Chapter 1

Introduction

1.1 Indoor Air Quality and Vapor Intrusion

Concerns about air quality are as old as civilization itself, ranging from beliefs that disease is caused by bad air - a *miasma*, to more recent concerns about exposure to combustion particulates, radon gas, or other air-borne pollutants. Since industrialization the number of potential hazardous pollutants has increased significantly, followed by increased concerns about air quality. At the same time, people now spend more time indoors now than ever before, with Americans spending up to 90% of their waking time indoors[**klepeis˙national˙2001**]. This change in human habitation has put a special emphasis on indoor air quality.

Some early scientific inquiries into indoor air quality focused on pollutant sources that were generated in the home, e.g. by heating and cooking systems, and these types of pollutants are still relevant today, but of particular concern in developing countries[**craig˙d.˙hollowell˙combustion-generated˙1976**, **world˙health˙organisation˙who˙2014**] Many buildings materials can also cause indoor air quality issues, with exposure to asbestos fibers being perhaps one of the more famous examples of this. Mold is another common indoor quality concern[**world˙health˙organisation˙who˙2009**].

In the 1970s, to address the growing public health concerns, research began into the potential exposure to radioactive radon gas in buildings. Radon gas, which is generated by the decay of naturally occurring uranium in soils and rocks, was found to be able to enter overlying building and expose the inhabitants. This phenomena came to the public attention in the mid 1980s, after a Pennsylvanian nuclear power plant worker set off radioactivity sensors at the plant, the cause of which was the high concentration of radon gas in the workers home[**noauthor˙health˙nodate**]. Exposure to radon gas can significantly increase the risk of developing lung cancer, and is to this day the second leading cause of lung cancer in many countries[**gaskin˙janet˙global˙nodate** With the discovery of radon intrusion into buildings, it did not take long for the same concerns to be extended to the entry of anthropogenic contaminant vapors - vapor intrusion (VI).

Vapor intrusion is the migration of contaminant vapors from a contaminant source, often contaminated groundwater, into the overlying buildings. These vapors evaporate from the contaminated groundwater and enter through cracks in the building foundation, gaps between walls and floors, sump pits, or other openings[**u.s.˙environmental˙p** In these aspects, VI is more or less similar to radon intrusion, and thus much of the early VI research was heavily influenced by the work done by radon intrusion researchers. This is largely true to this day, but vapor intrusion differs in some non-trivial ways, that make it an unique issue. Many of these differences stem from the properties of the contaminants themselves, and from the fact that many of the VI contaminants that we concern ourselves with, mainly volatile organic compounds (VOCs) and chlorinated solvents, are of anthropogenic origins.

One difference is that radon is unstable, and has a half-life of around 3.8 days (at least Rn^{222}, the only naturally occurring isotope of radon), and it follows that radon accumulation will be naturally mitigated, which is not the case with other contaminants[**schumacher˙fluctuation˙2012**]. The closest analogy is that certain VOCs of VI concern are able to be biodegraded by bacteria in the soil, but this effect can vary significantly as this process is oxygen limited[**u.s.˙environmental˙protection˙agency˙c** **abreu˙simulating˙2006**].

A more significant difference is the anthropogenic origin of VI contaminants. In VI, we often are concerned with a contaminated groundwater source underneath the afflicted building, and the source of the groundwater contamination typically originates from some contaminant spill at one or more sites in the surrounding area. Thus, a large number of buildings may be impacted by VI via a single contaminant source. The origins of such spills are numerous, but any activities that employ the contaminants of VI concern are possible culprits[**u.s.˙environmental˙protection˙agency˙oswer˙2015**]. In the United States (US), the Environmental Protection Agency (EPA) maintains a list of polluted sites throughout the country, so called Superfund sites, and as of 2020 there are 1335 recorded sites, many of which contain the contaminants of concern[**us˙epa˙current˙2015**, **u.s.˙environmental˙protection˙agency˙oswer˙2015**]. Additionally, many of the contaminants of concern do not readily degrade, and legacy contamination is an issue[**u.s.˙environmental˙protection˙agency˙oswer˙2015**]. It should also be noted that VI from a contaminated groundwater is only one type of contaminant source, with leaky subsurface tanks, spills into soils, etc., are likewise contaminant sources of concern. Figure 1.1 shows some of the VI processes.

