rates of advective flow of vapor would be expected due to increased depressurization rate and the contact surface with the subsoil, while in buildings installed on "*palafitas*" (a term used to designate buildings built on elevated structures in order to avoid direct contact with the ground, common in humid areas or wooden houses), the existing ventilation between the floor and the subsoil is increased, increasing the mixing rate with the outside air, thereby decreasing the rate vapor intrusion. These kinds of buildings are the only ones that can be considered intrinsically safe.

The vapor intrusion processes can occur regardless of the layout of the building assessed, even when the surface appears to be free of cracks or discontinuities.

Figure 02 illustrates the main types of construction considered when evaluating the intrusion of subsurface vapors indoors.

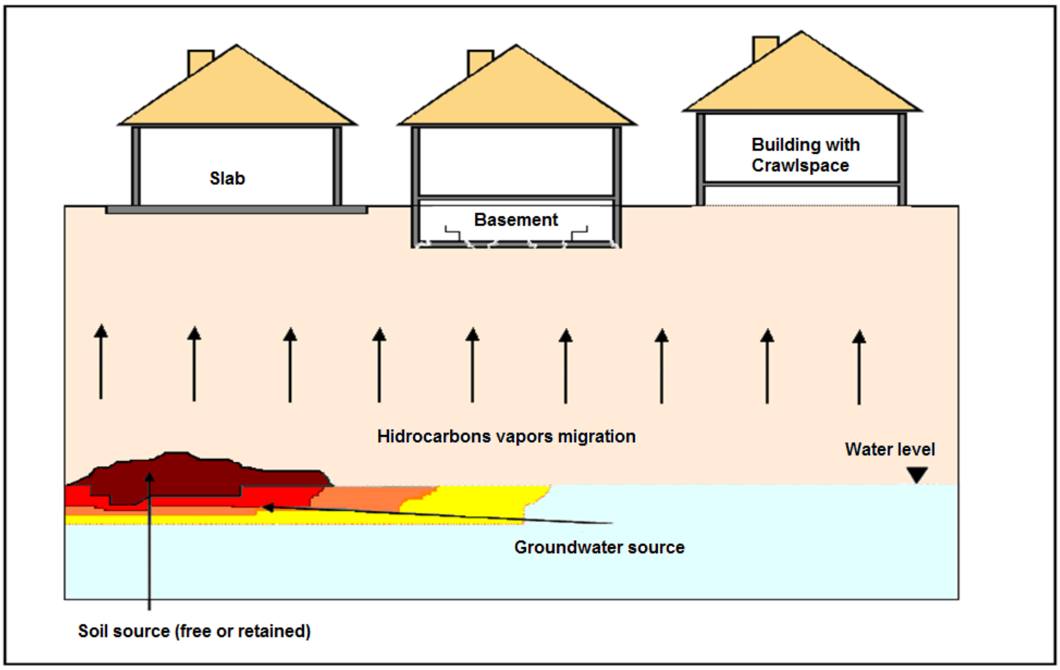


Figure 02 – Basic types of constructions considered in evaluating the indoor vapor intrusion processSource: Modified from API 2005

In some situations, during construction, mechanical barriers of plastic or asphalt material are installed (impervious webs), which can reduce the advective transport vapor (**Photograph 02**). But if the barriers are not installed properly, the diffusive flux of vapors through small perforations can be significant (HERS 2010).

Photograph 02 – Installation of asphalt barrier

Source: Hers (2010)

When subsurface vapors enter the interior of buildings, ventilation and air changes will result in dilution of concentrations from the subsurface by the air present in indoor environments. From the point of view of mathematical modeling, it is commonly assumed that the distribution of concentrations indoors is uniform.

It is important that during the preparation of the conceptual model, age-related construction data is collected, as well as type of pavement, presence of underground utilities that may represent preferred paths, layout and distance (lateral and vertical) in relation to the source of vapors.

3.2.5 Background Concentrations

During vapor intrusion evaluations, the possible influence of background concentrations should be considered, both from external sources and from existing sources inside the buildings evaluated. These sources can contribute to the presence of chemical compounds of interest in detectable concentrations or even higher than the environmental quality standards used as reference. The evaluation of the possible presence of background concentrations is important, especially when low concentrations are measured that may constitute long-term risk.

Potential alternative sources present indoors include cleaning products, consumer goods and building materials. Table 01 presents a summary relating the potential sources for release of BTEX indoors.

External sources include emissions from cars, industries, places with significant use and handling of chemicals, landfills, and others. In extreme cases, outside air concentrations may be higher than the indoor air target levels. Such considerations are especially important in densely populated and industrialized cities and should be included during the preparation of the conceptual model of the evaluated areas.

Table 01 – Potential sources of BTEX release indoors

Source	Compound			
	Benzene	**Toluene**	**Ethylbenzene**	**Xylene**
Latex-based paint	X	x		
Carpets	X	x		
Carpet Glue	X	x		
Wood Burning		x		x
Varnish remover		x		
Spray products				x
Scotch tape		x		
Cigarette smoke	X	x	x	x
Gasoline	X	x	x	x
Solvents		x	x	

Source: Adapted from Hers et al. (2001, p.180)

3.3 Vapor Transport Mechanisms in subsurface

The recognition of fate and transport mechanisms of vapors in the subsurface is critical to the interpretation of data collected during a specific assessment of vapor intrusion. Theoretical considerations regarding these processes should guide the development of conceptual and mathematical models for the scenarios evaluated.

The main fate and transport mechanisms of vapors in subsurface affecting indoor vapor intrusion process will be described in this chapter.

3.3.1 Diffusion

The diffusion process, from the physical and thermodynamic point of view, is a transport phenomenon associated with kinetic energy of molecules, where the chemicals of interest, solutes, migrate from areas with the presence of high concentrations to areas with relatively lower concentrations (NEW JERSEY, 2005). This process occurs regardless of the flow velocity, and can be observed inside solids, liquids and gases. In practical terms, diffusion can be exemplified by the scent of a perfume that spreads in an environment or a drop of ink that is diluted in water (**Photograph 03**).

Photograph 03 – Example of diffusion of potassium permanganate in water

Source: Kalipedia (2010)

Under steady state conditions, where the concentrations do not vary with time, the equation that correlates the diffusion flux (J) with the gradient of concentration (dC / dx) is called Fick's First Law:

$$J = -D \times \frac{dC}{dx} \tag{1}$$

Where:

J = Mass flow of solute per unit area per unit time;

D = Diffusion Coefficient (cm^2/s);

dC/dx = Concentration Gradient ($g/cm^3/cm$ or g/cm^4);

The negative sign in the above equation indicates that the flow is in the opposite direction to the concentration gradient, so, in the direction of high concentration to low concentration (NEW JERSEY, 2005). In Fick's first law, the thermodynamic potential or driving force in the diffusion phenomenon is the concentration gradient.

However, most practical situations involving the diffusion process occur at non-steady state conditions (transient conditions) where the concentration (C) in a given position (x) varies as a function of time (t). To describe the spread in non-steady state, the partial differential equation, known as the second Fick's Law, is used:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \times \frac{\partial C}{\partial x}\right) \qquad (2)$$

In situations where the diffusion coefficient is not dependent upon the composition (and thus the position), Fick's second law can be simplified to:

$$\frac{\partial C}{\partial t} = -D \times \frac{\partial^2 C}{\partial x^2} \qquad (3)$$

When boundary conditions that have a physical meaning are specified, it is possible to obtain solutions for Fick's second law. These solutions are functions C = f (x, t), which represent the concentration in terms of position and time.

In the porous environment, for example, in a free aquifer, the magnitude of the diffusion process is lower than that observed in a free solution. This reduction is associated with the tortuosity of the flow paths and retention of ions and molecules on the surfaces of the particles. To calculate the effect of this reduction, use the coefficient of Effective Diffusion D*:

$$D^* = \omega \times D_O \qquad (4)$$

Where: ω = tortuosity coefficient (BEAR, 1972)

Do= diffusion coefficient in a free solution.

The diffusion of volatile chemical compounds in vapor phase is an important mechanism of transporting contaminants in the non-saturated zone, and may occur in environments with the presence or absence of advective flow. In a porous environment, the diffusive flux of the chemical compounds of interest is proportional to the average diffusion coefficient in the environment and the existing concentration gradient. The diffusive flow rates may vary depending on various factors such as porosity and moisture content of the soil column, concentration gradients, temperature, size and structure of the molecules of the chemical compounds of interest, the viscosity of the fluid and the environment in which the diffusion will occur.

3.3.2 Advection

The advection process is characterized by the transport of molecules or ions through a moving fluid, where these elements move in the direction of the flux lines at an average speed equal to the fluid (NEW JERSEY, 2005). The equation that models this type of transport is the differential equation of transport by advection:

$$\left(\frac{\partial C}{\partial t}\right) = -V_X \times \frac{\partial C}{\partial_X} \tag{5}$$

$$V_X = \frac{K}{n} \times i \tag{6}$$

Where:

C = Solute concentration (g/cm^3);

V_x = percolation speed (cm/s);

K = permeability coefficient (cm/s);

n = porosity and;

i = hydraulic gradient.

When the fluids percolate through a porous environment such as soil, whose volume is partly occupied by solids, this phenomenon will occur predominately in media with high permeability such as sands, cracked clays and weathered, fractured rocks. Therefore, variables related to the physical properties of the environment, such as impermeable lithological layers and the presence of structures and floors that can redirect the advective flow, particularly to vapor phase, must be taken into account during the modeling.

Advective transport is a major process for the movement of vapors in the unsaturated zone. Advective flow may be related to temperature gradients, pressure gradients and density differences (vapors denser than atmospheric air tend to go down, accumulating along the capillary fringe while less dense vapors than air tend to rise, getting accumulated in layers nearest to surface

Temperature gradients can be related to seasonal or diurnal warming of the surface layers of soil. The differential pressures may be related to recharge fronts of groundwater that compress the vapors accumulated in the pores. Differential pressure can result from the ventilation systems in buildings and by wind-blown on structures that may result in advective movement of vapor from the soil to the indoors impermeable lithologic layers and man-made structures, such as decks and passive exhaust systems can redirect the advective flow of vapors and should be considered during modeling (NEW JERSEY, 2005).

3.3.3 Mechanical Dispersion

Mechanical dispersion results from the interaction between the moving fluid and the solid structure of porous medium. It is characterized by tortuous movement of fluids through the center portion of the flow, and results in mass spreading of the compounds beyond the region with predominantly advective flow. This movement can occur in both horizontal and vertical directions.

During the modeling of this process in water systems, the hydrodynamic dispersion coefficients are calculated using local soil characteristics related to dispersibility and advective speed of movement of vapors (FETTER, 1980). **Figure 03** illustrates the causes of mechanical dispersion in the size range of the pores.

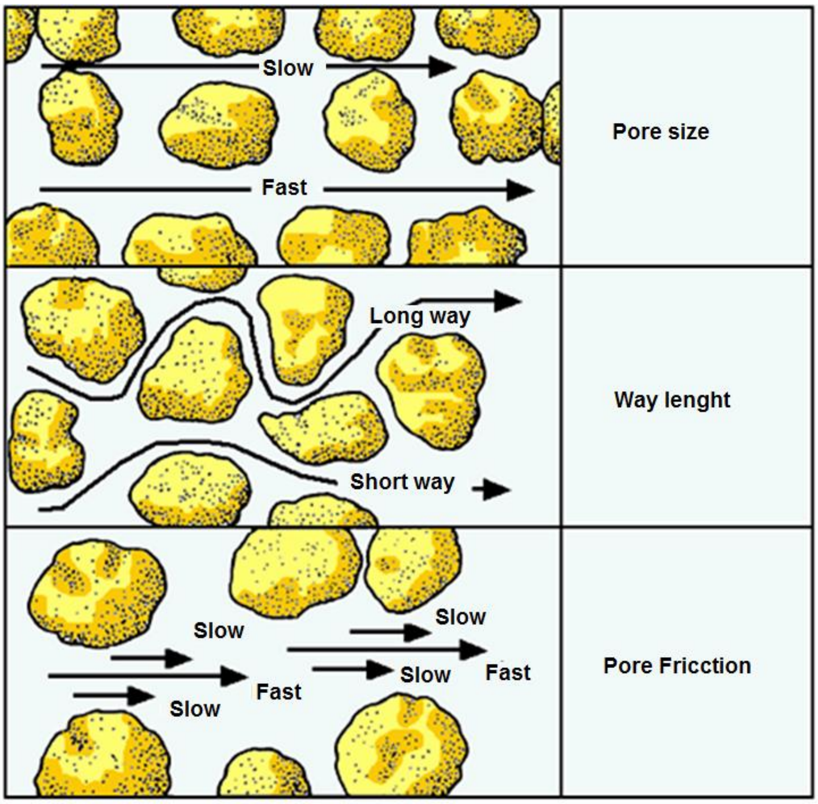


Figure 03 – Causes of longitudinal mechanical dispersion in the pore size scale
Source: Adapted from Fetter (1980)

The dispersibility is the amount of mechanical mixing that occurs as a result of local variation in the flow velocity around the center's predominant speed. This variable can be measured or estimated. Unlike the dispersion into aquifers, air dispersal incorporates the turbulent motion of the fluid in the center of the flow. The equations for calculating atmospheric dispersion require information on the emission rate or flow of vapors and particles in the subsurface, wind speed and steering, lateral and vertical scattering factors, subsurface characteristics and height of the mixing zone.

