CHEMICAL MANAGEMENT AND COMPLIANCE

PROGRAM FOR THE EMERGENCY PLANING AND COMMUNITY RIGHT-TO-KNOW ACT

By

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CHEMICAL MANAGEMENT AND COMPLIANCE

PROGRAM FOR THE EMERGENCY
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ACT

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PREFACE

Great amounts of time, energy, and money are expended annually in the fulfillment of compliance obligations mandated under Acts of Congress for the protection of the environment and human health and safety. Regulatory compliance programs have emerged from the private sector and from federally funded studies, in the form of software programs, database lists, support publications and step-by-step manuals. Their value notwithstanding, the need for a flexible, comprehensive chemical management program with inventory procedures built in, was indicated. Ways and means of organizing data and output documents into useful categories and summary reports were equally requisite. The foundation for the effort must be contained in a database flexible enough to respond to the special needs of different facilities and to changes dictated by on the job experience. The overall result of the Chemical Management Process would be a source-document serving to streamline compliance objectives across multiple EPA and OSHA mandates. The Chemical Management Program (CMP) presented here for critical review, initializes the ongoing effort to develop and perfect a customized environmental compliance tool, applicable to the manufacturing, non-manufacturing and construction industries.
I sincerely thank my thesis committee members--Dr. Jack Vitek (Advisor), Dr. James Lawler (Political Science and Law), and Dr. Paul Matthews (Dept. Head)--for guidance and support in completing the project. I would also like to thank Teresa Dustin for her role as liason and advisor to commuting students in the Department of Environmental Science and to Lori Chapman for sharing the task of constructing a chemical database from ground zero.
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NOMENCLATURE

1. See “Common Environmental Acronyms” pp 13-17, Section 1, Appendix A
1.0 INTRODUCTION

Acts of Congress evolved to sets of health and safety standards to meet the demands for action by involved community groups. Database systems for navigation and management of the maze of chemical and regulatory information are a natural compliment to the process. Computerized information of chemical hazards provides a base for controlling and organizing the progressive impact that added regulations have on the process of compliance. This is accomplished in part through chemical inventories and process accounting of chemical input-output streams. A basic requirement of the inventory process is a methodology inclusive of a set of steps identifying products used by a business, the hazardous constituents that compose chemical streams, estimated product amounts in pounds, and a product hazard profile.

Raw materials must be profiled for their unique identity. That identity may be unfamiliar in terms of chemical history and character, or it may be a reflection of well know constituents with a predictable activity range. Chemical constituents that comprise products or raw materials, often have recognized and listed physical properties, toxicological data, or an industrial activity record that provide as an existing information base for profile analysis. A keystone feature of the Chemical Management Program (CMP) is the interfacing of standardized chemical data with the information supplied for a product (unique) on a Material Safety Data Sheet (MSDS).
Contrasting product vs. chemical profiles creates two distinct points of reference or data reservoirs useful in determining combined chemical fates. This information is useful in a variety of decision making scenarios or in calculating the reapportionment of a product or constituent once it has entered the manufacturing or use cycle.

1.1 Background

Material Safety Data Sheets range from very informative to cryptic, elusive, non-committal or biased for favorable product image even to the point of supplying incorrect information based on regulatory interpretations. Managers or Safety Directors take the information supplied on an MSDS in good faith it is correct without an alternative source or sources of information to counterdict error. The discipline that the MSDS imposes on facility compliance is often limited to those compounds or processes in which relative large amounts of a substances are stored, processed or manufactured. An aggregating feature, such as provided by the CMP, which computes the quantities of hazardous chemicals reoccurring in several facility processes or tasks, is often missing. Equally important is a thorough comparison of chemical identities on hand with the occurrence on lists of chemicals controlled and regulated under various Acts of Congress. Thresholds for some substances under a particular regulatory framework may be as low as one pound, yet that fact goes unrecognized. It remains
no mystery then that facilities fail, years after enactment, to implement a program that fully complies with environmental statutes. The scope of such a project is not often understood by the individual assigned by management to complete it and is equally often underfunded. These factors understate the need for a comprehensive, turn key chemical management program.

1.2 Problem

The application of database technology to the tasks associated with industrial or commercial compliance objectives takes many forms. Chemical lists and hazard information layouts are common and supply good information for anywhere up to 100,000 chemicals. Cross references of chemical names and the synonyms to the status as regulated entities, are also ubiquitous. Most software packages marketed nationwide share a common characteristic—they are not customized to the individual needs of different manufacturers and the peculiarities of operations without incurring additional expense and time for recoding. The option to manipulate a system is most often reserved to the author, requiring long distance communication for requested changes in the system through the original provider.

The solution to this problem is the use of an object oriented database system providing flexible “object” (tables, queries, forms, and reports)
management. Changes and adaptations to the requests of facility managers used to organize data in a particular fashion require simple criteria manipulations in order to redirect or reshape data output. Specialized requests are easily accomplished through object queries, built-in auto functions and the availability of programmable modules. The system may be protected by reserving the individual company program in a read only format available to the client. Changes or alterations to the original format are easily produced as are updates or additions designed to improve access to information for the user. The selection of an object oriented database language establishes a foundation for problem solving that is workable, forgiving of mistakes, and ever adaptable to the demands of the hand of experience in the development of a Chemical Management Program (CMP).

1.3 Objective of the CMP

Federal environmental statutes have overlapping applications and varying compliance requirements that must be addressed in any database management system. The CMP was designed and modeled to comply with the Emergency Planning and Community Right-to-Know Act (EPCRA). EPCRA requirements reflect an administrative attempt to regulate the flow of chemical hazards to the environment, to foster source reduction initiatives, to standardize inventory methods, and to appropriate the process to a national database resource. Through EPCRA the
Environmental Protection Agency (EPA) consolidated in text and form, the physical and health hazard codes developed under previous Acts of Congress or adopted from professional organizations such as the National Fire Protection Association (NFPA). The hazard categories of Flammable, Pressure, Reactive, Acute Health, and Chronic Health represents the EPA’s attempt to groups hazards for Tier II Form reporting under EPCRA. These hazards are not reported numerically or in detail, but simply codified as an “x”. The CMP utilizes the EPA categories, but retains the detail afforded by the 23 Occupational Safety and Health Organization’s (OSHA) categories. Thus a “Flammable” is defined by its flashpoint at less than or equal to 141°F (code ‘F’), or ‘C’ for combustible at less than or equal to 200°F. An “Acute Health” hazard is coded for Irritant (‘IR’), Sensitizer (‘S’), Allergen (‘Allerg’), Corrosive (‘C’) etc. All categories and codes are outlined and defined in Group II of the Field Headings Definitions in Section I of Appendix A.