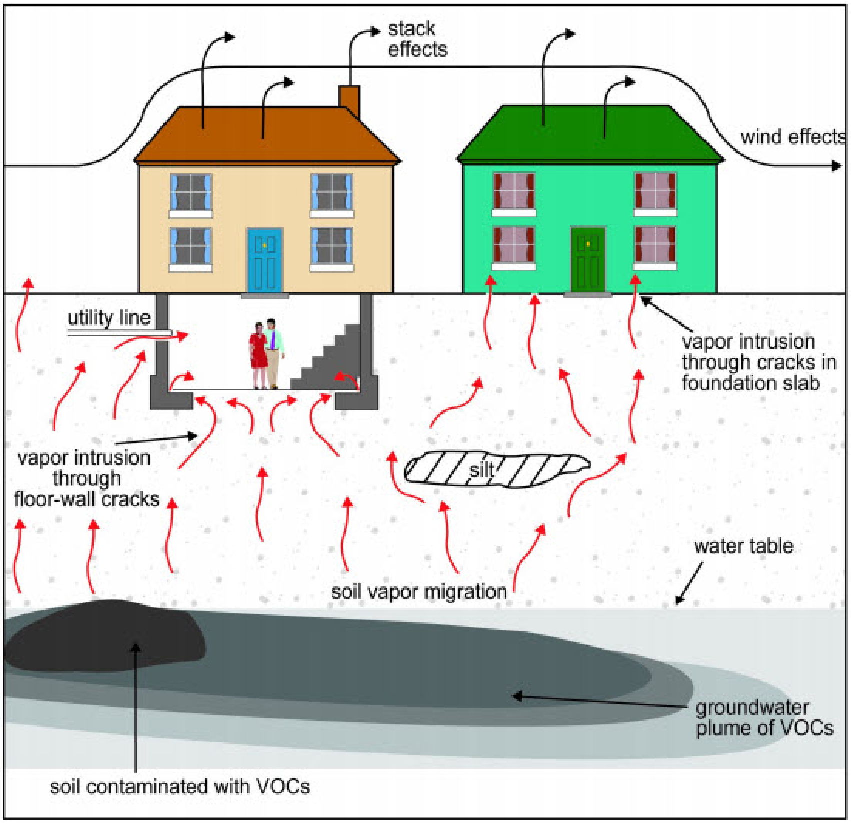

Figure 1.1: Vapor intrusion into a building can occur through a variety of means, from a variety of sources. Figure from the EPA[**us˙epa˙what˙2015**].

In VI, some common contaminants of concern are chlorinated solvents such as trichloroethylene (TCE), tetrachloroethylene (PCE), or chloroform. Various other organic compounds such as benzene, or other petroleum products are also of concern. Out of the various VI contaminants, TCE has emerged as of perhaps particular concern, mostly due to its associated cancer risk. TCE is an excellent degreaser and has seen extensive use as such, and has been commonly used by dry cleaners, the military, auto repair shops etc[**u.s.˙environmental˙protection˙agency˙oswer˙2015**]. A review study by **makris˙systematic˙2016**[**makris˙systematic˙2016**] showed that TCE may be associated with increased risk of congenital heart defects (CHD). But a more recent study by **urban˙systematic˙2020**[**urban˙systematic˙2020**] concluded that, mainly due to reproducibility issues and new studies, there is not adequate evidence to support that TCE causes CHD. Regardless, it is carcinogenic and despite concerns about its health effects, its use remains legal.

Considering the widespread existence of potential VI sites and the associated health concerns, an industry for finding these sites and either remediating or mitigating them has emerged. This is particularly true in the US, where the law dictates that the responsible party of the contaminant spill is liable for cleanup and mitigating human exposure; significant effort is spent on determining liability. Determining if VI occurs at a particular site, as we will see in this work, is not easy, and while VI has been studied for decades, many questions and challenges remain, in particular with regards to the great spatial and temporal variability that exist both within and between VI sites[**u.s.˙environmental˙protection˙agency˙oswer˙2015**].

1.2 Issues In Vapor Intrusion Investigations

Determining if vapor intrusion occurs at a building is often difficult. One might be tempted to believe that collecting an indoor air sample inside the building would be sufficient, i.e. that if the vapor contaminant concentrations is over some threshold in the house, proves that IV occurs, and the absence of contaminant vapors is proof that no VI occurs. However, this approach is too simplistic and may yield false positives.