3.3.4 Partition between phases

According to Hulling and Weaver (1991, and GALANTE, 2008, p. 24), the contamination in the saturated zone may occur in a NAPL phase, vapor phase, adsorbed phase or dissolved phase. The compounds present in vapor phase result from the volatilization of compounds present in the other phases.

Generally, the greater contribution of contamination comes from the NAPL phase. The potential for indoor vapor intrusion is proportionally greater for compounds that volatilize more easily.

The transfer of mass from a source of contamination to the vapor phase will depend on the vapor pressure of the pure compound, which corresponds to the maximum possible vapor phase concentration in a given condition of temperature and pressure. Partitioning from the free phase/residual phase to the vapor phase is governed by Raoult's law (partition from NAPL phase to the vapor phase) and partition from low concentrations in the dissolved phase to the vapor phase is governed by Henry's Law. Those phenomena are ruled respectively by the vapor pressure and the solubility of the compound, and vary depending on the pressure conditions and temperature.

3.3.5 Biodegradation

Biodegradation is based on processes in which there are biochemical reactions mediated by microorganisms. In general, an organic compound, when oxidized, loses electrons to a final electron acceptor, which is reduced (gains electrons). When present, oxygen commonly serves as the final electron acceptor, wherein the oxidation process of organic compounds, together with the reduction of molecular oxygen, is called heterotrophic aerobic respiration.

However, when there is no oxygen available, the microorganisms may use some alternative organic compounds or inorganic ions as final electron acceptors, which is known as the anaerobic condition. Anaerobic biodegradation may occur by denitrification of organic matter, iron reduction, sulfate reduction, acetate decarboxylation and CO_2 reduction (methane producing) (CORDAZZO, 2000).

Depending on the substrate, the VOC, the electron acceptors (i.e. Oxygen-O_2), and nutrients, biodegradation may be a limiting factor on the transport of organic vapors to indoor areas. However, most of the models used for risk analysis currently do not consider this process.

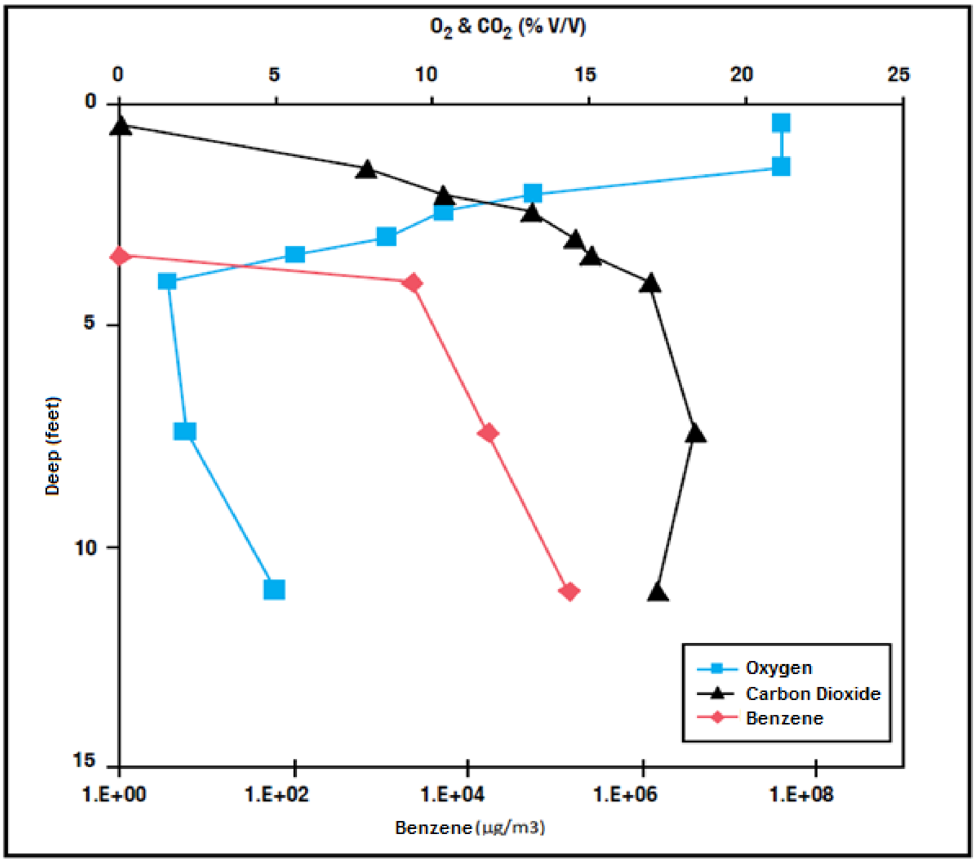
According to Hers et al. (2002), aerobic biotransformation of organic contaminants occurs in the non-saturated zone under suitable conditions, depending on oxygen availability, microbial population, moisture, nutrients and the presence of suitable conditions of pH, temperature and salinity.

De Vaull (1997, and HERS, 2002, p. 8), suggests that under conditions where the oxygen concentration exceeds 4% and where the concentration of dissolved nitrate present in the entrapped water from the pores exceeds 1 to 2 mg/L, biodegradation can be maintained. The results obtained by Zwick et al. (1995, and HERS, 2002, p. 8) suggest that aerobic biodegradation is significantly reduced as the moisture content present in the ground increases. These results are consistent with those obtained by Teixeira et al. (2009), who studied the aerobic oxidation of methane in three landfills in Brazil. The results of this study suggest an inverse relationship between the degree of saturation at the time of collection of the analyzed soil samples and the number of methanotrophic bacteria present in the soil profile.

This evidence indicates that the dissolved phase of volatile organic compounds is subjected to biodegradation processes in aerobic and anaerobic conditions in groundwater. Aerobic biodegradation of volatile organic compounds using alternative electron acceptors (i.e. Nitrate, sulfate) can occur in the groundwater at considerable rates, however, few studies have been conducted to demonstrate the extent of biodegradation in the unsaturated zone using these acceptors.

Other lines of evidence can be used to demonstrate the occurrence of biodegradation in the unsaturated zone, such as the presence of other gases in the soil. During the biodegradation process, oxygen is consumed and in its place, carbon dioxide is generated (HERS, 2002).

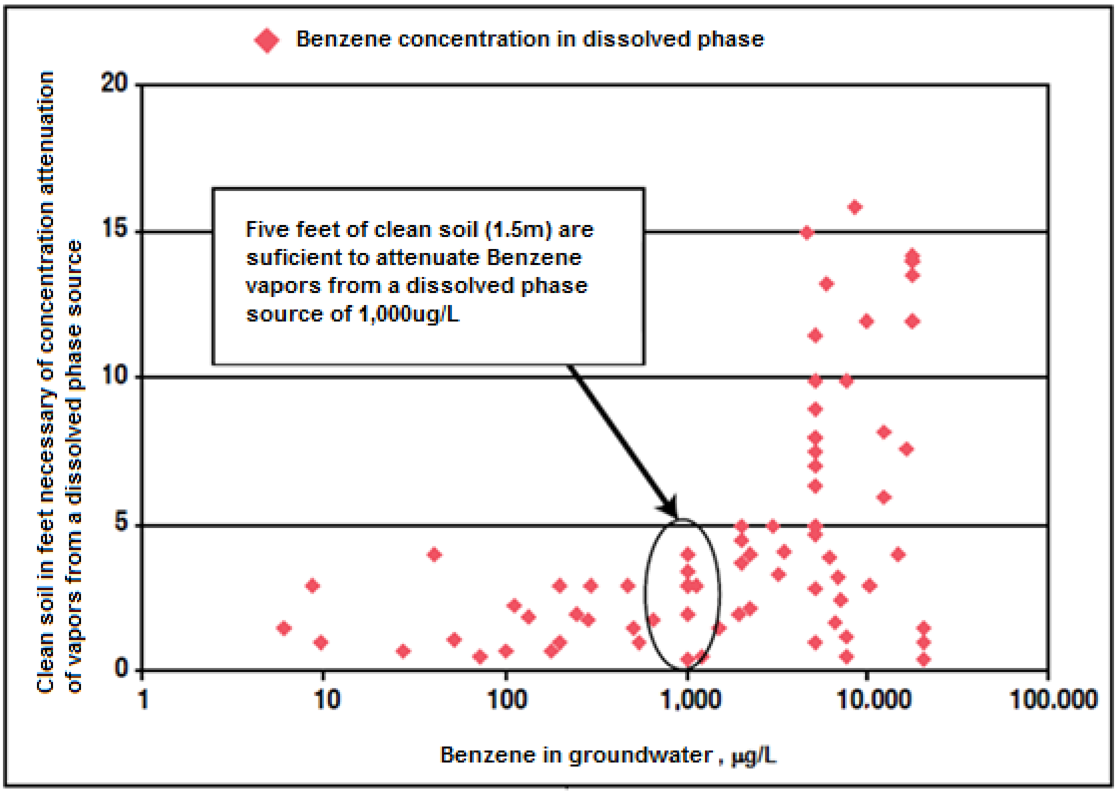
According to Davis (2009), the aerobic biodegradation of petroleum hydrocarbons can be recognized by a characteristic signature illustrated in **Graph 01**, where the concentrations of the vapor phase chemical compounds of interest are high close to the contamination source, accompanied by a reduction in oxygen and enrichment in concentrations of carbon dioxide. Above the contaminated zone, carbon dioxide and oxygen concentrations return to the expected conditions near the surface environments. This example demonstrates that the petroleum hydrocarbon concentrations in vapor phase, associated with highly dissolved concentrations (low persistence contamination sources) are attenuated by a factor of roughly one million for every 2.1 meters of clean soil layer over the source of contamination.



Graph 01 – Characteristic concentration profile indicating aerobic biodegradation of hydrocarbons

Source: Adapted from Davis, 2009

From a database of approximately 127 vapor and groundwater monitoring campaigns in several areas located in the United States and Canada, Davis (2009) established clean soil thickness over a contamination source necessary to mitigate concentrations of benzene vapor associated with various concentration ranges in dissolved phase, as illustrated in **Graph 02**.

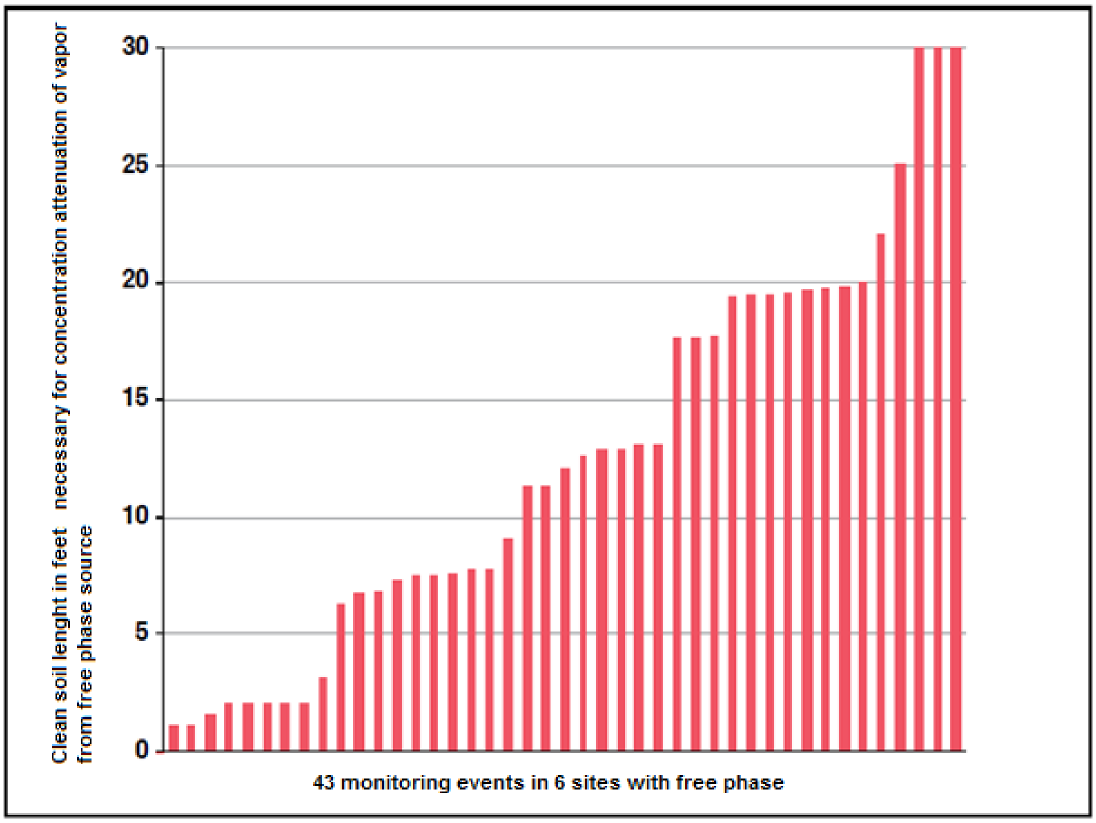


Graph 02 – Clean soil thickness necessary to mitigate concentrations of benzene in vapor phase associated with various concentration ranges in dissolved phase

Source: Adapted from Davis, 2009

The data obtained demonstrate that a layer of 1.5m in thickness of clean soil over the area source of vapor is sufficient to attenuate the vapor phase at concentrations associated with dissolved phase concentrations equal or greater than 1,000 µg / L benzene. Approximately 4.5 meters of clean soil are sufficient to attenuate benzene concentrations associated with dissolved phase concentrations greater than 25,000 µg / L.