The objective of complying with EPCRA presents an opportunity to maximize the chemical hazard inventory effort and to identify and segregate the regulatory citations under which those chemicals and hazards are listed and regulated. The detailed identification function of the CMP contains applications to Community Right-to-Know law and to Employee Right-to-Know law in the form of chemical lists, hazard identification, and chemical specific-work area details. The CMP is vested with an aggregation function
expressed in pounds for chemical amounts on hand at any given time and for amounts processed over an entire year. Those estimated weights can be utilized to indicate the potential for release to the environment and for potential employee exposure. Actual values for release and exposure must, of course, be determined under sets of additional physical and human factors. This concept is discussed in the Review of The Literature, Section 2, of this document.

The result of developing a chemical inventory with hazard profiles under the guidelines of EPCRA, sections 301-313, is a source-document for comprehensive environmental compliance. The basic task of identifying chemicals, estimating the amounts, and relating them to regulated chemical lists produces an information base that can be manipulated to comply with more than one set of compliance obligations. The continued development of the conceptual use of the CMP as a source-document is an overriding objective in current and future revised forms of the program.

1.4 Scope and Limitations

The CMP imposes a thorough, disciplined method on chemical inventory procedures. The inventory process narrows the margins for error in estimating the use, storage, and processing amounts of the products and chemicals that make up the chemical stream in a facility. The CMP imposes a housekeeping standard for MSDS control and product identification that
eliminates duplicity, updates out-of-date documents, and creates an umbrella view of product use within the facility. Inventories are organized into convenient alpha formats to expedite finding a particular chemical or product, either as a member of a report or in a master MSDS file book. This is a useful feature in terms of providing access to information for any individual or group of users. The CMP is intended for use by administrative agencies, facility management, employee personnel, and compliance engineers for various applications.

Questions must be raised as to the reliability of the sources for the CMP and the formalized output of data in reports (Sections IV.-VI. of Appendix A). Certain limitations precede the Chemical Management and Inventory Process. Material Safety Data Sheets are often the sole source for product identification and information relative to chemical management. The limitations of MSDS's have been previously discussed, but this does not diminish the role played in the inventory process. The hand of experience in extracting data from MSDS's is an essential component in recognizing information that is incorrect or somehow encrypted in the text.

The breakdown of the constituent composition of a product by percentages is an important function of the MSDS. Many times this information is left out on the basis that those elements do not constitute a hazard. This may be true, but may also be a misinterpretation of what constitutes a hazard and, therefore, qualifies for detailed composition. By definition a "Hazardous chemical" means "any chemical which is a physical
hazard or a health hazard” (29 CFR 1910.1200(c)). Reasonable interpretation of this definition includes hazards created by physical states that result in nuisance particulates, or ingredients of products that have the potential to sensitize or result in allergic reaction over extended exposure periods. Chemicals that form the composition of mixtures are exempted from health considerations at the 1% or .1% (carcinogens) thresholds if it can be reasonably anticipated that processing will not result in releases that exceed safe exposure limits set by the EPA in accord with the American Council of Governmental and Industrial Hygienists (A.C.G.I.H.). Completion of the CMP under circumstances of important missing information can often be corrected by a call to the manufacturer, even under Trade Secret exemption status. When these efforts fail a designation of “MWNS” or Manufacturer Will Not Supply is recorded to explain the missing information.

The estimation of product amounts relies on a combination of facility accounting and purchasing records and knowledge from the production “floor”. The first year estimates that supply the CMP output, are usually adequate and within the guidelines set by EPCRA, but will likely improve along with the inventory list, the second year. The process of discovery and organization varies from facility to facility depending on previous efforts to comply with EPCRA (or certain sections thereof) or with the Hazard Communication Standard.
The CMP, in its current state of development, is limited to the role of "Indicator" and "Identifier" of the chemical substances and associated hazards used, stored or processed in a facility. As will be shown in Section 4.6 developed uses and applications for CMP exist beyond its present scope. The additional inventory of factors associated with extended use of CMP data for Air Emissions Inventory, Title V of Clean Air Act, and Employee Exposure Determinations, requires extensive and additional effort to complete. As it now stands, CMP reports provide useful data in the completion of these and other compliance projects. Time and cost factors must be considered before adding to the scope of the CMP.

1.5 Relevance to Literature

Topics discussed in the Review of The Literature cover a range of ideas and concepts related to chemicals and poisons as social, medical, and economic phenomena. The discussion provides insight into attitudes that accompany chemical exposure among the working class and among the owners and managers of manufacturing operations. Toxicology is addressed because of its fundamental role in defining the hazardous nature of the chemicals we use and the certainty with which we can predict exposure. Human factors are considered for the overall influence on worker health in the context of working with hazardous substances. This discussion is designed to strengthen the role of comprehensive compliance tools, like the CMP, in addressing chemical health and safety concerns.
Rather than anticipating an imposed obsolescence for compliance programs in saturated domestic markets, the CMP concept looks to continued vitality as a hazard management tool, especially for small to medium size manufacturing concerns. Globally, the potential for educating and promoting chemical management for protection of the environment and for worker safety and health is practically unlimited.
2.0 REVIEW OF LITERATURE

2.1 Brief History of Chemical Exposure

The term hazard, from the French derivative hazander, is defined as “to expose to the operation of chance; to venture; to risk; to put in danger of loss.” Synonyms include perilous, unsafe, precarious, and uncertain. Chemical hazards are a predominant part of many hazard groups and affect societies at many levels. The awareness of chemicals as poisons from naturally occurring substances precedes the birth of Christ in legend and recorded history. Theophrastus of the Third century B.C., a well known Greek scholar, student of Aristotle, and admiral of inquest, documented knowledge of pisonous plants, laws against use, and other stories of political intrigue in De Causis Plantarum (Einarson, 1976).

Occupational exposure to hazardous chemicals was first recorded by describing the somewhat ominous effects observed among workers in 17th and 18th century Europe. Maladies described were “Grinder’s Rot”, “Phossy Jaw”, “Painter’s Colic”, “Chrome Itch”, and “Miner’s Phthisis” among others attributable to prolonged and concentrated exposure (Fairhall, 1957). Worker complaints were not generally well received by business owners of the day. Owners considered injury of any kind to be the result of worker immorality and character defect (Gordon, 1985). The effects mentioned were not universally observed leading to uncertainty of cause, and prolonging the validity of “other” explanations or “moral causes”
Prevalent notions among male populations of that period were influenced by macho attitudes toward strength, endurance, and invulnerability to industrial processes. An illness among workers was as likely to be viewed as elimination of a weak constitution (a sort of industrial natural selection) readily replaced by an eager new worker.

The large scale effects of the European Industrial Revolution resulted in the adoption of new technologies that gradually changed the continent from a complex of rural cottage industries, to large concentrations of expectant workers of all ages and gender. Bustling factories, squalid living conditions, inadequate sewage control, and shortages of food and water, contributed to a maze of adverse health factors. Extremes of poverty and wealth, the need and desire to work, and the absence of legal protection left little platform for complaints of exposure (Beales, 1958).

