Fugacity framework: web access and implementation for site assessment and rehabilitation


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Abstract

The fugacity-framework addresses multiple-media and multiple contaminant aspects of environmental site assessment. A U.S. EPA database of priority chemicals has been linked to the fugacity model for assessment of contaminant sources, transport and transformation, and exposure. Site-specific data are provided by the user. This tool provides a way for managers to visualize the behavior of toxic chemicals at a contaminated site, the effect of site-specific characteristics on contaminant distribution, the behavior of daughter products of degradation, and the associated risks to humans and the environment. The framework can be used to make decisions regarding protection of public health and the environment, site rehabilitation, and the sustainable development and economic recovery of impacted sites. The fugacity framework can be accessed at http://www.engineering.usu.edu/uwrl/, Utah Water Research Laboratory.

1 Introduction

Contaminated site rehabilitation involves an assessment of contaminant distribution from source(s) to receptor(s) that may include humans and the environment. Contaminants within sources generally spread through release and migration that expands to larger volumes of soil, water, air, and/or oil phases that result in large-scale exposure and receptor scenarios (Figure 1) that must be controlled through costly risk management technologies of containment,
removal, and/or destruction. The technologies selected often are not focused on the correct physical phase(s), resulting in inefficient or ineffective risk management and site rehabilitation efforts.

To address these issues of site rehabilitation, a fugacity framework for assessment of multi-media distribution (air, water, soil, and oil) of chemical contaminants in subsurface environments has been developed. The framework is utilized in an interactive mode and pedagogically designed for visual presentation to allow managers and decision makers to focus on making decisions regarding identification of information needs, site assessment, and site rehabilitation. This fugacity-based management system has been implemented to allow easy web access to users worldwide. This paper describes the three components of the fugacity-based management system, including: (1) fugacity framework and linked database, (2) instructional technology-based theory and tools for learning and user interaction, and (3) web-accessibility.

2 Objectives

The overall objective of this paper is to describe a web-accessible tool for managers, senior personnel, and other decision makers who may or may not have a technical background in mathematical modeling, multimedia contaminant behavior, and engineering treatment technologies.

The specific objectives of this paper include presentations of: (1) the fugacity-based framework as a useful tool for multi-media contaminant evaluation; (2) chemical database and site characterization requirements; (3) examples of applications of the fugacity framework; (4) instructional technology theory and application for learning and using the system; (5) web accessibility; and (6) future enhancements to the fugacity framework tool.
3 Fugacity-based Framework

The fugacity-framework is based on the conceptual site model (CSM) that consists of: (1) an Evaluative Site, (2) a chemical mass balance indicating distribution of contaminant(s) among physical phases at the evaluative site, and (3) a flow diagram to relate source(s) to receptor(s) pathways.

3.1 Evaluative Site.

The evaluator designs a “site,” then explores the likely behavior of chemicals in that site. A sensitivity analysis of the variables can be performed to focus the types of information needed to evaluate fate and transport, risk, and control options. The concept of “evaluative environments” was introduced by G.L. Baughman and R.R. Lassiter [1]. Evaluative aquatic environments were used to develop the U.S. Environmental Protection Agency (USEPA) EXAMS model of chemical fate in rivers and lakes.

Physical phases of a subsurface evaluative site (Figure 2) include a solid phase and three fluid phases. The solid phase is composed of soil organic matter (SOM) and inorganic components including sand, silt, and clay that comprise the subsurface texture. Fluid phases include the water or leachate phase, the gas phase, and the oil or NAPL (non-aqueous phase liquid) phase.

3.2 Mass Balance Approach.

A chemical mass balance approach is directed at evaluating how contaminant chemicals are distributed among the physical phases at a site. Chemicals at

![Figure 2. Evaluative site physical phases for fugacity framework.](image_url)

Brownfield sites are contained within the physical phases shown in Figure 2. One or more physical phases link contaminant sources to receptors. Therefore, a
mass balance approach is used to address: (1) chemical distribution among phases, (2) phase distribution at a site, (2) phase release or transport, (3) phase exposure/risk assessment, and (4) which phase(s) to manage with short-term or long-term technologies to prevent exposure. Chemical distribution among site phases can be determined through the application of fugacity calculations.