Graph 03 shows data obtained from 43 sampling campaigns at six areas where the occurrence of products in free phase were observed. These data indicate that concentrations of vapor associated with the presence of free phase are completely attenuated with a layer of nine meters of clean soil.



Graph 03 – Clean soil thickness necessary to mitigate concentrations of benzene vapor associated with sources with product free phase

Source: Adapted from Davis, 2009

According to Davis (2009), the relationship between concentrations present at the source, in free or dissolved phase, and the thickness of clean soil present on the source can be used as decision criteria to evaluate the relevance of the route of exposure associated with the intrusion of vapors indoors, guiding future actions related to environmental management of areas contaminated by the presence of volatile organic compounds.

3.3.6 Ethanol influence

According to Ferreira (2003), gasoline sold in Brazil receives the addition of anhydrous ethyl alcohol, also known as ethanol, into fractions which can vary from 20 to 24% in volume. The use of this compound in gasoline increases octane level and reduces carbon monoxide emissions into the atmosphere.

According to Chiaranda (2006), the addition of ethanol to gasoline affect the main properties that rule its distribution in the subsurface. When ethanol-containing gasoline is spilled into the unsaturated zone, the hydrophilic nature of ethanol causes it to partition into the water contained in the soil interstices and remain stored in this region due to capillary forces. The presence of ethanol in the unsaturated zone reduces the interfacial tension LNAPL-water, thus promoting the migration of LNAPL in the soil until it reaches the capillary fringe, where it starts to accumulate.

In quantities exceeding 10% by volume of the mixture, ethanol increases its saturation in the water, reducing surface tension and the ability of capillary forces to keep it in the unsaturated zone. Thus, alcohol also begins to migrate through the unsaturated zone to reach the LNAPL plume, increasing the solubility of pure product in water, an effect known as co-solvency (POWERS; McDOWELL, 2003).

The results obtained by Ferreira, Oliveira and Duarte (2004), who studied the relationship between the thickness found in monitoring wells and the porous medium, both for pure gasoline and for E-20 (80% gasoline and 20% ethanol) indicated that the BTEX concentrations are significantly higher in a dissolved phase plume of E-20, compared to pure gasoline (despite the mole fraction of BTEX being lower in the first, due to the addition of ethanol in the composition). In addition to increasing the mass transfer BTEX to groundwater, ethanol is also responsible for the increased length of the BTEX plume, because the reduction of the interfacial tension between the E-20 and the aqueous phase increases increase the migration capacity. Likewise, reduction of interfacial tension contributes to the reduction of the capillary fringe’s height, with the increase of the ethanol content in the saturated zone.

Due to the property of co-solvency, ethanol has also been applied in remediation where the persistence of residual gasoline phase is observed. Oliveira (1997) presented a detailed analysis of the pseudo-ternary diagram for fuel-water-ethanol. Results were obtained regarding the minimum amount of ethanol necessary for the fluid to reach the miscible displacement for complete removal of gasoline residues in a process of ethanol injection (flushing). The minimum amount of ethanol to incur a water miscible displacement corresponds to about 88% in ethanol weight and 12% water. Otherwise the miscibility is not achieved and the removal of gasoline residues is not complete.

Regarding the partition of volatile compounds to the vapor phase, the presence of ethanol in gasoline increases the vapor pressure of the mixture and consequently the tendency of loss by evaporation. The volatile organic compounds present in the fuel mixture, such as BTEX, tend to increase proportionally.

Finotti et al. (2009) quantitatively evaluated the influence of ethanol on the volatilization process of BTEX compounds in a mixture of gasoline and anhydrous ethanol 25% (v/v) in experimental columns that simulated soils contaminated with pure gasoline and gasoline/ethanol. The results showed that all BTEX compounds showed significant increase in volatilization rates in the column containing the mixture gasoline/ethanol.

According to Cruz et al. (2003), this phenomenon can be explained by the change of intermolecular bonds of hydrocarbons of gasoline caused by the presence of ethanol, which can occur in two ways:

> 1) For small amounts (up to 10%), all the ethanol molecules are surrounded by hydrocarbon molecules. The presence of ethanol causes the breaking of the intermolecular bonds of hydrocarbons, facilitating its evaporation and thereby increasing the vapor pressure of the mixture;
>
> 2) For higher ethanol levels, alcohol molecules are present in amounts sufficient to interact with one another and, since these interactions are stronger than the ones between molecules of

> hydrocarbons due to the higher polarity of the ethanol, the vapor pressure of the mixture starts to decrease.

Cruz et al. 2003 also showed that the effect of the presence of ethanol on vapor pressure becomes more pronounced as the temperature of the center increases.

3.4 Investigation of occurrence of vapor in the subsurface

Sampling of vapors present in the soil has been used as a tool to evaluate the spatial distribution of the chemical compounds of interest present in the soil and groundwater (MCHUGH; NICKELS, 2008). These data are commonly used to guide the environmental characterization of the areas under study, identify areas where soil and groundwater samples should be collected, and monitor the efficiency and effectiveness of remediation systems.

Since the results of this type of sampling generally do not provide specific concentrations in vapor phase of the chemical compounds of interest, the methods traditionally used during an environmental characterization are not suitable for assessing the impacts related to exposure to vapors indoors.

The collection of soil vapor samples for analytical determination of compounds and concentrations present to evaluate the vapor intrusion potential is a relatively new approach. However, in countries that already have specific guidelines, this method has frequently been used to provide a more accurate estimate of potential for contaminants in the subsurface to reach the receptors present indoors.

In this context, the aim of this chapter is to briefly present the main steps involved in a typical environmental investigation focused on the distribution of concentrations in vapor phase at places where, during the stages of confirmatory or detailed environmental investigation, concentrations of volatile organics in soil and/or groundwater exceeded environmental quality standards for the exposure route in question.

3.4.1 Development of the conceptual model

The development of conceptual models for assessing vapor intrusion has as main objective the three-dimensional presentation of specific data available for the study area, in the most comprehensive and clearest way possible, including all relevant characteristics. This model must be based on reliable data describing the sources of contamination, the existing release and transport mechanisms, the potential subsurface migration routes, potential receptors, as well as historical data on the use and occupation of the area evaluated and, possibly in some cases, the intended use in a future scenario (NEW JERSEY, 2005).

The conceptual model should include a consistent textual description, clearly distinguishing aspects that are known or determined in the field and assumptions based on empirical data. Its graphical representation must include the relationship between contaminants and possibly present receptors. Usually, it presents information related to the soil, geology, hydrogeology, heterogeneities, soil and groundwater contaminant concentrations, regional direction of groundwater flow, and features present in surface (i.e. presence of recharge areas, surface water bodies and ground cover). The conceptual model is a dynamic tool, and should be updated whenever there is new information available, as appropriate, after each new investigation stage.

The conceptual model is an essential tool to help in decisions related to environmental management. Therefore, it should provide all interested parties (e.g., legal representatives and managers) with a general understanding of the scenario, including the potential for exposure to the contaminants of interest. In this context, for developing a consistent vapor sampling plan and establishing site conditions, the conceptual model must contain at least the following information:

a) chemical compounds of interest currently present or previously stored or processed on-site (chlorinated solvents, gasoline, jet fuel, diesel, etc.);

b) concentrations detected in soil and / or groundwater, environmental standards used as a quality reference and applied analytical methods;

c) potential sources for release of vapors (presence of free phase, phase adsorbed to the soil, phase dissolved in the groundwater, etc.);

d) geological-geotechnical and hydrogeological conditions of the area;

e) approximate location of subsurface sources of vapor and distances (lateral and vertical) in relation to the assessed buildings;

f) types of flooring that might influence the flow of vapors between the subsurface and indoor air on the site;

g) presence of underground utilities;

h) characteristics of existing buildings (construction such as slab-on-grade or basement, size, age, presence of cracks in the foundation, etc.);

i) potential use of the area in a future scenario.

3.4.2 Selection of sampling points

For a consistent analysis, the expected conceptual model for the study area should be set prior to the selection of the depths and the points to be sampled, describing the main features of the sources of vapor, including their location, extent, characteristics of the physical environment, concentrations of the chemical compounds of interest and the expected variation in these characteristics over time (Ex. seasonal variations). The model may further include the expected distribution of the gases present in the soil along the profile evaluated, and the following basic information (API 2005):

a) stability of analyzed concentrations over time;
b) expected gas distribution profile, considering the influence of existing geological features in the area; and,
c) presence of underground utilities or other preferential pathways for migration of vapors.

3.4.3 Installation of monitoring wells for soil vapor sampling

The procedure for installing vapor monitoring wells, together or individually, is similar to that used for installing wells for groundwater sampling.

To install vapor sampling wells, manual methods are recommended, as these methods can be used in most soils present in the unsaturated zone. With manual methods, it is easier to be careful about the dimensioning of the bentonite seals and filling with pre-filter in the filter sections. Additionally, manual drilling is advantageous over more invasive methods (roto-pneumatic drill), because it minimizes disturbances in the distribution of vapor in the soil resulting from the drilling procedure, reducing the re-equilibration time (API 2005).

The drilling may be performed using manual auger of 4" in diameter. For the coating of the survey is recommended to use small diameter tubes (1/4 "), made from chemically stable material, such as stainless steel or Teflon® or nylon. The use of PVC pipes is not recommended, because this material may react to some volatile organic compounds (API 2005). The typical constructive profile for vapor sampling at different levels of depth can be seen in **Figure 04**.

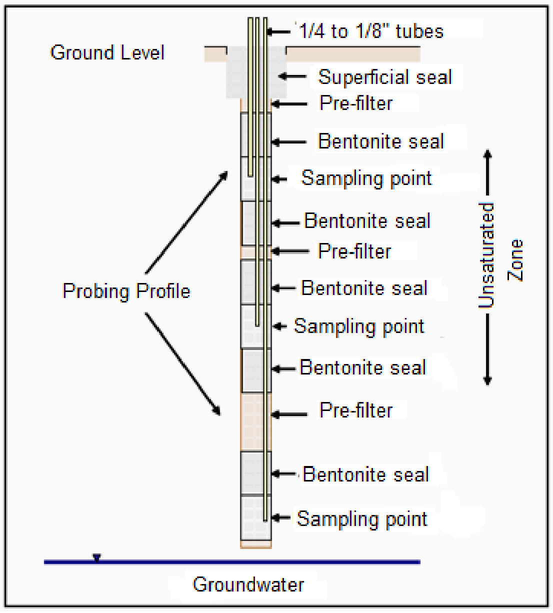


Figure 04 – Typical constructive profile for vapor sample wells

Source: Modified from API, 2005

Considerations when installing wells for sampling vapors (API, 2005) include:

a) the length of the filtering section must be short, between 15 and 30 cm;

b) for the installation of multi-depth wells, the filtering sections must be separated by efficient seals; the combined use of liquid and pellet bentonite is recommended;

c) the annular gap between the wall of the probe and the filter of the well should be filled with selected pre-filter with similar particle size fraction as that found in the soil profile in the evaluated area;

d) When wells are installed together (sampling at different depths), the filtering sections must be separated by approximately 50 cm in the shallower portions and between 1 and 1.5 m for deeper systems, according to the configuration illustrated in **Figure 04**;

e) it is necessary to describe in detail the lithological units that constitute the soil profile in the evaluated area, especially for samples collected near the source areas or near receptors. When layers with different permeability are present, sampling must be performed in higher permeability layers, as they may represent preferential paths for the migration of vapors;

f) in areas where the vapor source is located near the groundwater, it is advisable to install one or two sampling wells with a maximum depth of 60 cm above the highest water level in the area. Sampling at these points may provide more accurate data about vapor phase concentrations if conducted during periods when the free aquifer is deeper;

g) methods recently available on the market (e.g. direct push by GEOPROBE Systems®) enable greater precision during the process of installing permanent or temporary wells for sampling vapors in the soil. These tools increase the reliability and representativeness of the data obtained in the field (GEOPROBE SYSTEMS, 2006).