By the 19th century, half of the population of England resided in urban areas. Dense populations, unsanitary living conditions, and industrial exposure worked in tandem to send people to an ominous early grave (Beales, 1958).

The term “Phossy Jaw” describes a late 19th century chemical exposure problem in England and its industrial neighbor, France. White phosphorous, now a recognized extremely hazardous substance, was banned in 1898 and a suitable non-toxic substitute found. The pressure for change was a result of the work of members of the Match Worker’s Federation, most of which
were women. This is an important event in the growth of industrial hygiene and workers rights for that period of lower class status for all workers and extreme prejudice against women. The success of the women match workers among peers stands in contrast to similar exposures tolerated by male workers (Sax, 1984). The white phosphorous incident demarcated an era of improved working conditions based on the passage of industrial worker health and safety laws, many of them simply reducing the workday to 11 hours. Conditions such as “phthisia”, a precursor to tuberculosis and other lung ailments, dermatoses, rheumatism, etc. continued to be problems for workers in the cotton, silk, glass blowing, mining, iron, and other heavy industries (Gordon, 1985).

One might characterize the overview of industrial exposure to hazardous substances as having its roots in pioneering economies, social ignorances, and a complex of gender, ethnic, and economic biases. Health or safety conditions may be overlooked in favor of the opportunity to work and the pressure to support a family. Industrial booms carry a momentum that outpaces planning and management for items not built into the profit structure of the company. This is fertile ground for the suppression of worker health and safety concerns and to reinforce a psychological barrier to complaints, especially among women and minorities (Fuentes, 1983). The connection between 18th century England and multinational exploitation of lax environmental and labor laws in Third World countries,
exposes an innate tendency among business owners not to factor the cost of health and safety into their management plans. Even the development of a legal framework to foster third party or governmental protection of human rights, cannot ensure blanket application nor enforcement of those laws. At the root of this resistance to change is the dislike for outside interference in private affairs and the view that compliance is a cost burden. This view spills over in the international underwriting of the emerging economies of poorer nations. Industries are established without demanding the same level or sliding scale of protection found in developed economies (Fuentes, 1983).

The developed industrial powers of the world are a testimony to the compound effects of chronic chemical exposure. In our own country, the incidence of disease directly related to occupational exposure is documented in the sets of laws constructed to deal with the pain and suffering of past negligences. The coal mining (Black Lung disease), copper and other heavy metals, fiber related manufacturing, wood pulp, and other industries for which billions have been spent to rectify damage to workers and the environment, stand as monuments to the neglect of preemptive safety measures. In contrast, unregulated societies manage to make workers dependent and fearful of voicing occupational complaints thereby delaying the implementation of hazard controls (Ilo, 1985). Regulated societies continue to build consensus for compliance with the law based on
research, education, enforcement actions, and litigation. Thus, progress is possible where a legal framework is established, but it is not guaranteed. Additional tools and efforts to manage chemical hazards are required. The Chemical Management Program is a compliance tool with educational value nested in the procedures required for its completion and as such finds its place in the overall scheme of the environmental movement. The more time and money saving steps that can be incorporated into the initial chemical auditing and control process the more receptive owners and operators of industrial enterprise are likely to be.

2.2 Concept of Uncertainty of Exposure

Occupational exposure to chemical hazards is plagued by an innate amount of uncertainty in the diagnosis and confirmation process. Industrial exposure records sustain the effects of exposure for many chemicals such as heavy metals, acids, many dusts and fumes and certain organic compounds introduced in the 20th century. A host of compounds and mixtures still remain to be identified for exact effect on workers in occupational settings. The science of toxicology produces hard data by animal extrapolation (Calabrese, 1983) and as such must admit to uncertainty in many applications to human exposure. Exposure is regulated by numerous factors outside the toxicity of a substance or its mere presence in the workplace. Concentration of a compound, duration of
exposure, particle size, affinity for human tissue, solubility, grades of human sensitivity, and varying immune system response capabilities, affect actual hazard assessment and confirmation of exposure (Sax (1984), Clayton (1973), Amdur (1973), and Xintaras (1974). The Registry of Toxic Effects of Chemical Substances is noted for its disclaimer—"Under no circumstance can the toxic dose values presented with these chemical substances be considered definitive values for describing safe versus toxic doses for human exposure" (Lewis, 1982).

Test data may not always be correlated with environmental observations--pro or con. Data may be plentiful for elements or compounds but not for the thousands of resultant mixtures proffered from laboratories. Safe concentrations may still result in minor discomfort or over time accumulate a legacy of nonlethal, noxious insults capable of disabling basic body functions (Sax, 1984). The role of uncertainty in classifying a chemical substance serves as a guiding principle and reminder that the assessment process is dependent on many factors from different sources. Facts should be assembled from the field as well as the lab in order to reduce the level of uncertainty of a substance for its physical and health hazard status.

The concept of uncertainty is relevant to every step in the process of chemical analysis and characterization--to toxicology, MSDS preparation, factors of exposure, physio-chemical processes, and to the political
decision to ban a useful product from the marketplace. Though many chemicals have a level of toxicity that eliminates doubt as to the effects of exposure, many more substances and adverse effects are controlled by subtle use factors. To this end, uncertainty serves as a major influence of the conservative value system that has ruled in setting health and safety standards for chemical exposure by federal agencies for several decades. It is equally responsible for fueling debates over the entire chemical evaluation and certification process derived by animal extrapolation. A tug-of-war exists between economic interest and a public fear of chemicals fostered by a legacy of industrial abuses and political failures to intervene. In the words of Charles Thackrah in his treatise on occupational medicine, "Each master...has in great measure the health and happiness of his workpeople in his power...let benevolence be directed to the prevention, rather than to the relief of evils" (Clayton, 1973). Generally, this wisdom has not been applied until environmental contamination or worker health problems have been revealed.

The role of uncertainty in the whole process of establishing controls and mitigating the effects of chemical substances, is to promote due diligence, from discovery in the lab to hazard communication on the shop floor. Applied properly, uncertainty serves to buffer both the tendency to overreact to the threat (implied or otherwise) of chemical hazards and the
equal human tendency to ignore or understate the effects (subtle or otherwise) of chemical exposures.

2.3 Toxicology

Toxicology is rooted in the study of the nature and actions of poisons (Casarett, 1975). It is derived from the Greek term for the poison used to lace the arrows of warriors. Theophrastus has been discussed for his knowledge of poisonous plants and the laws accompanying their control. The fateful death of Nero, Emperor of Rome is attributed to foul play and a lethal potent. Toxicology has an ancient relationship with government and social order (Bury, 1958).