3.2.1 Fugacity

The word fugacity is derived from Latin meaning “to escape or to flee,” and refers to the escaping tendency of a chemical from a particular subsurface phase. Fugacity was introduced by C.N. Lewis in 1901 and has been widely used in chemical process calculations. Fugacity is applicable to organic chemicals, but not to metals and other inorganic chemicals. Its convenience in environmental partitioning calculations became apparent after 1980. Donald Mackay, Professor of Chemical Engineering at the University of Toronto, Canada, introduced the concept of fugacity in the 1970’s to express the distribution of organic pesticides among phases of the environment. His books “Multimedia Environmental Models – The Fugacity Approach” [2, 3] describe the basis and applications of fugacity for handling chemical distribution, reaction, advective flow, and diffusive and nondiffusive transport in multimedia environments.

Fugacity modeling provides a way for conducting a chemical mass-balance analysis. Fugacity uses partition coefficients for a chemical contaminant between soil and water (Kd), air and water (Kh), and oil and water (Ko) to describe the distribution of chemicals among physical phases comprising a multi-phase evaluative site. Physical phases can be evaluated with regard to: (1) sources, (2) transport and transformation, and (3) exposure.

Fugacity has the units of pressure (Pa). Relevant equations for Level I fugacity (equilibrium conditions among phases) are described below.

\[ C_i = \frac{f_i Z_i}{Z_i} \]  

where: 
- \( C_i \) = concentration of chemical in phase i, (moles/cubic meter)
- \( f_i \) = fugacity in phase i (Pa)
- \( Z_i \) = fugacity capacity of phase i (mole/Pa-cubic meter)

The fugacity capacity of each phase can be determined using the following equations.

\[ Z_a = \frac{1}{RT} = 4 \times 10^{-4} \]  

where: 
- \( Z_a \) = fugacity capacity of the air phase
- \( R \) = university gas constant and \( T \) = temperature (K)

\[ Z_w = \frac{1}{H} \]  

where: 
- \( Z_w \) = fugacity capacity of the water phase
- \( H \) = Henry’s Law constant (Pa-cubic meter/mole)

\[ Z_s = K_p \rho_s Z_w \]  

where: 
- \( Z_s \) = fugacity capacity of the soil-solid phase
- \( K_p \) = soil partition or distribution coefficient
- \( \rho_s \) = soil dry bulk density

\[ Z_o = Z_w K_{ow} \]  

where: 
- \( Z_o \) = fugacity capacity of the oil phase
- \( K_{ow} \) = octanol-water partition coefficient

The amount (moles, m) in each phase is: 

\[ m_i = C_i V_i = f_i Z_i V_i \]
where \( V_i \) = volume of each phase

At equilibrium, since \( f_1 = f_2 = f_3 = \ldots = f \), then \( f = M / \sum (Z_i V_i) \) \hspace{1cm} (8)

Thus, the equilibrium fugacity can be calculated from knowledge of the volumes and fugacity capacities of the subsurface phases and the total mass of chemical in the evaluative site. Then for each phase it is possible to calculate: (1) chemical concentration using equation (1), and (2) mass of chemical using equation (7). Fugacity has been used by Sims [4,5,6] for subsurface assessment.

When the amount of chemical released to the subsurface is not known, then a percentage, proportion, or relative amount, of chemical mass in each phase can be determined by substituting the value one (1) for the variable ‘M’ in equation (8). Volumes can also be estimated as percentages such that the sum of the four phases equals 100%. Such a determination is useful to indicate the phase(s) that would likely contain the most mass (%) of chemical. Field determination of chemical concentration could be used with an estimate of phase volume to determine the mass of chemical in the target phase. An estimate of the total mass of chemical at a site is possible since the mass percentage of chemical in each phase is known through the use of the fugacity calculations.