Many common consumer products contain the same contaminants that are of concern in VI, and the presence in the home of e.g. a petroleum containing gasoline tank may be the culprit. Not all indoor contaminant sources are so obvious though, and many contaminants may be inadvertently introduced, such as by bringing home newly dry-cleaned clothing (a common source of PCE). Great care is taken to eliminate such indoor sources during formal VI investigations, but can be challenging[**u.s.˙environmental˙protection˙agency˙oswer˙2015**].

A compounding issue related to this is that many of the contaminants can sorb onto/into various materials and subsequently desorb for significant periods of time, potentially extending the influence of indoor sources beyond their removal[**meininghaus˙diffusion˙2000**, **meininghaus˙diffusion˙2002**]. This a phenomena, among other related issues with sorption, we will discuss in Chapter **??**.

Since indoor air sampling may not alone prove that VI occurs, investigations usually involve further steps. One is to collect air samples right below the foundation of the building, and if contaminant vapors are found there, as well as in the indoor air, that is more compelling evidence that VI occurs. However, as work by **holton˙creation˙2018**[**holton˙creation˙2018**] has shown, contaminant vapors in the indoor environment may migrate from inside the building to the subslab, creating a contaminant cloud in soil beneath the building that may persist for significant periods of time.

Collecting samples from the contaminant source, such as the groundwater underneath a building, to determine the presence of contaminants can be used as potential evidence of VI. However, even identifying such a potential source is not enough evidence of VI, as the presence of a contaminant source does not mean that the contaminant vapor actually enters the overlying building. **folkes˙observed˙2009**[**folkes˙observed˙2009**] conducted a decade long study of VI sites in Redfield, Colorado, and a 19 month long study in New York showed that many of the sites, even though they were above a contaminated groundwater source, were not impacted by VI.

Often investigators take samples from different locations, those already discussed as well as soil-gas samples, and compare the relative decrease in contaminant vapor concentration from the source to the indoor to establish what is termed a "completed pathway". This decrease is called *attenuation* and is quantitively represented in concentration from one point to the next as an *attenuation factor*. For example, the indoor contaminant concentration is divided by the contaminant concentration at the soil-gas groundwater interface. α is commonly used in this work we will often use a subscript to denote attenuation from one measurement point to another. In the case of groundwater attenuation for instance, one would divide the indoor contaminant concentration by the groundwater contaminant vapor concentration (that is when the contaminant concentration is in equilibrium with air, e.g. Henry's Law).

$$\alpha_{\mathrm{gw}} = \frac{c_{\mathrm{in}}}{c_{\mathrm{gw}} K_H} \tag{1.1}$$

Where α_{gw} is the attenuation from groundwater; c_{in} $[\mathrm{mol\,m^{-3}}]$ is the indoor contaminant concentration; c_{gw} $[\mathrm{mol\,m^{-3}}]$ is the groundwater *liquid phase* contaminant concentration; and K_H is the dimensionless Henry's Law constant.

Over time, the U.S. Environmental Protection Agency (EPA) has compiled data on attenuation factors relative to different source depths and types. Using these data, standards as to which attenuation factors are expected have been established to help guide investigators and regulator determine the VI risk. This is helpful, but often we are faced with VI sites that render these sort of standards difficult to use. For instance, the EPA recommends that an attenuation from the subslab region to the indoor of $\alpha_{\mathrm{subslab}} \approx 0.03$ for determining if VI occurs. In reality, attenuation factor values can vary by orders of magnitude due to a variety of factors, and that these recommended values can therefore be too conservative[**yao˙examination˙2013**].

Some of these factors are soil heterogeneity, nonhomogeneous contaminant source concentrations, as well as differences in the nature of the source (e.g. a contaminant spill in the soil itself vs. a leaky underground chemical tank). These can all contribute to significant spatial variability in contaminant concentration at a site.

A good example of this is seen in a study by **luo˙spatial˙2009**[**luo˙spatial˙2009**] where contaminant concentration beneath a building foundation varied from 200 to less than 0.01 mg/L. **bekele˙influence˙2014**[**bekele˙influence˙2014**] also found that TCE soil-gas concentration could vary by an order of magnitude underneath the foundation of another site.

Likewise, not all indoor environments are perfectly mixed and indoor contaminant concentration can vary significantly between different rooms or compartments in a building. This was observed at a site in Boston, Massachusetts by **pennell˙sewer˙2013**[**pennell˙sew** who found that the indoor contaminant concentration was significantly higher in the upstairs bathroom than in the basement, where one typically would expect higher concentrations.