Modern toxicology can be traced to advances in methods of recognition and analysis of chemical substances in deceased animals and men. Matthieu Joseph Bonaventura Orfila (1787-1853) was a Spanish physician in the Court of King Louis XVIII. He is reported to have given known quantities of drugs and poisons to animals and to have recorded the symptoms, performed autopsies of organs, and further analyzed tissue samples (Calabrese (1983) and Loomis (1968). Orfila’s pioneering work laid a foundation for expanded research with more substances by C. Bernardo in his 1850 treatise on “Mechanisms of Action of Strychnine”. A century of development in the science of the “action of poisons” on
biological tissue capitulated with the work of P. Muller on the effects of DDT and related insecticides and with the work of G. Schrader’s 1952 *Introduction and Study of Organophosphorus Compounds* (Casarett, 1975).

A toxic agent has the following characteristics:

- A chemical agent capable of producing a response
- Has biological tissue as the site of the response
- Produces adverse effects relative to dose

These characteristics form basic assumptions in the discussion of the topic (Casarett (1975), Jameson (1984), and Rodrigs and Jardiff (1982). The dose-response relationship for lethal effects unifies the attempt to define the point at which a chemical causes serious harm to biological tissue (Loomis (1968), Calabrese (1983), Casarett and Doull (1975) and Manahan (1989). Dose is a unit per body mass of a toxicant to which the organism is exposed, usually in mg/kg body weight. Response is the observable or obtainable effect due to exposure (Manahan (1989), and Casarett (1975).

The introduction of the “LD50 dose response” level (Trevan, 1927) set a standard or rationale for toxic effects testing. The median lethal dose may be depicted on a statistical curve for percent deaths plotted against log dose (Manahan, 1989). The same relationship may be depicted as well on a Gaussian distribution curve of the typical bell shape for survival to death ratios (Casarett, 1975). This is the frequency response among members of the test species. The cumulative response curve is sometimes
spoken of in terms of a “probit” in which a probit of 5 equals the LD50 and differences of 1 probit correspond to ± 1 Standard Deviation of the mean LD50. Sixty-eight percent of all values on the dose-response curve within 1 Standard Deviation represent a range of lethal effect from LD16 to LD84.

The range for lethal effects can be qualified for Effective Dose (ED), Toxic Dose (TD), and Lethal Dose (LD) in order to establish a range of safety or therapeutic index (Casarett, 1975) as introduced by Paul Ehrlich in 1913. The therapeutic index is a function of the ratio of dose required for toxic effect to that required for desired therapeutic result. The use of such an index is not limited to substances that have medicinal value, but includes a host of common elements or compounds that fluctuate between nutrient and toxin based on dose. The argument is made that the therapeutic index is a better marginal indicator of safety that the lethal index alone by providing shades of subtle change in toxic character (Casarett, 1975).

The LD50 cumulative response curve for lethal effects is also useful in comparing the “potency” of two substances based on dose requirements (Loomis, 1968). Over time the comparative values among dose responses for hundreds of tested chemical substances have evolved into a categorization of toxicity. The relationship between chemical concentration and observed effect produces a descending classification system for toxic
effect. Table 1 compares level of toxicity, dose range, and equivalent measure for comparison:

Table 1. Toxic category, dose level and liquid equivalent.

<table>
<thead>
<tr>
<th>Toxic Category</th>
<th>Dose Level</th>
<th>Liquid Equivalent</th>
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<tbody>
<tr>
<td>EXTREMELY TOXIC</td>
<td>&lt; 10 mg/kg</td>
<td>&lt; 14 drops</td>
</tr>
<tr>
<td>HIGHLY TOXIC</td>
<td>10 - 50 mg/kg</td>
<td>&lt; 1 tsp.</td>
</tr>
<tr>
<td>TOXIC</td>
<td>50 - 500 mg/kg</td>
<td>1 tsp - 1 oz.</td>
</tr>
<tr>
<td>MODERATE TOXICITY</td>
<td>500 - 1500 mg/kg</td>
<td>1 oz. - 3.5 oz.</td>
</tr>
<tr>
<td>SLIGHT TOXICITY</td>
<td>1500 - 5000 mg/kg</td>
<td>3.5 oz. - 1 pt.</td>
</tr>
<tr>
<td>NEARLY NON-TOXIC</td>
<td>5000 - 15000 mg/kg</td>
<td>1 pt. - 1 qt.</td>
</tr>
</tbody>
</table>

Table 1 values vary slightly among select authors. The values for “toxic” in row three represent the definition for the term found in 29 CFR 1910.1200 and incorporated into the terminology and symbolism of the Chemical Management Program. The Liquid equivalents are based on the conversion of mg/kg animal dose to equivalent measure for a man average weight of 68 kg or approximately 150 pounds. The density or specific gravity standard is water at 1 gram per cubic centimeter. Chemical substances of all kinds hover above and below this value such as benzene at .899 g/cm³ or acetone at .792 relative to water = 1.0. One cubic centimeter is equivalent to one milliliter is equal to about 20 drops.
Further evaluation of dose-response data plotted on a frequency distribution curve allows for generalizations to be made about population responses. It is common to speak of “normal, hypersensitive, and hyposensitive” members of a species test group (Loomis, 1968, Casarett, 1975, Manahan, 1989, Goldberg, 1983, and Rodricks and Jardiff, 1982). The hypersensitive / hyposensitive individual represents a deviation from the mean culture of respondents. Though outside the normal response range for a population, such effects are given thoughtful consideration in the final assignment of human personal exposure standards. Part of the value of animal experimentation is the discovery of the type of toxic action related to a dose and the ability to distinguish variable effects by different routes of entry. Thus, an oral dose may prove not toxic or lethal to a specimen but may very well generate characteristic irritant properties at low dosage levels. A substance may be lethal upon inhalation and also exhibit the ability to sensitize skin or eye tissue after repeated doses at low levels. The overall value of any animal extrapolation study for toxicity of a substance should be reviewed according to the testing protocol used (Fairhall (1957), and Choudhary (1981).

The previous discussion on dose-response relationships focuses on the acute effects. This may only be the first step in a thorough assessment of the toxicological properties of a chemical. Subacute toxicity studies
preempt the need for extended assessment testing periods in order to assess the chronic effects of exposure. Subacute data can be used in the assessment of closely related groups of chemicals, reducing the necessity for long term chronic evaluation. Chronic evaluations may extend from 2-7 years depending on the species and require supporting data on population mortality, life-span, growth rate, food consumption, appearance, and behavior characteristics (Casarett, 1975).