### 3.3 Flow diagram

A flow diagram incorporates site-specific data into an evaluative site and site specific mass balance information to assist in organizing the information to identify priority source phases with regard to release, secondary sources of contamination, exposure and the need for phase control to accomplish risk management and site rehabilitation (Figure 3). A flow diagram also serves as a common communication tool for site owners and operators, regulators, and consultants.

**Site Conceptual Exposure Model**

![Flow diagram](image)

Figure 3. Flow diagram identifies priority physical phases that connect source to receptor through migration and exposure. Risk management technology selection is based on priority phase management goals.

### 4 Chemical database and site characteristics required

Fugacity calculations require numerical values for properties of chemical substances for the calculation of fugacity capacities, as shown in equations (3) through (6). Calculation of Henry’s Law constant (eq. 3) involves water
solubility and vapor pressure; calculation of $K_p$ (eq. 4) can be accomplished through a knowledge of $K_{oc}$ and the fraction of soil or aquifer solid phase organic carbon ($f_{oc}$). Calculation of $Z_o$ (eq. 5) requires a value for the octanol-water partition coefficient ($K_{ow}$). The chemical properties required are provided in an embedded chemical database as part of the fugacity framework.

The chemical database utilized in the fugacity framework was developed by the U.S. Environmental Protection Agency (U.S.EPA) [7] to provide information pertaining to fate and transport properties for contaminants commonly found at Superfund sites. The U.S. EPA database of approximately 70 chemicals therefore provides the values used for chemical properties required for fugacity calculations for chemicals relevant to Brownfield and other sites, and also serves as a peer-reviewed reference.

Site characteristics required for fugacity analysis include the volume (cubic meters) of each physical phase (air, water, soil or aquifer, and NAPL). If the volumes are not known, then relative percentages of the volumes can be estimated and used in the fugacity calculations so the total percent of all phases equals 100. In addition, the soil organic carbon, as percent by weight of the soil phase, and the soil dry bulk density (kg/cubic meter) are required.

5 Examples of applications of the fugacity framework

Examples of the applications of the fugacity framework include: (1) distribution of trichloroethylene (TCE) in the subsurface as influenced by the NAPL phase, (2) distribution of TCE parent compound and daughter products dichloroethylene (DCE) and vinyl chloride (VC) within the same subsurface site conditions, and (3) Provo City Ironton Economic Redevelopment Project, Utah.

Figure 4 illustrates the distribution of TCE in a subsurface environment composed of 2% NAPL, 25% air, 23% water, and 50% soil by volume, and represents a source area of TCE contamination. The majority of TCE (87%) is located within the NAPL that comprises only 2% of the volume of the subsurface, while only 7% is present in the soil-solid phase.

Figure 5 represents the subsurface environment downgradient from the source where NAPL is absent (NAPL volume = 0%). With only air, water, and soil-solid phase present, the majority (55%) of TCE is present in the soil phase that represents a large increase in the %TCE in soil phase from 7% in Figure 4.

Using the same site characteristics as identified in Figure 4 for TCE, the distributions of daughter products of anaerobic biodegradation DCE and VC are shown in Figures 6 and 7, respectively. Figure 6 shows that DCE is present in air (34%) compared to 2% for TCE, and Figure 7 shows that VC is present almost exclusively in the air phase (96%). Therefore in the subsurface, anaerobic transformation from TCE to DCE to VC results in a different
LEVEL 1 FUGACITY MODEL

**CHEMICAL CHARACTERISTICS**
- Entry the compound name: Trichloroethane
- Enter the molecular weight: 131.4
- Enter water solubility (mg/L): 1.206E-03
- Enter Henry's law constant (L/mole*atm): 6.882E-03
- Enter Log Kow: 2.1