3.4.4 Procedures for soil vapor sampling

Collecting and storing vapor samples can be accomplished by means of various equipment, such as Summa Canisters, TedLar®Bags, tubes with adsorbent materials, glass cylinders and sampling syringes. Equipment should be selected according to the objectives of the investigation, the inherent methodological requirements and the necessary detection limits for the assessment of exposure to vapor-phase compounds. **Table 02** presents a summary of the sampling methods commonly used to collect subsurface vapors. Currently, there are a number of manuals and guides that guide the collection and validation of data in the field (USEPA, 2002, API, 2005, ITRC, 2007, 2014), addressing sampling techniques, appropriate analytical methods, and the elaboration of specific conceptual models. In countries where the assessment of vapor intrusion is already an established method, the environmental regulatory agencies have their own procedures covering various techniques and specific equipment. For further readings on sampling procedures, it is recommended to consult the following documents: ASTM, 1992; API 2005; USEPA, 2002.

Table 02 – Summary of sampling methods commonly used to collect subsurface vapors

Method	Description	Advantages	Disadvantages
TedLar® Bags	TedLar®Bags can be found in volumes ranging from 10 mL to 10 liters. For vapor sampling in the soil, 0.5-liter bags are usually used. Samples can be collected with the following technologies: 1) pump with a small electric battery; 2) Syringe 3) peristaltic pump or; 4) the vacuum chamber The vacuum chamber method involves placing a bag in a sealed chamber which has been evacuated. This causes the bag to suction vapors from the soil, making it ideal for low permeability soil.	When using peristaltic pumps, the device does not contact the sample, eliminating the risk of cross-contamination; Easy to sample, can be completed using several methods; Disposable material, eliminating the possibility of false positives; Lower cost when compared to other vapor sampling methods.	Electric pumps are subject to cross-contamination and appropriate decontamination is necessary at every collection point. Additionally, in situations requiring the application of strong vacuum, leaks may occur; There may be significant leakage from TedLar®Bags during the first 24 to 48 hours after collection. Therefore, samples should be sent for chemical analysis as quickly as possible in order to ensure better representation
Glass cylinders	Glass cylinders can be found in various volumes. Generally, 1 liter cylinders are used for sampling soil vapors; Glass cylinders are normally supplied by the laboratory responsible for chemical analysis, filled with high purity nitrogen.	The glass cylinder is installed in line, between the probe and the sampling pump, avoiding the risk of cross-contamination.	The samples collected by this method should be analyzed within 24-48 h. Unfamiliar and unaffordable method for most consultants
Syringes	Syringes are typically used to collect small volumes of sample (normally 5 to 60 ml).	Expeditious method, simple and easy to use during sampling; Lower cost when compared to Summa Canister and tubes with absorbent materials.	The samples must be analyzed in a short period of time after collection (30 min). Therefore, this method is only recommended for analysis on site using portable chromatographs.

Cont. Table 2 - Summary of sampling methods commonly used to collect subsurface vapors

Method	Description	Advantages	Disadvantages
Tubes with adsorbent materials	There is a wide variety of adsorbent materials (Ex. Tenax®, Carbotrap®), which should be selected based on the chemical of interest and the expected concentrations for the area. Generally, sampling rates used are between 100 and 200 ml / min, and the flow rate provided by the sampling pump must be accurately determined. The sampling time will depend on the expected concentration, the flow rate and the desired detection limits.	The tubes are installed in line between the probe and the sample pump, avoiding cross contamination. Easy to carry.	High cost when compared to other sampling methods
Summa Canisters	Summa canisters can be found in volumes ranging from 400 ml to 6 liters. They are previously evacuated, and vacuum is measured before and after transportation in order to detect possible leaks. The sampling rate is controlled by a flow regulator attached directly to the container.	Samples can be stored for up to 30 days before chemical analysis; Requires no pumps or other devices for sampling.	The container is used in various sampling campaigns, and decontamination is performed by the laboratory responsible for chemical analysis. Proper decontamination could be a critical factor; High cost when compared to other sampling methods.
Passive samplers	Passive samplers are those whose sampling principle is based on passive adsorption of contaminants in an adsorbent material. There is no need to use sampling pumps. Passive sampling may last from days to weeks and is used to identify potential routes of vapor intrusion and determining the lateral extent of the contaminants.	The identification of contaminants can reach the level of ng or ug; Effective in low permeability soil; Reduces the effects of varying the concentrations of the vapors over the time.	Does not allow vertical profiling of concentrations of vapors; The data are reported in mass and not in concentration units for risk assessment; It is not applicable for methane and other non-adsorbable compounds.

Source: Modified from New Jersey, (2005)

3.4.4.1 Soil Vapor Re-equilibration Time

The installation of vapor monitoring wells and the operation of remediation systems may affect the distribution of vapors in the soil. Prior to sampling, the distribution profile of vapors in the soil must be re-equilibrated. Some best practices can help ensure the accuracy of samples:

a) after the installation of wells, sufficient time should elapse before actual sampling, so that an equilibrium can be established between the gases present in the soil and in the pre-filter;

b) an equilibrium time of 48 hours (API 2005) is recommended for wells installed using manual methods;

c) for wells installed with more invasive methods, such as roto-pneumatic equipment, disturbances caused by drilling may be greater. Therefore, the equilibrium time can vary from days to months after the installation of wells; and,

d) testing for leaks using tracer gas (e.g. helium) and portable detectors can be done to determine the presence of disturbances in the soil at the drilling site and integrity of the seal of the installed wells, thus reducing the possibility of cross-contamination with atmospheric air during the sampling.

3.4.4.2 Purge

To ensure equilibrium between the equipment used and the sampled medium, besides guaranteeing a representative sample, it is necessary to carry out purge procedures prior to sampling. The volume of the purge must be compatible with the sampled medium and the equipment used. For an accurate estimate, one must consider the inner diameter of the tubing used for the installation of vapor monitoring wells, the length and internal diameter of the tubing used for attaching the well to sampling equipment, and the volume of the container used for sample storage.

The typical volume used for purging is between 1 to 5 times the total volume of the sampling system. Empirical data (API, 2005) indicate that the most appropriate procedure is to minimize the purge volume during sampling, in order to reduce uncertainty regarding the representativeness of the sampled point (e.g., entry of vapor system from other portions of the soil, entry of vapors from the surface [short-circuit], etc.). You can set a number of volumes to purge (e.g., three times the system volume), or calculate an appropriate purge volume based on specific variables, such as permeability, and stability of the concentrations in the field (measured with portable vapor analyzers). Vacuum or peristaltic pumps are recommended for purging, since the purge volume can be controlled with greater accuracy.

3.4.5 Analytical Methods

The analytical methods for determining the COC concentrations present in soil vapors were defined mostly by the USEPA. Currently, there are several methods applicable for the quantification of COCs in vapor samples, however, the methods should be selected according to the intended use of the sampling results and the technical requirements from regulatory agencies (in case the methodology is recognized by the local environmental agency). To select the most appropriate method, some fundamental issues need to be evaluated:

a) the analytes that need to be identified/quantified in the analysis;
b) the detection limits suitable for the evaluation of risks associated with exposure to COCs;
c) the methodology used to collect the samples;
d) laboratory certification by the environmental agency and certification of selected analytical method;
e) expiration date of the sample; and,
f) the analytical method suitable for analyzing soil vapors.

Table 03 presents a list of analytical methods commonly applied for this type of analysis.

Table 03 – Summary of analytical methods for quantification of compounds in vapor phase

Analyte	Field Method	Laboratory Method
Benzene, toluene, ethylbenzene, xylenes, MTBE	Gas chromatography using method 8260	Gas Chromatography using the methods TO14, TO 15 , TO 17or 8260
TPH	Gas chromatography using method 8215	Gas Chromatography using method 8015
Oxygen	In situ measurements with electrochemical cell	Gas Chromatography/TCD using method 3C
Carbon Dioxide	In situ measurement using infra-red analyzer	Gas Chromatography/TCD using method 3C
Methane	In situ measurement using portable detector	Gas Chromatography/TCD using method 3C
Nitrogen	In situ measurement using portable detector	Gas Chromatography/TCD using method 3C

Source: Modified from API, 2005

The precision of the analytical method used will depend on sample handling and preparation, and maintenance conditions of the analytical equipment. Most methodologies describe the minimum quality controls to be observed, such as calibration of the equipment used and their accuracy. Further details on the quality control of selected analytical methods can be checked in the procedures described in USEPA, 2002.

3.4.6 Interpretation of results

A preliminary review of the results is necessary to ensure the quality and consistency of the risk assessment and the proposed conceptual model, as well as assessing the uncertainties of the method used. After this review, the importance of the vapor intrusion exposure route in the study area should be evaluated and the possible receptors (present or future) considered in the risk analysis. To assess the importance of this route of exposure, the following comparisons must be made:

a) if the concentrations of COCs present in soil vapors are lower than the specific target calculated for indoor inhalation (SSTL), the route of exposure is not completed;

b) if the concentration of the COCs present in the soil exceed the Site-Specific Target Level calculated for indoor inhalation of vapors

(SSTL) in one or more sampling points, it must be determined whether the concentrations are reduced (both vertically and laterally) between the vapor source and foundation of the building enough to become lower than the target. If it is verified that COC concentrations do not reduce below the target calculated specifically for soil vapors (SSTL) between the vapor source and the building, this route of exposure is considered significant for the area.

According to API (2005), COC concentrations of the determined directly in certain buildings have values in the order of 1000x lower in relation to soil vapor concentrations obtained immediately below the foundation of those buildings. This relationship is consistent with published data on studies conducted by Nazaroff et al. (1987), and the results obtained from the model developed by Johnson and Ettinger (1991). However, there are limitations to this relationship. Soil vapor concentrations measured near the surface and just below the buildings can vary significantly due to short circuit potential (contamination with surface air) from samples collected from the surface. SSTLs for each mode of this transport in the area (groundwater, soil, soil vapor, outdoor air and indoor air) must be used. Alternatively, modeling can be performed using the concentrations present in groundwater, calculating the equilibrium relationships and partition between the air and groundwater (USEPA, 2002; ASTM 1992).

3.4.7 Evaluation of vapor intrusion according to standards established on Board Decision No. 263/2009 of CETESB

The procedures for assessing vapor intrusion in São Paulo are included in the current roadmap for undertaking detailed site investigation and intervention plan development for fuel retailers (CETESB - São Paulo State Environmental Company from the Board Decision No. 263/2009, published in Diário Oficial do Estado de São Paulo on October 20, 2009).

Based on the mapping of the spatial distribution of contamination plumes during the detailed investigation stage, the roadmap determines a number of additional steps for intervention, including developing a conceptual model, evaluating types of intervention that could be applied, and establishing an action plan based on the exposure pathways and receptors in the evaluated area.

The need for intervention measures is assessed by comparing the concentrations of Chemicals of Concern (COCs) detected in soil and groundwater samples to the Maximum Acceptable Concentrations at the Point of Exposure (MCAs - POE) as a function of the distance between the source and the exposure point, as well as other Applicable Legal Standards (ALSs).

The maximum acceptable concentrations for indoor inhalation of vapors, listed in the document *Ações Corretivas Baseadas em Risco (ACBR) Aplicadas a Áreas Contaminadas com Hidrocarbonetos Derivados de Petróleo e Outros Combustíveis Líquidos – Procedimentos*, are based on mathematical models that estimate the concentrations in the vapor phase that will intrude into buildings. In these models, the concentrations in vapor phase that will reach the interior of the buildings are calculated based on the concentrations in soil samples and/or groundwater and the conduction properties, equilibrium relationships, and existing partition between these media and air, for the "average" geological and geotechnical condition existing in the site’s broader region (USEPA, 2002 and ASTM 1992).