2.4 Factors of Exposure

The application of comparative lethality indexes to human safety standards is inadequate (Sunshine, 1988). Guidelines set exposure limits based on probable duration of exposure to a toxicant and an estimate of dose to the target entry site based on absorption / elimination rates. The expected outcome for exposure is of course an observed absence of adverse effect. Rates of absorption by routes of entry for administered doses to test specimens in descending order are intravenous, inhalation, intraperitoneal, subcutaneous, intramuscular, intradermal, oral and topical. Hazard determination in the lab is designed to correspond with the likely route of exposure on the job. The designation of “acute” toxic effect is derived from a single dose capable of producing an observable health effect. Chronic effects are relative to low level doses. The importance of route of entry as an exposure factor is illustrated by the contrast of the
response of rats to administered doses of cocaine. Cocaine, injected intravenously results in convulsions and death, whereas the same dose injected subcutaneously manifests only excitable behaviour (Casarett, 1975).

Dosage as a factor of adverse exposure must be considered for two refining characteristics: reversability and accumulation. The acute observable effect that is completely reversible differs from the same effect that results in scar tissue, allergic reaction, sensitization, or delayed immune response. Chemicals that accumulate in fat or muscle tissue represent a potential long term health threat of unpredictable proportion (Sunshine (1988), Casarett (1975), Manahan (1989), Loomis (1968) and Hamilton (1974). The impact of multiple chemical exposures may work to diminish the protective value of limits designed to intercept the acute or chronic effects associated with certain toxins (Mason and Johnson, 1986). The level of uncertainty in confirming exposure increases as we move from the lab to the workplace, from acute toxicity to chronic effects, and from single compound-single route of entry exposure to multiple insults of multiple compounds at multiple sites.

Once a substance has been assessed for local effects and route of entry, the actual effects are dependent on systemic absorption factors. The ability of chemicals to cross membrane barriers, to react with biological chemicals, to metabolize, and to interfere, disrupt, or shut down
a physio-chemical process, are major influences in classifying a toxic substance (Sunshine, 1988). Chemical exposures may be site limited with varying observable effects from irritation to corrosive damage of tissue layers. Delayed chemical reaction or solubility on exterior tissue may result in direct adverse reaction, or the build up of fluid as edema.

Chemicals that bypass membranes may suffer several fates: (1) a direct digestion to excretion path; (2) metabolism of the parent compound to excretion; (3) detoxification in the liver; (4) distribution for storage in bone or fat; (5) binding to receptors in blood or potential passage across cell membranes. These and other options for systemic effects complicate the process of confirming exposure and determining long term effects of individual and group substances. Alternative research is currently underway to relate the structure activity relationships (SAR) (Patnaik, 1992) between chemical composition and reactions with biological tissue. More generalized testing protocols for chemical groups (perhaps by molecular configuration as with SAR’s) will give researchers an edge in predicting systemic effects. SAR is one of a host of alternative approaches to chemical testing and extrapolation for toxicological data being explored (Jameson (1984), Cairns (1986), Hollaender (1985), Calabrese (1983), and Patnaik (1992). For example, models used to estimate the effects of a toxicant(s) on an ecosystem rather than a single species may have applications to human regulatory mechanisms affecting
exposure such as pulse, blood pressure, body temperature, heart rate etc. (Cairns (1986) and Calabrese (1983)).

The discussion of factors of exposure from the physio-chemical and metabolic point of view suggests an expanded role for the industrial hygienist beyond the measurement of exposure limits or simply generic safe work practices. Linking the details of the work environment and factors surrounding human subjects with advancing research in toxicology holds the promise of improving the results of industrial chemical hazard assessment and the criteria used to suggest or implement changes. The goal should be two-fold: (1) to reexamine the factors of exposure used in determination and, (2) to be willing to extend the examination process beyond the standard inhalation test for exceedance of Personal Exposure Limits or Standard Limit Values. As will be evident in the next discussion, the hygienist or safety director seeking to implement new ideas or improve the information gathering process must be aware of the obstacles to hazard assessment presented by a broad spectrum of human factors.

2.5 Human Factors and Predicting Exposure

Industrial hygiene control methods form a basis for worker safety and protection in a variety of hazardous environments (National Safety Council). Ideal control methods are the combination of efforts to prevent,
reduce or suppress the escape of hazardous substances and to engineer or vent the offending fumes, mists, dusts or vapors. Human factors (Salvendy, 1986) consist of multiple elements of human behavior, physiology, personal habits, etc... that affect contact with, absorption of and systemic outcome of interaction with hazardous chemicals. Consideration of these factors in the context of major routes of entry and the absorption process is essential in the effort to circumscribe all the factors relevant to actual exposure.

Exterior surfaces of the human body considered targets for exposure include the skin, nails, hair, ears, eyes, teeth, oral passages, nasal passages, trachea, esophagus, lungs and digestive tract (Manahan (1989), Xintaras (1974), Loomis (1968), and Brown (1988)). Human factors affect rates of absorption forming a risk scale associated with specific body sites. The skin is the largest area of the body exposed to the most types of hazard forms including gases, liquids, and solids and to the most sources from air, work surfaces, tools and equipment, and direct handling of chemical substances. Skin exposure is scaled according to the physical state of the substance and the degree of thickness of the horny epidermis. Hands and bottom of feet are least absorbent while the scrotum is most vulnerable. Toxic substances exhibit varying capacities to remove oil from the skin causing it to dry out, or resulting in degrees of irritation or burning, or to transverse the permeable membranes of cell
layers and enter the bloodstream. Toxic substances showing no acute symptoms of exposure may have chronic carcinogenic or mutagenic effects after prolonged use (i.e. coal tar).

The eye is often placed in vulnerable positions relative to chemicals in use. It is easily irritated and sensitive to particulates and as such should serve as a warning of exposure from dusts, fumes, mists or solids transferred from hand or finger to the eye. The eye is a resilient organ even when damaged by acute trauma. Its nemesis is prolonged, consistent exposure to materials that dissolve the conjunctive membrane covering its surface. Removing or compromising this layer leads to permanent disabilities in the layers beneath.

The oral cavity including the throat and esophagus are subject to absorption of chemicals by contact with fingers or by inhalation. Substances may be carried by saliva or mucous into the digestive tract, trapped in the cavity by teeth or tissue, or absorbed across membranes into the bloodstream. Nicotine is a powerful poison, soluble in the mouth and the direct cause of malignant activity in the oral tissue of tobacco users.

Absorption through the lungs carries the highest route of entry risk factor where chemical substances become air borne as mists, fumes, or vapors or where processes solids fragment into particulates (Salvendy, 1986). The lungs average 70 M$^2$ of surface area compared to 10M$^2$ for
the gastrointestinal tract and $2M^2$ for the skin (Mason and Johnson, 1986). The passageways to the lungs contain fine structural cilia that function as filtering devices to particulates which can be further trapped in mucous and swallowed or expectorated. Soluble substances may be dissolved in combinations of saliva and mucous and never reach the lungs. The risk of lung exposure is predicated on its role as the site of gaseous exchange in the alveoli (one cell partitions) that border vessels carrying either oxygenated or deoxygenated blood. Gases, vapors, and some fumes (particulates at the micron level) may pass into this exchange system or the finest of particulates that are insoluble may become imbedded in lung tissue. The degree of absorption and adverse response to toxins is heightened in the lungs (Manahan, 1989).