The work by **pennell˙sewer˙2013**[**pennell˙sewer˙2013**] further revealed that VI could occur through sewers and enter the building through broken plumbing fixtures, which requires considering another level of complexity in VI - associated with the existence of preferential pathways. A preferential pathway is a term used describe something permitting enhanced contaminant vapor transport to near or into a building, in contrast with the more "traditional" view that contaminant transport occurs through soil. **mchugh˙evidence˙2017**[**mchugh˙evidence˙2017**] studied a VI impacted building in Indianapolis, Indiana, and found that the sewer system there acted as a preferential pathway bringing contaminants into the house (in addition to the soil pathway from the contaminated groundwater). There contaminated groundwater infiltrated into the sewer system a few blocks away from the site.

Similarly, **guo˙identification˙2015**[**guo˙identification˙2015**] studied a site in Layton, Utah, that was found to be impacted by a sewer connected land drain that allowed contaminant vapors to be transported to the near-slab region beneath a house (and close to a visible breach in the foundation). The results of this study and the role of the preferential pathway is a significant focus of this work and will be discussed in more detail in Chapter **??**.

holton˙temporal˙2013[**holton˙temporal˙2013**] (same group as **guo˙identification˙2015**) demonstrated the very significant temporal variability in indoor contaminant concentrations that exist at some sites, where they found close to four orders of magnitude in variability during the multi-year study period. **hosangadi˙high-frequency˙2017**[**hosangadi˙** studied another site in San Diego, California, that likewise showed orders of magnitude temporal variability, albeit on a shorter time scale. Likewise, the aforementioned site in Indianapolis exhibited significant temporal variability[**schumacher˙fluctuation˙20**

This temporal variability often has a seasonal component, and the highest indoor contaminant concentrations are usually found during the colder months of the year[**schumacher˙fluctuation˙2012**, **holton˙temporal˙2013**], although there are cases when the opposite is true. **steck˙indoor˙2004**[**steck˙indoor˙2004**] shows this at a radon impacted building in Minnesota, where the highest radon levels where observed during summer. Some authors such as **bekele˙influence˙2014**[**bekele˙influence˙2014**] suggest that it may be necessary to collect samples at intervals across a full year, to account for all seasonal effects, to avoid mischaracterization of VI.

The complexity and nuances of VI has made it necessary for a multiple lines-of-evidence (MLE) approach to be taken when determining if a building is impacted by VI[**u.s.˙environmental˙protection˙agency˙oswer˙2015**, **pennell˙field˙2016**]. However, the complexities associated with this approach has prompted the development of new methodologies and techniques that can reduce the uncertainty and complexity associated with conducting VI site investigations.

1.3 Innovations In Vapor Intrusion Investigations

In an attempt to reduce the uncertainty in determining human exposure due to vapor intrusion caused by the significant spatial and temporal variability in VI, a number of new investigatory techniques and methods have been proposed, but in general their efficacy is yet to be fully established[**mchugh˙recent˙2017**]. This work won't deal with all of these exhaustively, but rather primarily address two approaches (together with other topics related to variability.)

1.3.1 Controlled Pressure Method

Most buildings are naturally depressurized relative to atmosphere due to the operation of heating, ventilation, and air conditioning systems, and the so-called stack effect, a topic that will be covered in greater detail in Chapter **??**. This depressurization induces a flow of air from soil into the building; this flow can carry contaminant vapors into the building. (This view is rather simplistic, as will be discussed throughout this work, but suffices for now.) Using this idea, the controlled pressure method (CPM) was suggested, where blowers are used to control the depressurization of the building, and thereby more effectively controlling the indoor environment (see Figure 1.2). The basic ideas was to create a "worst case" scenario in which contaminant soil vapors are induced to enter the building.