For each COC whose concentrations in soil (unsaturated zone) or groundwater (saturated zone) have exceeded at least one of the CMAs - POE or ALSs, a risk map should be prepared in accordance with the intervention framework. Risk maps should include the iso-concentration curves corresponding to all CMAs - POE and ALSs that have been exceeded, and should describe a conceptual model that identifies the retained and dissolved contamination plumes and the location of potential recipients. In the risk maps prepared for the exposure scenarios for vapor inhalation from soil and groundwater, the limits of iso-concentration curve of CMA - POE should be extended by 10 meters. It should also be considered that the first receptor identified in the external area must be a residential receptor in the scenarios of indoor vapor inhalation from soil and groundwater.

3.4.8 Evaluation of vapor intrusion according to EPA’s 2015 technical guide

The document issued by the USEPA titled "OSWER Technical Guide For Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air," published in June 2015, provides a structured approach to investigating vapors, and details measures that can mitigate and eliminate the vapor intrusion route.

During the investigation planning stage, the conceptual model for the area should be developed and any underground interferences (sewer pipes, water, energy, gas, etc.) identified. The investigation should only evaluate the COCs that are known or reasonably expected to be found in the area under evaluation.

As vapor concentrations decrease along the distance from a source in the subsurface, the concentration may become negligible at a certain distance. EPA indicates, for certain cases, an “inclusion zone” of 100 ft (30,5m) from the boundaries of a vapor-generating anomaly. That distance should also be considered when planning the investigation.

Due to the variability of several factors (temperature, humidity, air exchange volume, among others), EPA believes that a simple sample of the air present in the building, collected on a randomly selected date, is insufficient to estimate the average exposure to the chemical compounds of interest. Multiple samples are recommended in order to estimate an average of long-term exposure and allow the assessment of risks to human health.

For human health risk evaluations, ambient air samples over a period of 24 hours in residential areas and 8 hours in commercial/industrial areas are recommended.

EPA recommends some vapors mitigating factors that should be considered when interpreting the results. These factors were developed using EPA's database.

For example, the average attenuation factor for sub-slab samples in residential buildings is 0.03. Thus, the Vapor Intrusion Screening Level, indicative of the risk of inhalation of vapors, can be calculated from the equation below:

(7) $$C_{VISL} = C_{target,ia} / \alpha_{VI}$$

where:

C_{VISL} – Concentration of *Vapor Intrusion Screening Level* (VISL);

$C_{target,ia}$ – Risk rate for indoor environments according to *Regional Screening Levels* (RSLs) for *Chemical Contaminants at Superfund Sites* da USEPA; and

α_{VI} – Attenuation factor recommended for subsurface air indoors.

EPA emphasizes that attenuation of vapor intrusion into buildings is usually not a suitable substitute for the mitigation and elimination of subsurface vapor sources. EPA recommends a variety of engineering responses and institutional controls for addressing vapor intrusion, both for existing buildings and future construction.

3.4.9 Technical guides to handle petroleum vapor intrusion

Considering the fact that petroleum hydrocarbons degrade rapidly under aerobic conditions and their intermediate degradation products are generally less toxic than the original hydrocarbons, there is a lower potential for vapor intrusion. Therefore, traditional approaches used for chlorinated solvents and other non-biodegradable VOCs in aerobic environment may not be appropriate.

The technical guide about the intrusion of petroleum vapors developed by ITRC in 2014, PVI (Petroleum Vapor Intrusion), deals with vapor intrusion from petroleum hydrocarbon compounds and non-chlorinated volatile organic compounds, or other non-persistent and non-petroleum hydrocarbons.

This guidance document explains the principles of PVI and assists with the following tasks: PVI identification on sites contaminated by petroleum hydrocarbons, decision-making for PVI risk management, and selection of measures to reduce or eliminate the effects of PVI indoors.

The guide’s method for identifying PVI is based on the vertical distance from the source to the base of the foundation of a particular building (**Figure 5**).

For this purpose, as well to optimize the required information that must be collected, the required minimum distances necessary for biodegradation to occur were compiled from empirical studies conducted in several cities with hydrocarbon sources (underground or aerial storage of fuels, such as stations or bases). However, this approach requires utilization of hydrogeological and geological data for the site, gathered in previous studies, to prepare a Conceptual Model of Exposure (CME).

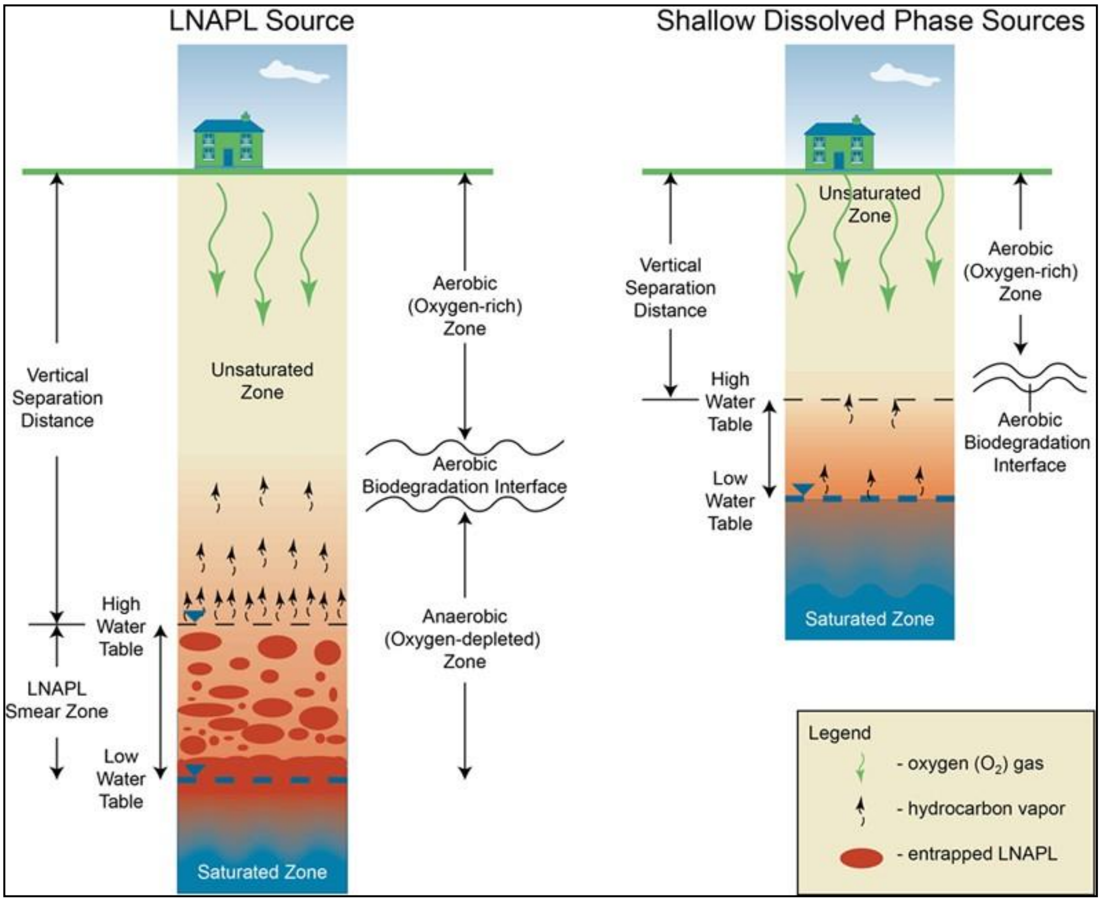


Figure 05 – Conceptual model of Vapor Transport from a source of LNAPL or from Dissolved Phase

Basically, three steps to define the vertical distance are indicated:

- Step 1: The CME should be developed using data obtained from environmental assessments, information about groundwater sources (underground or overhead tanks of oil fuel storage or areas with industrial petroleum), type of vapor source (free or dissolved phase), the vertical separation distance, and other relevant factors present at the site;

- Step 2: Evaluation of the area of interest regarding Barriers and Horizontal Dispersion: If barriers are present, further investigations are necessary. Otherwise, it should be checked whether the current or future buildings are on zones of lateral vapor dispersion, which leads to Step 3. If the building is not in a zone of lateral vapor dispersion, further evaluation is not necessary.
- Step 3: Delimiting of the vertical separation distance: the distance between the base of the building foundation and the top of the source of vapor emissions (free or dissolved phase plume).

Three models are used to evaluate PVI:

- Empirical models: Use data based on assumptions from other studies (mitigation factor). This model uses an appropriate distance or an attenuation factor derived from the evaluation of data from the area with potential PVI or for estimating vapor concentrations in buildings. This model’s output is a vertical separation distance;
- Analytical models: mathematical equations based on simplifications of the conditions of the area of interest (e.g., the Johnson and Ettinger model, 1991). In this model, PVI evaluation is exclusively unidimensional or assumes that the source, at a certain depth, is a flat and uniform surface. A distinctive feature of this model is the consideration of biodegradation processes. The model BioVapor (DeVaull, 2007) is an adaptation of the Johnson and Ettinger model, with the incorporation of limited biodegradation by O2, as well as: options for setting different O2 refill conditions for the subsurface and the sum of Petroleum Hydrocarbons present. The model of biodegradation limited to O2 content only simulates biodegradation in the unsaturated zone when there is sufficient O2, essential for the biodegradation process. This model has undergone several revisions and the EPA is in the process of developing a new version;
- Numerical model: Allows multidimensional transport simulation and generates a more realistic representation of the specific conditions of the area of interest. This model has the advantage of including details such as the medium’s heterogeneity, geometric complexity and temporal

variation. The PVI numerical model has been applied to understand in detail the causes and effects of transport and attenuation of vapors. Due to the complexity of this model, acquiring specific information is required, which can lead to increased costs, making it less practical and rarely used.

In 2015, the EPA released the Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites (USEPA, 2015), which was designed to regulate procedures in the United States.

The procedure recommended by EPA to evaluate these areas includes identifying and mitigating imminent risk, characterizing the site and developing a conceptual model of the area, delimiting a lateral inclusion zone, determining the vertical separation distance, evaluation of source and attenuation of petroleum hydrocarbon vapors, and vapor intrusion mitigation actions if necessary.

The lateral inclusion side is used to orient the investigations in areas most prone to intrusion of vapors. For each building within the lateral inclusion zone, additional samples must be taken to determine the vertical separation distance, which is defined as the thickness of clean biologically active soil separating the contaminants in soil and/or groundwater from buildings and potential receptors.

The EPA technical document points that, depending on the vertical separation distance, a more detailed vapor intrusion investigation is unnecessary in some scenarios.

The attenuation factors listed in the document *Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* by the USEPA (2015), as previously mentioned, are not applicable to intrusion of petroleum vapors from leaking underground storage tanks, because they do not account for the biodegradation that occurs in unsaturated aerobic soil. Thus, EPA recommends sampling to measure the actual attenuation that occurs due to the aerobic biodegradation.

Modeling can be used to better estimate the attenuation factor, but only if the current specific conditions of the area are the ones assumed by the model. The recommended models are Abreu, Ettinger and McAlary (2009), Verginelli and Baciocchi (2014) and the BioVapor model (DeVaull, 2007). EPA has developed a model called PVIScreen specifically for cases of petroleum vapor intrusion.

This document does not address specific remediation techniques, and its recommendations include interrupting the path between the source of contamination and the potential receptor, remediating the source of contamination (including the removal of LNAPL when present), and establishing institutional controls to limit or prohibit access to affected areas.

3.5 Mathematical Modelling and Calculation of Target Levels

There are three options for assessing the relevance of exposure to vapors that migrate from a subsurface source to the proximities of the foundations of buildings and other confined spaces.

In the first approach, samples are taken directly inside the buildings and the concentrations are compared directly with the reference values for indoor air. In the second approach, existing experimental data (underground vapor sampling) for the area are compiled and analyzed, establishing a comparison between the actual and expected conditions for the area. In the third approach, models that consider the specific conditions of the area (geology, concentrations of the chemical compounds of interest in soil, vapors and groundwater, etc.) are used to predict concentrations in indoor air.

These three approaches do not need to be mutually exclusive, and each can play an important role in an integrated assessment of potential impacts of the intrusion of subsurface vapors (USEPA, 2002).

Since performing regular indoor air monitoring can often be impracticable, models have played an important role to predict concentrations indoors. The applications of these models include:

a) estimating the potential impact of vapor intrusion in specific areas;

b) identifying areas that require more specific analysis;

c) obtaining specific target levels for the areas under study; and,

d) identifying how the target levels or concentrations obtained for the indoor air may change due to variations in the concentrations in groundwater and soil or due to the chemical characteristics of compounds of interest.