Once toxins have entered the bloodstream by any of several routes, the fate of those substances is in part dependent on the ability of the liver to detoxify the substance(s) or its metabolites. Predicting the fate of toxins in the bloodstream must be done on a case by case basis relative to biochemical research on the composition of the compound. The pathways of metabolism of foreign compounds in the body leads to knowledge of parent compounds that are traceable through the body or metabolite offspring that end up in the urine of the worker. An example is the assessment of benzene exposure based on the analysis of phenol in subject urine (Amdur, 1973). Toxicologists can use the results of
intraperitoneal injections of toxins which have a direct path to the liver for comparison with intravenous injections. A higher LD50 for the “ip” injection (lower toxicity) than for the “iv” injection would suggest a detoxifying role for the liver (Amdur, 1973). Biochemical studies for the fates of parent compounds define toxic action in the body and locate the agent of adverse action. An example among relatives of a chemical group is the dominance of triethyl lead as cause of nervous system damage among specimens also injected with di, tetra, and lead acetate (Cremer in Amdur, 1973).

Additional human factors that influence the intensity and perhaps duration of a toxic agent include, the age and general health of the individual, personal diet, smoking and alcohol consumption, genetic susceptibility, and gender. Behavioral attitudes toward safety in general play a major role in predicting exposure. Resistance to the use of provided safety equipment, poor hygiene between meals, and methods of job performance that unnecessarily increase exposure. Physical environmental factors either at home or on the job can influence the overall susceptibility to low level doses of toxic agents. In the workplace elevated temperatures, high humidity, and labor intensive job tasks (elevated heart rate and respiration--open pores and perspiration) create conditions that elevate rates of exposure by normally resistant routes. Physical and mental factors combine and manifest as stress related
symptoms in employees (Smith, 1986) aggravating the effects of low level exposures. Such factors need to be considered in the process of determining not only an employee’s risk of exposure from the hazardous chemicals in his work area but from internal / external factors that exacerbate the effects of low exposure or weaken natural defense systems.

2.6 Workplace Applications of Exposure Factors

Asserting the “uncertainty” involved in predicting workplace exposure does not diminish the importance of factors that can be measured. Absorption through the lungs averages 25 liters per minute under conditions of light work. This translates to an average consumption of 10 cubic meters over the course of the eight hour workday. Concentrations of gases, vapors and fumes are measured in mg/M$^3$ as a function of molecular weight per constant volume under the ideal gas law. The weight to volume measure is easily convertible to volume to volume as parts per million (ppm). Many gases or vapors may enter processes in the liquid state and therefore the weight to volume measure also has a liquid equivalent based on the density of a substance relative to water at 1g/ml. Thus 1 mg/M$^3$ of water equals $1ul/L$ liters equals 1ppm. The inventory process of the Chemical Management Program inputs values for specific gravity in order to convert product amounts of any physical state
to pounds providing a foundation for further weight to volume comparisons.

Safety standards promulgated by the A.C.G.I.H. range from .00006 mg/M$^3$ for proteolytic enzymes to 9000 mg/M$^3$ carbon dioxide (Mason and Johnson, 1986). The majority of substances fall between .1 and 10 mg/M$^3$ in Table 2 of this subsection. The liquid equivalent for the vast majority of substances controlled for exposure is $\leq 10$ml or about 2 tsp.

Concentrations of gases are computed according to the ideal-gas equation in which one mole of gas at standard temperature and pressure fills a volume (V) of 22.41 liters, and the molecular weight (MW) of the substance. The ratio of the (MW) to (V) for flourine, for example, is a calculated density of .84 g/l. For practical applications the ideal gas volume is adjusted to room temperature at 25°C. (77°F.) value which expands the volume to 24.5 liters (Brown and LeMay, 1988). Threshold Limit Values for air contaminants (TLV’s) represent 8 hour time weighted averages for maximum allowable exposures over the course of the workday. Values expressed in ppm and mg/M$^3$ are convertible as follows at Standard Pressure of 1 atmosphere (760 mmHg) and room temperature:

$$\text{PPM} = \frac{24.5}{\text{MW}}$$

$$\text{mg/M}^3 = \frac{\text{MW}}{24.5}$$

[2.6.1]

Thus 200 ppm acetone $= \frac{200 \times 58.08}{24.5} \text{ L}$ or 474mg/M$^3$
Upon consulting the TLV value for Acetone (29 CFR 1910.1000 (Table Z-1)) the ppm is 750 and the mg/M$^3$ 1800. This ratio is consistent with the results of the formula [2.6.1].

Substances regulated for exposure limits are subject to the rule of mixtures in which more than one constituent may consort to create additive value in terms of overall toxic effect. Under this rule the ratios of concentrations of contaminants (C) to specified exposure limits (L) are added and shall not exceed unity (1) (29 CFR 1910.1000 (d)(1)(ii)). In short, the ratios of concentrations to TLV values must not be greater than one if it is conceivable the components have additive value (Sunshine, 1988). Otherwise, they can be assessed independently.

Vapor pressure is an inventory component of the CMP whenever provided by the MSDS. Vapor pressure presents another method or option of solving for T (TLV) where a mixture of (N) components conceivably have additive effects. Each component mole fraction times the partial pressure at 25°C is divided by that same value over the registered TLV (Sunshine, 390):

\[
T = \frac{F_1 P_1^o + F_2 P_2^o + \ldots + F_N P_N^o}{P_1^o \frac{T_1}{T_1} + P_2^o \frac{T_2}{T_1} + \ldots + P_N^o \frac{T_N}{T_1}} \quad [2.6.2]
\]

Solving for components Trichloroethylene (1) and Methylchloroform (2):

\[
T = \frac{38.2 + 59.2}{38.2 + 59.2 + 100} \cdot \frac{1}{350} = 97.4 = 177 \text{ppm}
\]
OSHA limits for air contaminants contain designations for “skin” effects and for “ceiling” limits which are exposure thresholds never to be exceeded. Approximately 150 chemicals qualify for the skin designation whereas about 45 chemicals in Table Z-1(29CFR 1910.1000) qualify for a ceiling. Chemicals with skin designations form an important group to consider whenever an assessment for PEL or TLV compliance is being conducted. As will be discussed, the gas, vapor, or liquid states provide the same opportunity for exposure and absorption via the skin as would be expected for the respiratory path. The surface area presented for absorption in the lungs is greater than that for the skin and the rates are higher, but as will be shown the amount of contact per surface area required for absorption to occur is relatively low.