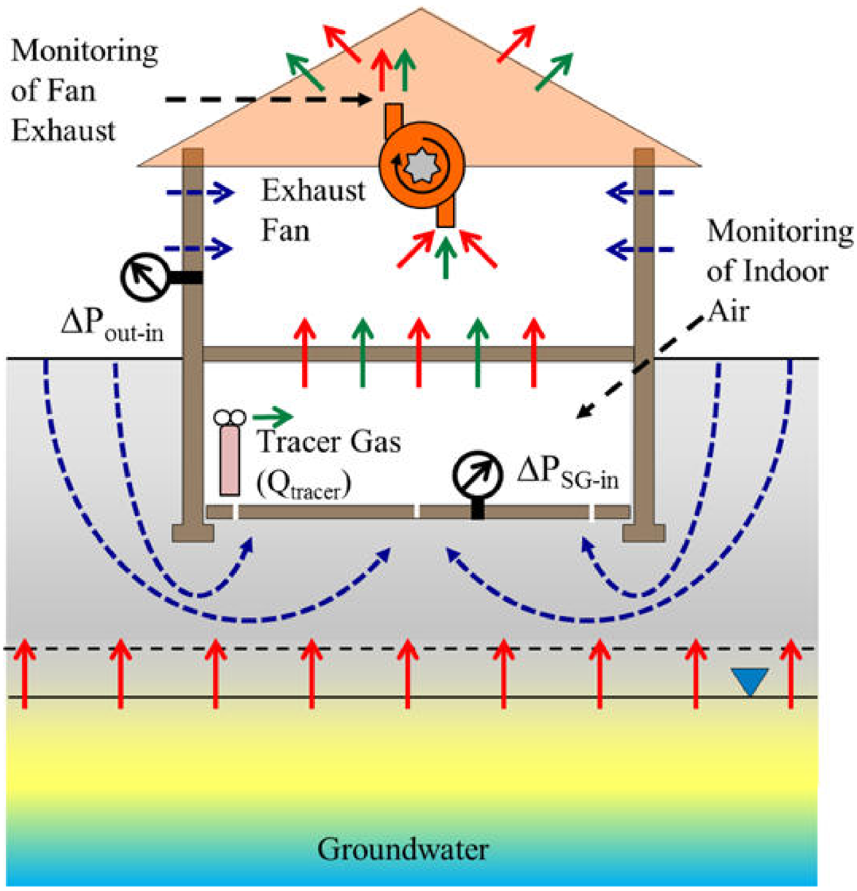

Figure 1.2: Conceptual idea of the controlled pressure method - a VI impacted building is forcefully pressurized using a blow, theoretically controlling the contaminant entry into the building. Figure from **holton˙long-term˙2015**[**holton˙long-term˙2015**].

Within the CPM framework, overpressurizing a building will then prevent contaminant entry from occurring. Thus, this can be used to identify indoor contaminant sources, as the presence of any contaminant vapors in the indoor environment in the overpressurized building have to originate from such a source. This approach can be applied as needed and hopefully will reduce the uncertainty and difficulty of VI investigations[**mchugh˙evaluation˙2012**].

1.3.2 Indicators, Surrogates, & Tracers

The conventional sampling schemes currently employed, due to the spatial and temporal variability of VI, has a propensity for creating false positives and negatives. While one solution to this problem is to increase the scope of VI investigations of a particular site, by for instance continuously monitoring the indoor contaminant concentration or by collecting an increasing number of samples, this approach is not practical, especially when numerous sites are involved. Thus, there is a need to develop guidelines that help reduce the sampling requirements and scope of VI investigations, while retaining the same degree of confidence that the relevant level of VI has been determined[**schuver˙chlorinated˙2018**].

To achieve this, it has been suggested to use indicators, surrogates, and tracers (ITS) to determine when to conduct a VI site investigation. For example, can meteorological ITS be used to determine when VI is expected tp be the largest, e.g. at which temperature and barometric pressure is, for instance, the 95th percentile indoor contaminant concentration most likely to be found[**schuver˙chlorinated˙2018**]? This is a promising approach, because as we have already discussed, many VI sites have the highest indoor contaminant concentration during colder seasons. So far this is more of a qualitative observation rather than quantitative guidelines for use in VI site investigations.

1.4 Issues With Applying CPM and Using ITS

On the surface, the CPM and ITS methods are two different approaches that try to address the same problem. However, they both attempt to utilize some external variable, such as building pressurization, and either manipulate it directly, or by inference, to determine or predict the indoor contaminant concentration.

The issue with these approaches is that they assume that different VI sites will respond comparably to these external variables, which in reality is not the case. **guo˙identification˙2015**[**guo˙identification˙2015**] used CPM to (inadvertently) identify a preferential pathway at their site, closed it, and noticed a markedly different relationship between indoor contaminant concentration and building pressurization for the period before and after the closing of the preferential pathway.

The reason for this change in behavior will be elaborated on in Chapter **??**, but consider that contaminant transport from soil into a building across a foundation breach occurs through two means - diffusion and advection. If advective transport dominates, then one would expect a strong correlation between building pressurization and contaminant entry rate, which determines the indoor contaminant concentration; if diffusive transport dominates, this relationship would be absent or weak.