3.5.1 Johnson and Ettinger Algorithm

The Johnson and Ettinger model (1991) and its extensions (i.e. API Publication, 2005), are currently the most widely used models worldwide for evaluating the subsurface vapor intrusion pathway for buildings. Johnson and Ettinger’s algorithm combines equations that determine the partition of the contaminants at the vapor source, transport in the vadose zone, transport through the slab of the building and mixing with the air present indoors.

The results of these equations will depend on the data used for input, which include specificities of the local soil, characteristics of buildings and physical and chemical parameters of the compounds of interest. The model produces an estimate of vapor attenuation factor, which is the ratio between the concentration measured indoors and the concentration of vapors in subsurface soil:

$$\alpha = \frac{\left[\frac{D_T^{eff} A_B}{Q_B L_T}\right] \exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right) + \left[\frac{D_T^{eff} A_B}{Q_B L_T}\right] + \left[\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right]\left(\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack}^{eff} \eta A_B}\right) - 1\right)} \qquad (8)$$

Where α = (C_{indoor}/C_{source}), and:

A_B = Surface area of the building in contact with the ground (m^2);

D^{eff}_{crack} = Global coefficient of effective diffusion of vapor through cracks in the walls and foundation [$m_{crackeff}^2$/d];

D^{eff}_T = Global coefficient of effective diffusion of the vapor phase in the soil column between the foundation and the source [m^2/d];

L_{crack} = Slab thickness of the building [m];

L_T = Distance (depth) to the vapor source or other point of interest below the slab [m], measured from the slab towards the vapor source or other point of interest;

Q_B = Volumetric air flow [m3/d]. Generally estimated as the product of the building volume (VB [m3]) multiplied by the ratio of air exchanges between indoor air and outside air (EB [1/d]);

Q_{soil} = Gas flow from underground directed by pressure to the building [m^3/d];

η = Fraction of the surface area of the building open to intrusion of vapors [m2/m2]; commonly referred to in the literature as "crack factor". This can be estimated as the total area of cracks, fractures, discontinuities and perforations on the surface in contact with the ground, divided by the total area in contact with the ground;

C_{indoor} = Concentration in indoor air;

C_{source}= Concentration in the source.

Figure 06 illustrates the conceptual basis of the algorithm and the relationship between the eight primary input parameters.

It is worth noting that Equation 7 is, in practice, the version most often used of the algorithm. This version considers that the vapor source is in steady state, so, concentrations do not vary over time. There is also a version of the equation that considers the reduction of concentrations over time by the vapor source area.

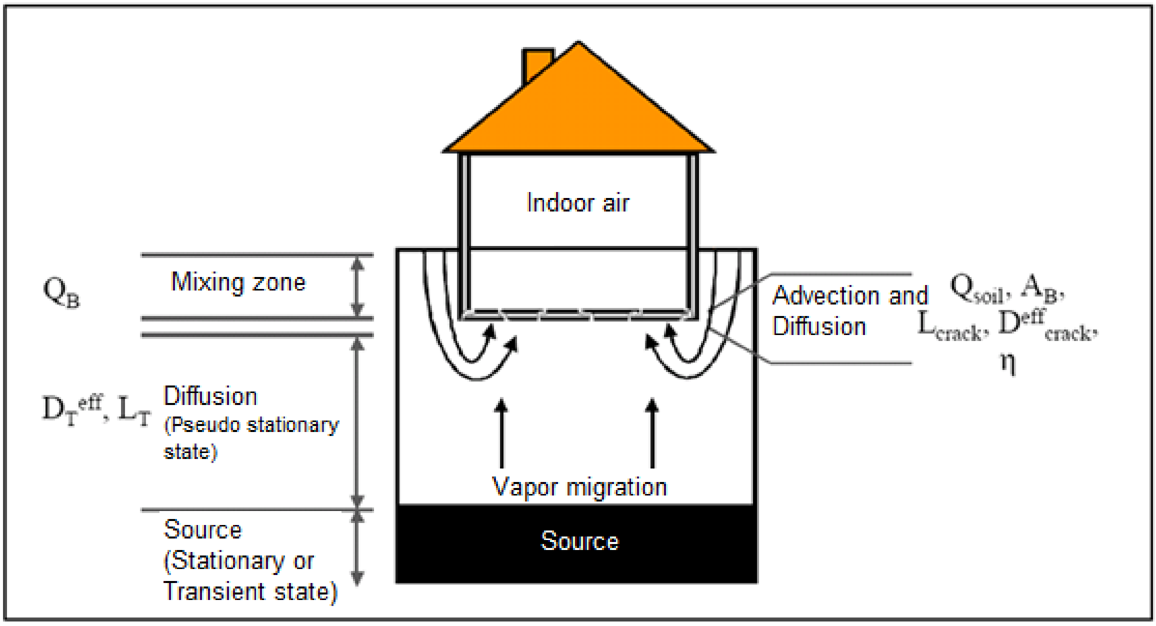


Figure 06 –Conceptual basis of Johnson and Ettinger algorithm and the relationship between the eight primary input parameters on the primary model

Source: Modified from Johnson, 2002

3.5.2 CETESB spreadsheets for risk assessment in contaminated areas

In order to standardize and optimize the implementation of risk assessment studies in São Paulo, since the publication DD 263/2009, CETESB published the worksheets for risk assessment in contaminated areas under investigation. Spreadsheets were developed in Microsoft Excel™ platform and are divided into four files, representing the possible types of receptors present in the areas under investigation:

a) Residents in urban areas (represented by adults or children);

b) Residents in rural areas (represented by adults or children);

c) Commercial / industrial workers; and,

d) Civil construction workers.

Spreadsheets allow the quantification of risks for both non-carcinogenic and carcinogenic substances, individual and cumulative, in various exposure scenarios. It also calculates the MACs for these substances.

The calculations are based on the procedure described in RAGS - Risk Assessment Guidance for Superfund - Volume I - Human Health Evaluation Manual Part A (USEPA, 1991) for quantifying the exposure and risk, as well as the Johnson and Ettinger (1991) model for vapor transport in the saturated zone. Spreadsheets include information on the physical-chemical and toxicological properties of 631 substances. All input parameters of mathematical models were defined so that values for the exposure factors and the physical environment given are applicable to the reality of São Paulo state.

As a result of modeling, spreadsheets provide standardized reports, including the quantification of the risk to human health and the determination of MACs for exposure scenarios that should be considered during preparation of the Intervention Plan.

3.5.3 USEPA Spreadsheets

The publication of the "Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils” (USEPA, 2002) established a series of procedures for evaluating the indoor intrusion of volatile organic compound vapors from a subsurface source of contamination.

The relevance of the vapor intrusion route of exposure in question is evaluated in a 3-Tier Assessment. These tiers analyze the site with progressively more detail as the presence of vapor is confirmed. These tiers include:

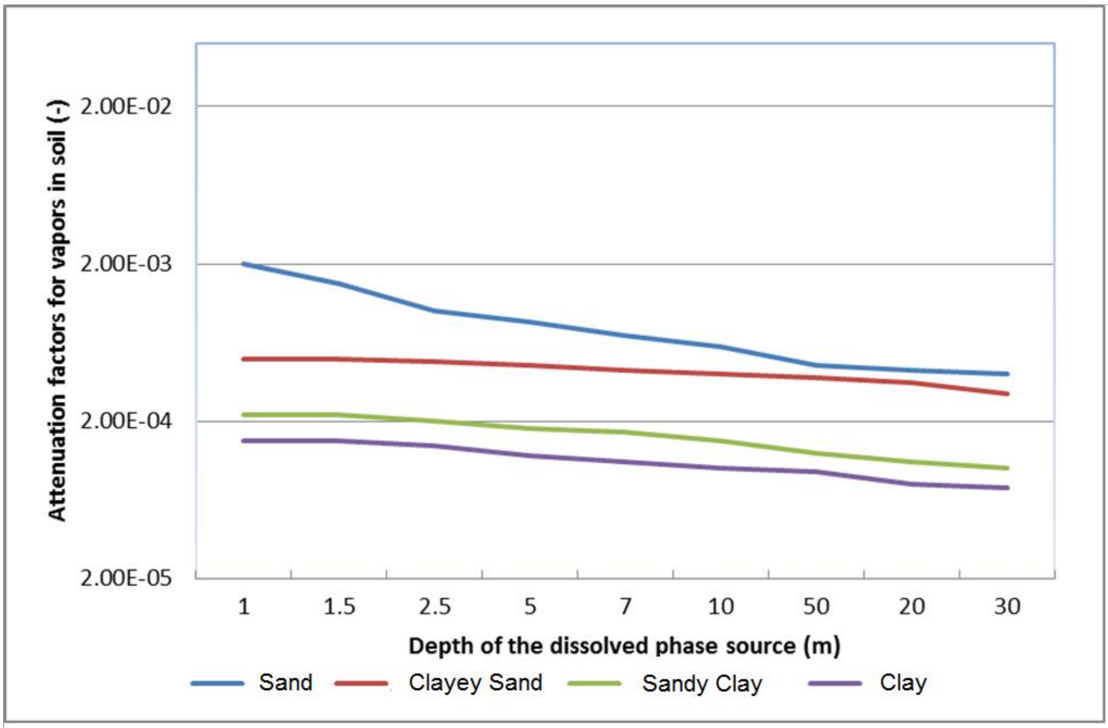
1) *Tier 1* – Preliminary evaluation;
2) *Tier 2* - Comparing the concentrations in dissolved phase with generic reference values (or semi-specific); and,
3) *Tier 3* - Specific evaluation contemplating the investigation of vapors in the soil.

The Preliminary Assessment (Tier 1), addresses three primary questions:

1) presence of VOCs;
2) distance to existing buildings;
3) imminent risk (explosion or toxicity);

If the answers to these questions indicate the potential for vapor intrusion, evaluation proceeds to a second stage (Tier 2). Concentrations of the chemical compounds of interest in the dissolved phase, obtained directly in the evaluated area, are initially compared to generic reference values (Preliminary Remediation Goals). The detected concentrations are also compared to "semi-specific" values, calculated from generic mitigation factors that consider the geotechnical characteristics of the area. Typically, the attenuation factors are obtained from tables and pre-established reference charts generated from the USEPA database. **Graph 04** below shows the attenuation factors depending on the depth and soil type.

If the concentrations obtained exceed the reference values calculated from the attenuation factor, the evaluation proceed to a more specific level (Tier 3) where data is collected directly from vapor phase (indoor or below the slab) to assess more accurately the relevance of route of exposure for the area and the level of risk for the receptors in these environments.



Graph 04 – Attenuation factor for vapors in the soil depending on the depth of the source of vapors in dissolved phase