Mason and Johnson (NIOSH, 1987) have constructed a set of practical tables, formulas and examples of relationships between TLV’s and the potential absorption of common contaminants through the lungs, skin, and eyes. The tables reveal general trends and associations between the TLV ranges and absorption under different work load levels. Another example gives the liquid contact required to absorb the daily doses implied by the TLV at light (average) work loads. The intent of this final discussion is to reconstruct these tables and paraphrase the discussion in order to show direct application of values obtained in the CMP inventory to health and safety initiatives of any industrial environment.
Table 1 related TLV ranges to liquid equivalents such that for some chemicals permissable exposure in any one hour of an 8 hour day ranges from a fraction of a drop to about 2 teaspoons. In the following Table (2) TLV’s are related to the potential for daily absorption in the lungs based on light and heavy workload.

**TABLE 2  Summary of TLV’s and Potential for Daily Absorption from the Lung at Light and Heavy Work**

<table>
<thead>
<tr>
<th>TLV Range (mg/m³)</th>
<th>Number Substances</th>
<th>Weight</th>
<th>Volumeᵃ</th>
<th>Weight</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; = 0.1</td>
<td>59</td>
<td>1mg</td>
<td>1ul</td>
<td>3mg</td>
<td>3ul</td>
</tr>
<tr>
<td>&lt; = 1</td>
<td>129</td>
<td>10mg</td>
<td>10ul</td>
<td>30mg</td>
<td>30ul</td>
</tr>
<tr>
<td>&lt; = 10</td>
<td>162</td>
<td>100mg</td>
<td>100ul</td>
<td>300mg</td>
<td>300ul</td>
</tr>
<tr>
<td>&lt; = 100</td>
<td>88</td>
<td>1g</td>
<td>1ml</td>
<td>3g</td>
<td>3ml</td>
</tr>
<tr>
<td>&lt; = 1000</td>
<td>82</td>
<td>10g</td>
<td>10ml</td>
<td>30g</td>
<td>30ml</td>
</tr>
<tr>
<td>&lt; = 10000</td>
<td>37</td>
<td>100g</td>
<td>100ml</td>
<td>300g</td>
<td>300ml</td>
</tr>
</tbody>
</table>

ᵃ Volume at specific gravity of 1.0 relative to water. Equivalent volumes for most substances will vary proportionately with specific gravity. Ranges of sp gv of 0.61 to 1.5 will decrease volume by as much as 1/2 for the denser substances and increase volume to one and a half times for the lower densities.

Experimental data for amounts of substances inhaled (I) for 30 minutes and absorbed (A) has been reported for various concentrations of exposure (in mg/m³) and various workloads (resting, light, medium and heavy). Experimental exposure/absorption data can be use to generalize about substances for which data may be sparse. Exposure concentrations of
butyl alcohol of 300 mg/M$^3$ for 30 min. are multiplied by a factor of 16 for an 8 hour day and by a factor of 20 for a 10 hour shift. For light work then, the daily absorption for light work is 220mg x 16 or 3.5g and 460 x 20 or 9g for heavy work. Table 2 generations of potential for absorption for TLV ranges of 300 mg/M$^3$ by linear extrapolation are approximately 3g and 9g for light and heavy columns respectively. The ratios for Butyl Alcohol Absorbed (A) to Inhaled (I) (Table not shown) are 81 to 220 and 193 to 460 mg/M$^3$ light and heavy work. The values for the ratios indicate about a 36% absorbency rate for light work and about 40% for heavy. The Table 2 equivalent volumes are approximately 1ml and 3.6ml respectively. It can be concluded from the discussion that:

- Concentrations of exposure indicate potential only.
- Inhalation of potential contaminant concentrations increases with workload and rate of respiration, generally by a factor of 2 from light to heavy assignment.
- Absorption rate is approximately 1/2 that of exposure.
- The TLV summary in Table 2 is a valid tool to predict or estimate exposure and relative absorption at various concentration rates.

Absorption through the skin is likely to occur in the hands or forearms as any other place. OSHA has placed skin designations on numerous chemicals because of the widespread incidence of dermatoses associated with the use of solvents and other organic substances. Xylene for example has a TLV of 435 mg/M$^3$ which can be extrapolated for potential respiratory absorption (light load) of about 4.3g of which only about 2g
would account for actual absorption. The absorption rates for substances on skin vary widely from as low as $2\mu g / \text{cm}^2$ per min. for m-xylene to rates of 200 for styrene, 300 for toluene and 100 for xylene (mixed isomers).

If 2g of xylene is the estimated actual absorption over an 8 hour period and the absorption rate is $100 \mu g / \text{cm}^2$, then the surface area required to complete 2g of absorption would be 20,000 square centimeters total exposure. The area of the hand is about 500 square centimeters which equates to holding the hand submerged in xylene for 40 minutes to get the same approximate exposure to atmospheric xylene at the recommended TLV.

Table 3 illustrates the liquid exposure required in cm$^2$ per min. that would actually result in a daily dose implied by a chemicals TLV. The first value in the table that generates the series of ranges and linear extrapolations is calculated according to the following formula:

$$0.1 \text{mg/m}^3(\text{TLV}) \times .025\text{M}^3_{\text{resp. rate}} \times 480 \text{ min./day} \times .5(\text{absorp.factor})$$ [2.6.3]

The amount absorbed is 600ug.

<table>
<thead>
<tr>
<th>Absorption Rate (\mu g/cm$^2$ · min.)</th>
<th>0.1</th>
<th>1.0</th>
<th>10</th>
<th>100</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>6000</td>
<td>60,000</td>
<td>600,000</td>
<td>6x10$^6$</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>600</td>
<td>6000</td>
<td>60,000</td>
<td>600,000</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>60</td>
<td>600</td>
<td>6000</td>
<td>60,000</td>
</tr>
<tr>
<td>1000</td>
<td>0.6</td>
<td>6</td>
<td>60</td>
<td>600</td>
<td>6000</td>
</tr>
</tbody>
</table>
The gray shading pinpoints the area for high average absorption rates (xylene e.g.) for TLV ranges 1 to 10 mg/m$^3$. This emphasizes that a representative number of hazardous chemicals (162 fr. Table 2) require contact on anywhere from a couple of fingers to the entire hand in order to absorb the maximum dose allowed by the Threshold Limit Value. This knowledge can be translated first into a review of the pounds of a particular hazard (perhaps a volatile solvent) on hand at any given time, the manner in which it is used by a worker or in a process, and then a simple observation of actual, repetitive skin contact. Other questions and steps to remedy actual contact would proceed from those points of reference.