**SITE CHARACTERISTICS**
Enter the following:
- Volume of air (m³): 25
- Volume of water (m³): 25
- Volume of soil (m³): 50
- Volume of NAPL (m³): 2
- Total Volume (m³) tot: 100
- Enter the % organic saturation in soil (%): 0
- Enter the Soil Phase Density (g/m³): 1200
- Enter the total mass of the compound in the system (g): 1.00E+05

**RESULTS**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
<th>% Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.00E-04</td>
<td>2%</td>
</tr>
<tr>
<td>Water</td>
<td>1.38E-03</td>
<td>38%</td>
</tr>
<tr>
<td>Soil</td>
<td>1.38E-03</td>
<td>38%</td>
</tr>
<tr>
<td>NAPL</td>
<td>2.00E-04</td>
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Figure 4. Fugacity Analysis of TCE in a subsurface environment with 2% (volume) NAPL.

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Figure 5. Fugacity Analysis of TCE in a subsurface environment with 0% (volume) NAPL.
distribution of daughter products. These assessments have implications with respect to which phases to monitor for which chemical, as well as the appropriate phase for control and treatment to prevent exposure to human health and the environment for each contaminant at a site.

The Provo City Ironton Economic Redevelopment Project was initiated in 1996 with a grant from the US EPA. The project involves the redevelopment of land contaminated with polycyclic aromatic hydrocarbons and metals, and includes citizens, local businesses, and local industry. The fugacity framework is applicable to the evaluation of PAH source assessment and risk management with respect to human exposure and land rehabilitation.

6 Instructional technology - theory and application for learning and using the system.

6.1 The instructional problem.

Given the complex nature of the fugacity-framework, two instructional challenges were presented: 1) quickly help users understand the important concepts of fugacity and 2) teach them how to use the web-accessible fugacity-framework tool. Both novice and experienced users will need to understand and use the system. While novices may need considerable instructional aid, experienced users prefer quick access to the desired information with as few mouse and keyboard operations as possible. Whatever the case, a thoughtful design will help individuals and groups effectively make informed decisions regarding risk management and associated costs for control and treatment of toxic chemicals in subsurface environments.

6.2 Criteria.

There are several different potential use cases. Novices might want to simply explore the concepts and interface features or have direct instructional assistance.
Experienced users may want to seriously explore different “what if scenarios,” the how and why fugacity works, or evaluate specific sites. The framework could also be used in educational settings by classroom teachers or individual students.

The criteria for this instructional design required a quick direct interaction between users and the model for these different purposes. Therefore a variety of features are required to meet the range of needs.

- Easy to use
- Intuitive
- Process to directly evaluate sites
- Method to track, record, compares, and saves past experiments
- Explanations
- Attention focusing to possibilities offered by the framework

6.3 Principles of solution

A theory of instructional design that humans learn from interacting with models of environments, cause-effect systems, and expert behavior was selected. Model-centered instruction as characterized by A.S. Gibbons [8] prescribes methods for making human/model interactions effective by promoting model observation, interaction, and problem solving. MCI’s central premise is “that the most effective and efficient instruction takes place through experiencing realia or models in the presence of a variety of instructional augmentations designed to facilitate learning from the experience.” The interface was designed to be intuitive to incorporate the criteria that users need to quickly learn how to use the fugacity framework. Features were utilized that meet the needs of both novice and experienced users. The instructional interface incorporates a visually simple design with minimal text. The user control options are clear with quick access to required information.

Instructional features were provided for both the novice and experienced user (see Figure 8). Features provided for the novice user include: sequenced demonstrations based on problem solving that range from easy to complex, embedded didactics that provide explanations of important functions, instructional road signs that point out key events, and coherence between visual elements of the interface and the model. Features that are included for the experienced users are: quickly accessible data and results, a multi-problem representation trace that allows the user to visualize inputs and results from different initial conditions over a series of “what if scenarios”, and downloadable results in the desired format.

Figure 8 shows subsurface display elements that correspond to the novice and expert user features described previously.