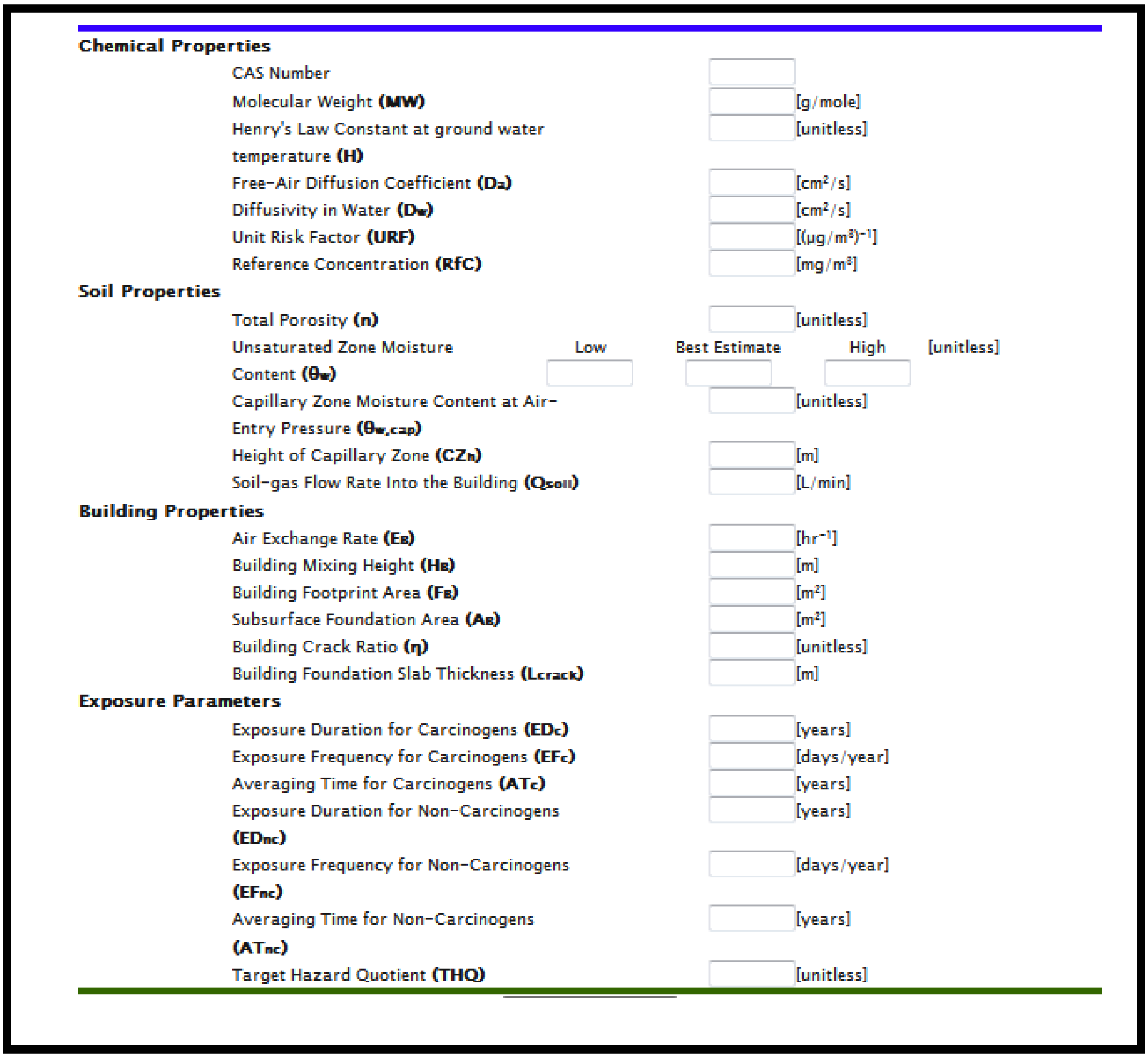
Source: Modified from USEPA, 2002

In Tier 3, target values for comparison are derived by applying the Johnson and Ettinger (1991) model, providing the mitigating factors "α" specific to the geotechnical conditions of the site evaluated. The modelled attenuation factor is used to derive risk rates, reference values for vapor concentrations at specific depths and vapor concentrations expected for evaluated buildings.

To facilitate the use of the Johnson and Ettinger model (1991), the USEPA has developed spreadsheets in the Microsoft Excel™ platform and general guidelines (USEPA, 2002). These worksheets have user-friendly interface that makes the application of the model easy.

Spreadsheets from USEPA are divided into two different calculation formats. One produces risk indices resulting from existing concentrations (dissolved phase or vapor phase) and the other takes as an input the acceptable risk value (options including 1.00E-4, 1.00E-5, and 1.00E-6, depending on the current legislation for the rated site) and calculates the appropriate reference values (backward mode). Both worksheets can be filled out at the EPA’s Web site from inside the Web browser, and the results are obtained immediately. The site has the option of exporting the inputs and outputs of the calculations in a standardized report.

Figure 07 partially illustrates the input screen for the backwards spreadsheet, in which physical parameters of the evaluated area are used as input to obtain the target concentrations.



Chemical Properties

CAS Number
Molecular Weight **(MW)** [g/mole]
Henry's Law Constant at ground water temperature **(H)** [unitless]
Free-Air Diffusion Coefficient **(D_a)** [cm²/s]
Diffusivity in Water **(D_w)** [cm²/s]
Unit Risk Factor **(URF)** [(µg/m³)⁻¹]
Reference Concentration **(RfC)** [mg/m³]

Soil Properties

Total Porosity **(n)** [unitless]
Unsaturated Zone Moisture Content **(θ_w)** Low Best Estimate High [unitless]
Capillary Zone Moisture Content at Air-Entry Pressure **($\theta_{w,cap}$)** [unitless]
Height of Capillary Zone **(CZ_h)** [m]
Soil-gas Flow Rate Into the Building **(Q_{soil})** [L/min]

Building Properties

Air Exchange Rate **(E_B)** [hr⁻¹]
Building Mixing Height **(H_B)** [m]
Building Footprint Area **(F_B)** [m²]
Subsurface Foundation Area **(A_B)** [m²]
Building Crack Ratio **(η)** [unitless]
Building Foundation Slab Thickness **(L_{crack})** [m]

Exposure Parameters

Exposure Duration for Carcinogens **(ED_c)** [years]
Exposure Frequency for Carcinogens **(EF_c)** [days/year]
Averaging Time for Carcinogens **(AT_c)** [years]
Exposure Duration for Non-Carcinogens **(ED_{nc})** [years]
Exposure Frequency for Non-Carcinogens **(EF_{nc})** [days/year]
Averaging Time for Non-Carcinogens **(AT_{nc})** [years]
Target Hazard Quotient **(THQ)** [unitless]

Figure 07 – Input screen of the reverse calculation spreadsheet of USEPA

Source: The author

The worksheets require a large number of input parameters and, as a result, relations between inputs and outputs of the model may be misunderstood, since many users are not able to identify the critical variables. This has caused some disagreements about the utility of this model (JOHNSON, 2002). Since USEPA spreadsheets are commonly referred to in professional circles as "Johnson and Ettinger model," it is useful to point out some fundamental differences between the application of these spreadsheets and the original Johnson and Ettinger algorithm (1991). These differences are summarized in **Board 01** below:

Johnson & Ettinger (1991)	USEPA Spreadsheets (1997, 2000)
Model output is the attenuation factor α	Spreadsheet outputs are the level of incremental risk, index or target levels for remediation of soil and groundwater resulting from certain incremental risk levels. Alpha attenuation factor is an intermediate part of the calculations and does not appear in the final results page.
Gas underground flow directed by pressure to the building (Q_{soil}) is defined as a primary parameter input.	The gas flow in underground directed by pressure to the building (Q_{soil}) is an intermediate calculation, and does not appear in the final results page. It is obtained through input parameters defined by the user as soil permeability, differential pressure, length of the perimeter of fractures, etc.
Humidity and thickness of the capillary fringe are defined by the researcher	Humidity and thickness of the capillary fringe are defined from soil description tables with predefined categories
The calculation is focused on the relationship between vapor concentrations indoors and the concentration of vapors in the soil at a defined depth	Partition between retained phase and vapor is introduced; initial application of the sheet is limited to individual compounds, where contaminants in immiscible phases are not present, although this is not clear to the user
For both models it is necessary to ensure consistency in the relationship between the input parameters (e.g., total porosity and moisture in the unsaturated zone).	

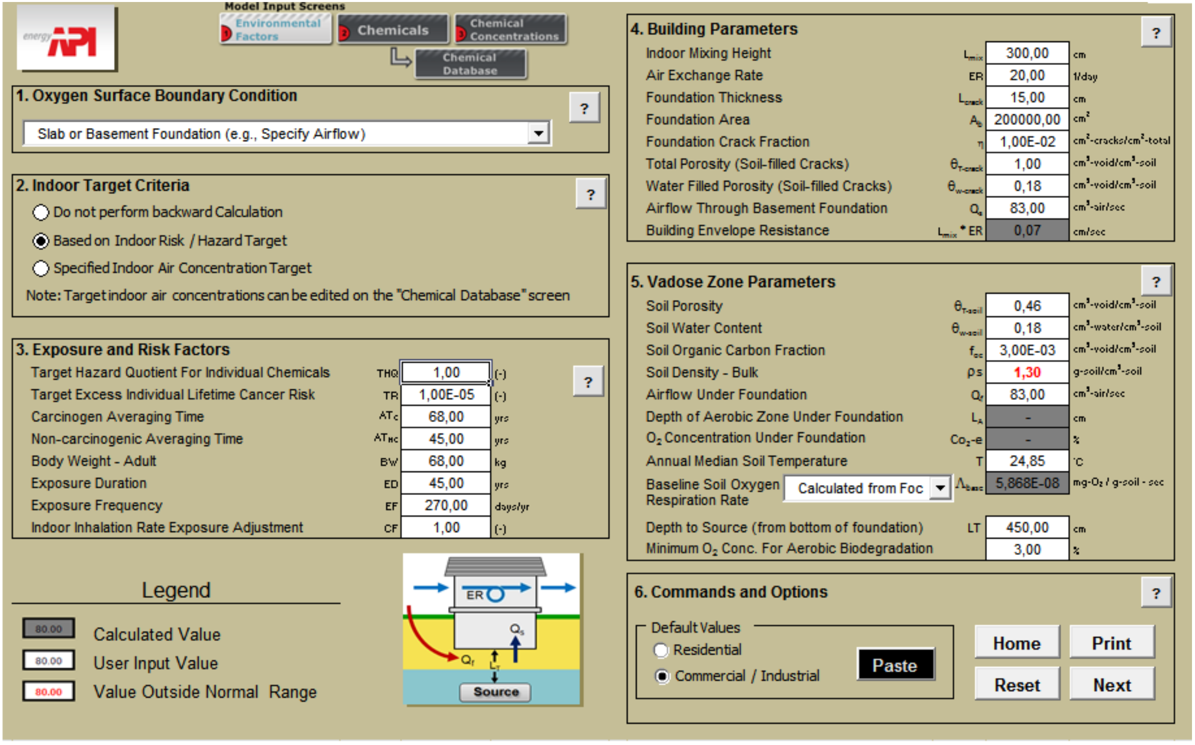
Board 01 – Summary of fundamental differences between the model of Johnson and Ettinger and USEPA's spreadsheets

Source: Johnson, 2002

3.5.4 BioVapor

The BioVapor model (API, 2009) adds to the Johnson and Ettinger model (1991) by accounting for the aerobic biodegradation potential. It features a user-friendly interface, using spreadsheets where input data are inserted and model outputs are presented. **Figure 08** shows the software entry screen and the fields that must be filled with data on exposure and physical environment.

In its design, the model considers a source of gasoline vapors in steady state (the concentrations of the source do not vary as a function of time), with diffusion being the main vapor transport mechanism in the subsurface. The soil profile is divided into a surface layer where aerobic biodegradation is predominant and a deeper layer where anaerobic biodegradation occurs.



1. Oxygen Surface Boundary Condition

Slab or Basement Foundation (e.g., Specify Airflow)

2. Indoor Target Criteria

- ○ Do not perform backward Calculation
- ● Based on Indoor Risk / Hazard Target
- ○ Specified Indoor Air Concentration Target

Note: Target indoor air concentrations can be edited on the "Chemical Database" screen

3. Exposure and Risk Factors

Target Hazard Quotient For Individual Chemicals	THQ	1,00	(-)
Target Excess Individual Lifetime Cancer Risk	TR	1,00E-05	(-)
Carcinogen Averaging Time	AT_c	68,00	yrs
Non-carcinogenic Averaging Time	AT_{NC}	45,00	yrs
Body Weight - Adult	BW	68,00	kg
Exposure Duration	ED	45,00	yrs
Exposure Frequency	EF	270,00	days/yr
Indoor Inhalation Rate Exposure Adjustment	CF	1,00	(-)

Legend

80.00	Calculated Value
80.00	User Input Value
80.00	Value Outside Normal Range

4. Building Parameters

Indoor Mixing Height	L_{mix}	300,00	cm
Air Exchange Rate	ER	20,00	1/day
Foundation Thickness	L_{crack}	15,00	cm
Foundation Area	A_b	200000,00	cm^2
Foundation Crack Fraction	η	1,00E-02	cm^2-cracks/cm^2-total
Total Porosity (Soil-filled Cracks)	$\theta_{T\text{-}crack}$	1,00	cm^3-void/cm^3-soil
Water Filled Porosity (Soil-filled Cracks)	$\theta_{w\text{-}crack}$	0,18	cm^3-void/cm^3-soil
Airflow Through Basement Foundation	Q_s	83,00	cm^3-air/sec
Building Envelope Resistance	L_{mix} * ER	0,07	cm/sec

5. Vadose Zone Parameters

Soil Porosity	$\theta_{T\text{-}soil}$	0,46	cm^3-void/cm^3-soil
Soil Water Content	$\theta_{w\text{-}soil}$	0,18	cm^3-water/cm^3-soil
Soil Organic Carbon Fraction	f_{oc}	3,00E-03	cm^3-void/cm^3-soil
Soil Density - Bulk	ρs	1,30	g-soil/cm^3-soil
Airflow Under Foundation	Q_f	83,00	cm^3-air/sec
Depth of Aerobic Zone Under Foundation	L_A	-	cm
O_2 Concentration Under Foundation	Co_2-e	-	%
Annual Median Soil Temperature	T	24,85	°C
Baseline Soil Oxygen Respiration Rate: Calculated from Foc	Λ_{base}	5,868E-08	mg-O_2 / g-soil - sec
Depth to Source (from bottom of foundation)	LT	450,00	cm
Minimum O_2 Conc. For Aerobic Biodegradation		3,00	%

6. Commands and Options

Default Values

- ○ Residential
- ● Commercial / Industrial

Figure 08 – Example of data entry screen of the BioVapor *software*

Source: API, 2009

The model is solved iteratively by varying the depth of the aerobic zone to match the oxygen demand required. The model results are calculated for intervals of concentration at the source, soil characteristics in the unsaturated zone and the physical parameters of the evaluated building.