Thus, to reliably apply any technique such as CPM or to use ITS, one needs a good mechanistic understanding of how, for instance, contaminant transport occurs at a VI site, and how the various site specific characteristics give rise to different transport phenomena. Assessing this in the field can be challenging, and therefore we turn to the use of numerical models of VI scenarios, guided by a first-principles perspective, which gives the ability to study physical phenomena in great detail.

1.5 Mathematical Modeling of Vapor Intrusion

Early in the history of VI, mathematical models of VI were formulated to aid investigators and regulators predict human exposure risk. Most of these adapted

work done by **nazaroff˙predicting˙1988**[**nazaroff˙predicting˙1988**] who had developed mathematical models of radon intrusion. Perhaps one of the more well-used VI models was the one developed by Johnson and Ettinger in 1991[**johnson˙heuristic˙1991**]. This analytical model could be used to describe the transport of various VI contaminants from a groundwater source into the overlying building, and it was quickly adopted by the EPA as a spreadsheet tool that has seen widespread use since[**u.s.˙environmental˙**
Over time more advanced numerical models were developed, which allowed for more physics and VI scenarios to be modeled in greater detail. Some notable examples are the work by **abreu˙effect˙2005**[**abreu˙effect˙2005**] and **pennell˙development˙2009**[**pennell˙c**

A benefit of using models in VI, besides as a predictive tool, is that their use allows the user to inspect in detail the role that various physics plays in determining VI. In a field that is dominated by empirical field studies of VI sites (which are environments that are difficult to control), models are an invaluable tool that help deepening our understanding of the VI phenomena. Already these have been used to investigate topics such as the role of soil moisture in VI transport[**shen˙influence˙2013**], how different foundation features affect contaminant entry[**yao˙simulating˙2013**], or how wind and outdoor temperature affects building air exchange with the outdoor and pressurization[**shirazi˙three-dimensional˙2017**].

In this work, we will likewise use numerical models, in combination with analysis of field-data from well-studied VI sites to explore the nature of contaminant transport. Some specific topics that will be covered include analysis of how preferential pathways can fundamentally change contaminant transport, and how the lessons learnt can be used to aid in resolving some of the issues in VI investigations, and broaden our understanding of the temporal and spatial variability at VI sites. The role that sorption of contaminant vapors on soils and in the indoor environment, a largely unstudied phenomena, will also be explored, and some of the implications discussed.

1.6 Outline

Numerical models of VI scenarios will be used throughout this work, and understanding the underlying mathematics that governs VI, as well as how these models are implemented, are crucial for understanding this work. Chapter **??** covers these aspects of VI modeling, where we develop a model of a hypothetical VI scenario. Here, the governing equations will be introduced, as well as the finite element method (FEM), which will be used to solve our model. In this process, we will cover the work of constructing a model geometry mesh, configuring solvers, post-processing results, and a variety of practical considerations when modeling VI. Lastly, a brief summary of VI models and recent developments will be addressed.

With this knowledge of VI modeling, we will first use them to tackle the issues of preferential pathways in Chapter **??**. A significant focus is placed on modeling and analyzing the preferential pathway found at the "ASU house" VI site in Layton, Utah. This work will demonstrate how and why preferential pathways can contribute so greatly to temporal and spatial variability in VI. The preferential pathway at "EPA duplex" VI site in Indianapolis, Indiana, will also be explored here.

From the work in Chapter **??**, we find that it is important to consider if vapor contaminant transport from the subsurface into a building is dominated by advective or diffusive transport, a topic that will be further explored in Chapter **??**. Here we discuss some of the site specific conditions that give rise to either of these transport mechanisms to dominate. These conclusions have wider implications for CPM or using ITS, and their efficacy can hinge on characterizing the dominant transport mechanism at a site. We also explore how weather conditions and outdoor temperature can be used to predict building pressurization, which becomes an important potential ITS for advection dominated sites.

In Chapter **??** the role that sorption of vapor contaminant in the indoor environment and onto soil particles is explored. The capacity of a variety of common materials to sorb TCE are measured at relevant conditions, where we find that these capacities can vary by orders of magnitude. These sorption data are then applied to a VI model, where the potential influence of these sorption effects on contaminant transport, VI investigations, and application of mitigation systems.

Lastly, Chapter **??** provides a summary of the conclusions and findings in this thesis, and suggestions future work.