1. **Chemical.** Selects the chemical and displays the properties.
2. **Environmental Distributions.** Displays how contaminant chemicals are distributed among physical phases.
3. **Evaluative Site.** Shows a subsurface representation of the contaminant distribution for the selected chemical.
4. **Site Characteristics**. Selects and displays the percent of physical phases in the subsurface environment.

5. **Representation Trace**. Records and displays from a series of “experiments” or “what-if scenarios.”


7. **Practice**. Presents the user with various problems or case studies.

Not shown in the diagram is the export feature that enables users to save a session’s data into portable file format.

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**Chemical**

**Fluorene**
- mol wt. = 166.22
- Vap Press = 6.67E-04

**Environmental Distribution**

**Site Characteristics**
- Soil 22%
- Air 3%
- Water 10%
- NAPL 65%

**Evaluative Site**

**Representation Trace**

Figure 8. User Interface for Fugacity framework for site assessment.

### 6.4 Conclusion

The primary challenge of the instructional design was to enable users at all levels to quickly understand the concepts of fugacity and teach them how to use the web accessible Fugacity based management tool. Model-centered instruction with an intuitive interface and relevant instructional augmentations was selected to provide users with instructional experiences of the fugacity model. In the end, meeting these challenges will enable users at all levels to characterize and evaluate their own specific sites, engage in fruitful dialogue with other stakeholders, and make informed decisions regarding risk management and associated costs for control and treatment of toxic chemicals in subsurface environments.
Web accessibility and downloading to the local computer

There is a continuing and rapid change in internet technology and development tools. The number and types of development products, and the uncertainty associated with the longevity of each introduces major complexity into the selection process. We considered the three implementation paradigms for delivering the model over the internet: 1) running the model on the server, 2) downloading the model to the local computer, and 3) a combination of both where the database resides on the server and an executable module is downloaded to the local computer. Each method has advantages and disadvantages in terms of accessibility, standardization, support, and extendibility.

Accessibility to applications running on the server “server apps” is independent of the local platform (i.e. the model can be accessed by a variety of operating systems found on MacIntosh and PC computers); the only requirement is a conventional web browser and online connection to the internet. Applications designed for downloading to the local computer, “local apps”, are specific for each class of operating systems (e.g. Mac and PC), and separate executable modules must be coded and compiled specifically for each.

Standardization in this case means that at any time all users are operating with the same model version and dataset. If strict consistency is an issue then standardization is essential.

Continuing support is a major issue for all models. Rarely is a model released and not modified shortly thereafter. Each update to a local app has to be distributed to the entire user group; only one update implementation is needed for a server app. This issue applies to both the model itself and to the training materials for the operation of the model.

Extendibility refers to the architecture of the model - can it be enhanced with major new features while maintaining the basic features and look-and-feel of the original.

Comparing the server app with the local app, the server app has a clear advantage in standardization and support. In terms of accessibility the server app can be operated from any local computer having a conventional browser while the local app is specific to a particular platform. On the other hand, the user must be connected to the internet in order to use the server app. Extendibility weights heavily in favor of the local app because server apps are constrained by the functionality and speed of the browser.

The fugacity model was developed as a local app because extendibility was a major issue. Borland Delphi® (object Pascal) was used as the development tool. Delphi provides a tight compiled module that can be easily downloaded and installed onto the local computer from the internet. Delphi is a powerful computer language with excellent interface components, and we have found that Delphi is good compromise between MS Visual Basic® and C++. Delphi combines much of the ease-of-use of Visual Basic with the programming power of C++. 
8 Future enhancements to the fugacity framework tool.

A web-accessible database of risk management technologies and associated costs for control and treatment of toxic chemicals to prevent human and environmental exposure will be linked to the fugacity modeling framework in future enhancements. In addition, the number of chemicals and chemical properties contained in the chemical database will be increased to more comprehensively represent Brownfield chemicals.

References


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