In general, the results from this model indicate that the potential for vapor intrusion is significantly lower compared to models that do not consider the biodegradation process.

4 - USE OF COMPOUND-SPECIFIC ISOTOPE ANALYSIS (CSIA) TO DIFFERENTIATE INDOOR POLLUTION SOURCES

4.1 - Introduction

Compound-Specific Stable Isotopes have been used in environmental applications to assess biodegradation, as well as for forensic investigation of environmental compounds that may have caused contamination of soil or groundwater. An example would be determining the origin of a possible leak. CSIAs have been successful when assessing Volatile Organic Compounds (VOC) dissolved in groundwater, which led to increased interest in the use of CSIA for VOC vapor, determining attenuation processes in the vadose zone and the potential in differentiating the sources of indoor contamination. This chapter provides a brief explanation of the use of CSIA, new methodology for collecting and analyzing vapor samples (from the interior of the buildings), potential applications and field studies considering their potential relevance for use in Brazil.

4.2 - What is an isotope?

Isotopes are formed when atoms have different numbers of neutrons, which produces variations in molecular weight (the sum of the number of protons and neutrons). Isotopes can be unstable (radioactive, for example, C14) or stable, (for example, C12 and C13, which have 6 and 7 neutrons, respectively). For decades, isotope chemistry has been used in various industries. Its application in environmental chemistry has been relatively recent, as analytical methods now have lower detection limits than in the past. CSIA has been increasingly used in various environmental applications (USEPA, 2008).

Isotopes are mainly used to evaluate the degradation of the chemical compounds of interest in groundwater. Some isotopes are lighter, having lower molecular weight, and bonds are more likely to be broken. These features allow these isotopes to be preferentially degraded by microorganisms and, over time, this process results in the enrichment of heavier isotopes, in this case C13. This process is known as "kinetic isotope effect". This can confirm the occurrence of the biodegradation process, and in some cases, allow quantification of such degradation rates. This process is graphically illustrated in **Figure 9** (Wilson et al., 2005). Currently, the use of isotopes in this application has involved the carbon atom in compounds like PCE and TCE (Shouakar-Stash et al. 2003; USEPA, 2008; Hunkeler et al., 2004).

It is also possible to analyze multiple stable isotopes on the same molecule, for example, carbon and chlorine (CL37) on PCE or other chlorinated solvent. This process, known as "double" isotope analysis, improves the evaluation of biodegradation, given that the enrichment of isotopes simultaneously generates more conclusive data about the degradation in progress (Palau et al., 2014). Previous studies have focused only on organic compounds, but many scientists are now considering the deterioration of metals such as mercury (Kritee et al, 2007), chromium (Raddatz et al, 2011), lead (Mukai et al., 1993, Cheng, H. & Hu, Y., 2010) and zinc (Aranda et al., 2012). CSIA has also been employed in forensic investigations, for example, where several sources of contamination (a common scenario) were evaluated using three stable isotopes (carbon, chlorine and hydrogen in the case of chlorinated solvents).

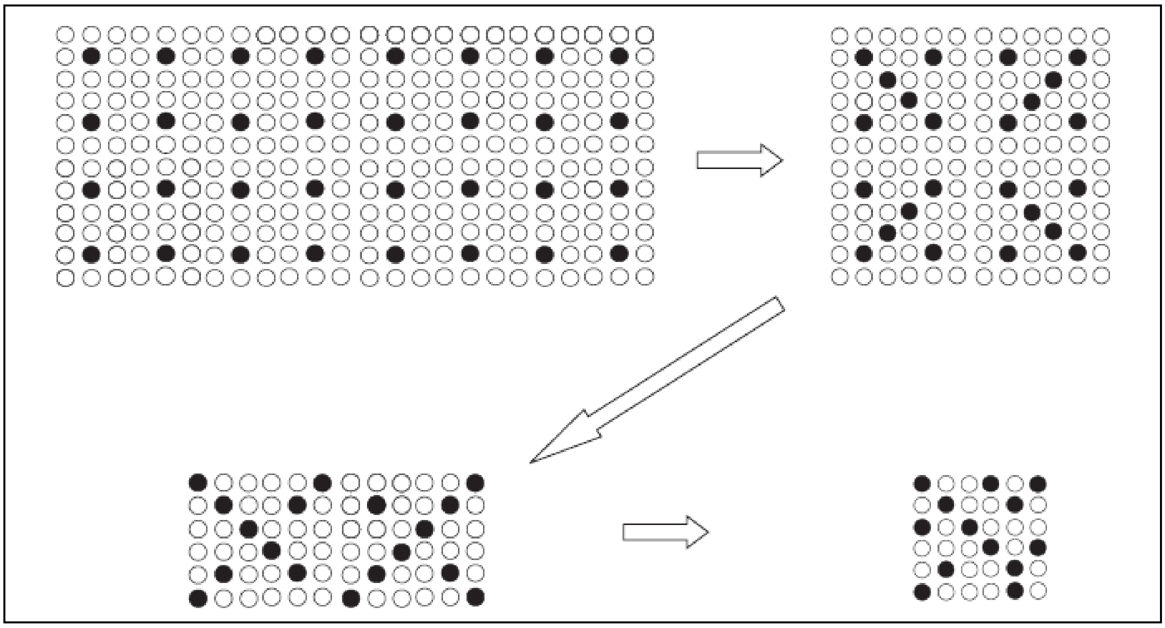


Figure 09 - An illustration of the kinetic isotope effect. This example demonstrates the enrichment of black dots, or fractionation of the proportion of black dots to white dots, where the rate of removal of white points is faster than the removal of black spots (Wilson et al., 2005).

4.3 - Use of CSIA on Vapor Phase

Some recent studies focus on the effects of the isotopic composition at the stage of volatilization of contamination in dissolved phase into the vadose zone, a process that often results in reverse enrichment, since the light isotope, e.g. C12, partitions with greater ease from the dissolved phase than other heavier isotopes (Kuder et al., 2009). As vapors tend to rise, is possible to trace the effects of isotopic composition to an underground structure of a building, or on the soil surface. Where there are buildings and air can accumulate in enclosed environments, it is also possible to analyze the intrusion of vapors to determine the effects of this process through isotopic signatures (**Figure 10**) (MCHUGH et al., 2011).

Alternative sources in buildings can be isotopically analyzed, showing that a direct exposure source on the surface is predominant relative to the intrusion of vapors originating from a subsurface source. Isotopic analysis also allows us to differentiate such sources that produce these vapors (**Figure 10**) (MCHUGH et al., 2011).

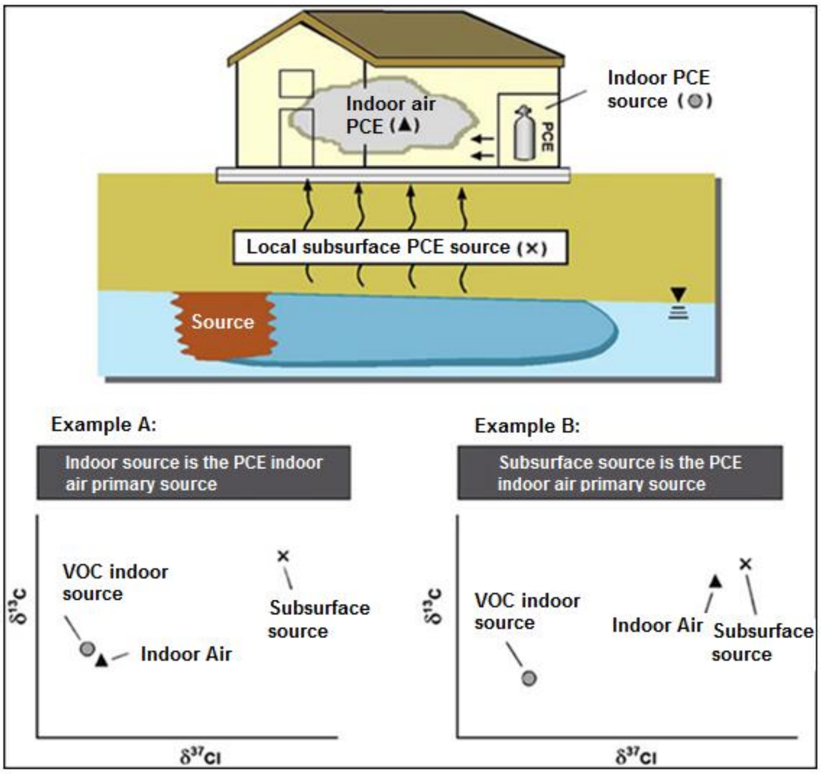


Figure 10 - Conceptual Model, Vapors Intrusion

Source: (MCHUGH et al., 2011)

4.4 - Methodology of isotope testing for indoor contamination

Several methods can be employed to differentiate indoor vapor sources. There is ongoing work to differentiate the sources of contamination inside the buildings using analysis of stable isotopes. Generally, this procedure involves the use of canisters, which is illustrated in **Figure 11** (USEPA, 2015).

Figure 11- SUMMA Canister
(USEPA, 2015)

Another approach used for sampling VOCs, the dissolution tube, involves the use of a liquid organic solvent for dissolving the contaminants of interest (**Figure 12**) (BOUCHARD et al., 2015). Initially, laboratory experiments were carried out to evaluate the efficiency of VOCs dissolved in liquid solvents during the process of continuous air injection, for determination of what would be the suitable liquid solvents (solvent volatility, VOC solubility) and to assess the reproducibility of isotopic signatures of the selected VOCs (benzene and trichloroethene) (BOUCHARD&HUNKELER, 2014).

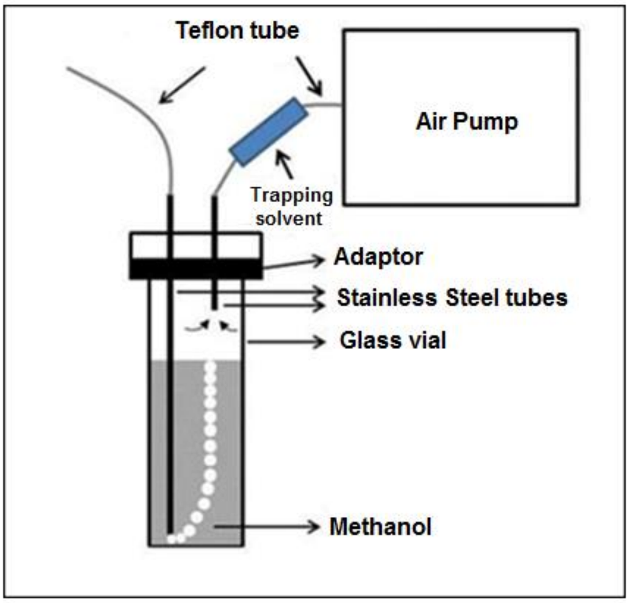


Figure 12: Schematic representation of the dissolution sample tube device (BOUCHARD et al., 2015)

This methodology was applied during an experiment carried out in an old industrial building (BOUCHARD et al, 2008a; BOUCHARD et al, 2008b.). A source of TCE (liquid phase) with known isotopic composition (δC13 and δCl37) was used to create a plume in vapor phase inside an insulated room. The vapor accumulated in this room was sampled with the dissolution tube. While passing the liquid solvent, VOC in vapor phase is dissolved and accumulated. The results are compared to samples with use of canisters, indicating that there is excellent correlation in the measurement of δC13 for TCE between the two methods used. Furthermore, the values of δC13 and δCl37 measured for the sampled TCE with the dissolution tube were similar to the known values of the source.

4.5 - Case Study in Brazil

As this technique is under development, specific applications in Brazil need more study.A case brought by this Working Group involves the evaluation of stable isotopes of methane gas generated by biodegradation processes (Freitas et al., 2010) at the municipal park in the city of São Paulo. The use of isotopes in this case has identified particular mechanisms of biodegradation. This information can be used for forensic investigation to determine the specific source of methane in the area of interest (FREITAS et al, 2010).

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