Potential exposure may be estimated by knowing what volume of a liquid is required to generate a concentration of (x)ppm in a defined cubic volume of space. A convenient volume is of course the cubic meter which is the volume limit for exposure sanctioned by OSHA and referred to as the average working air space. For this calculation the following formula may be used:

$$V_x = \frac{C \times MW \times 298 \times P \times V_T}{p \times 24.45 \times 760 \times 10^6} \quad [2.6.4]$$

This formula can be used to establish the liquid equivalent of the TLV or PEL value with which we may be concerned. The PEL value for Acetone is 1000ppm. Find the liquid volume required to produce that concentration in the workspace of the employee:
$C = \text{desired concentration (1000ppm)}$

$MW = \text{molecular weight of Acetone (58.08)}$

$p = \text{density of Acetone (.7899)}$

$V = \text{volume of tank, room or space (1000L/M}^3)$

$T = \text{temperature in degrees Kelvin (273)}$

$10^6 = \text{conversion factor}$

Solving:

$$V_x = \frac{58,080,000}{(0.7899)(24.45)\text{L}} \times 740 \times 298 \times 1
\times \frac{1}{760 \times 273 \times 10^6}$$

$$V = 3.19 \text{ ml}$$

The overall objective under the EPCRA mandate is to aggregate chemical substances in pounds and to compare these figures against Emergency Planning Thresholds. Aggregate amounts in pounds also have direct applications to health and safety through the conversion methods previously discussed and as a basis for converting liquid pound volumes to cubic feet of potential vapor by the following formula:

$$\text{Cu.ft per lb.} = \frac{\text{liters/mole} \times \text{grams/pound}}{\text{liters/cu.ft} \times \text{g / mole}} \text{[2.6.5]}$$

Liters per mole at 24.45 and grams per pound at 453.6 and liters per cubic foot at 28.32 form a constant of 391.61 at room temperature. This value can be divided by the molecular weight of any volatile substance to get the cubic feet of vapor. Thus, one pound of acetone ($MW = 58.08$) produces 6.74 cubic feet of vapor. Expanding the application: The amount of acetone held by a facility is a 55 gallon drum; the specific gravity of Acetone is .7899; total pounds on hand $55 \times 8.345 \times .7899 = 362.45$ pounds Acetone. If one drum is used per week in a parts washing operation, it is reasonable to consider the potential release of this very
volatile substance to be 362.45 pounds x 6.74 cu.ft. = **2443.54 cu.ft. of vapor** (Olishifski, 1988).

That amount of vapor would have to be attenuated to keep exposure levels below TLV values by sufficient amounts of ventilation or engineered evacuation at the site(s) of liquid release. General ventilation is often employed in facilities that are older and have not implemented forced ventilation. They rely on general ventilation relative to the size in cubic feet of the building and open doors or windows for fresh air sources. In the winter those types of ventilation can fail to supply an adequate ratio of fresh air to concentration of chemical vapor. In the example above the estimated release of about 2450 cu.ft. per week translates to 490 cu.ft per day pure vapor. In a building with dimensions of 100 x 50 x 10 ft. the volume space would be 50,000 cu.ft. Over the period of a day if approximately 8 fresh air exchanges occurred, in the building, then the cubic footage of attenuating space is 400,000 cu. ft. By this logic the PEL limit of 1000 ppm is equal to .001 decimal fraction per 1,000,000 cu.ft. In order to maintain a safe PEL level in our example building, the ratio of cu.ft. of vapor to the attenuating space must be below .001. The ratio of 490 cu.ft. pure vapor to 400,000 is .001 and technically complies. The extended application of industrial hygiene in this scenario would be an attempt to either increase the volume of fresh air input or the amount of liquid volume being used in order to broaden the range for a safe PEL limit.
In conclusion, the CMP inventory process for aggregating amounts of chemicals in pounds and characterizing products and chemicals using the factors of specific gravity, molecular weight, vapor pressure, percent volatility and other health factors, has direct application to health and safety estimates of exposure and absorption in processing scenarios. Coupled with an awareness of the Factors of Exposure and Human Factors engineering, discussed in Section 2.4 and 2.5, the CMP stands as a powerful complimentary tool to the overall goal of a safe and healthful workplace.
3.0 METHODOLOGY

3.1 Assembling Sources

The process of organizing and extracting information from MSDS’s requires the assembling of additional texts of reference for support in the data entry process. The CMP is designed to provide an existing database built on chemicals, identified by Chemical Abstract Numbers (CAS#), with physical and health hazard information provided by the National Fire Protection Association manual, the *Registry of Toxic Effects of Chemical Substances*, the *Hazardous Chemical Data Book* by Weiss, the *Dangerous Properties of Industrial Materials* by N. Irving Sax, and the United States Code of Federal Regulations. Additional on hand resources include the *Handbook of Chemistry and Physics* by Weast, *A Comprehensive Guide to the Hazardous Properties of Chemical Substances* by Pradyot Patnaik, and the *Fundamentals of Industrial Hygiene* by the National Safety Council. Information supplied by MSDS’s is challenged by the accuracy of these sources or information that is missing or incomplete on an MSDS regarding a particular compound may be extracted by researching this reservoir of information.

The other aspect of assembling sources of input data comes from the inventory process used in a facility. Regulations for Emergency Planning under EPCRA depend on estimates of “amounts on hand at any given time”
in order for Local Emergency Planning Committees (LEPC), the State Emergency Response Commission (SERC), and the local Fire Department to know ahead of time the degree of hazard associated with a facility’s chemical use or storage. That estimate per chemical or unique mixture must be in pounds. The CMP requires the following sets of data:

\[
\text{MWR}^* = \text{Maximum Weight Recorded for each Product with an MSDS}
\]

\[
\text{ETO} = \text{Estimated Time the Amount Ordered is on hand (in days)}
\]

\[
\text{MAXWT} = \text{Maximum Weight of Product on Hand Any Given Time}
\]

\[
\text{CHEMWt} = \text{Chemical Weight of any constituent by percentage compos.}
\]

\[
\text{CHEMavg} = \text{Chemical Average of the constituent over the period of time indicated by ETO.}
\]

\[
\text{AREA} = \text{Location in which each product is found}
\]

\[
\text{CONT} = \text{Container Code approved for Tier II reporting forms}
\]

*These and other acronyms or abbreviations used in the CMP are fully identified by the Field Heading Master List in Section I of Appendix A.

The maximum amount on hand any time becomes a function of the annual weight (MWR) \( \div 365 \) days \( \times \) the inventory turnover rate (ETO). Instead of just walking into a facility and seeing 2 drums of a product on hand and using that liquid volume to convert to pounds, the correct amount is garnered either from purchasing records or from experienced floor personnel. The 2 drum estimate might as easily be 4 based on established ordering patterns for the product. The result of the above formula is the MAXWT or amount on hand any given time in pounds. From this estimate
for a product, the percentages of constituents provided on the MSDS give the CHEMWT of each component on hand any given time. It is a simple matter of taking the MWR associated with any product times a percent composition to get the annual amount for a chemical associated with a particular product. Database calculations use the Product and Chemical estimates in pounds to aggregate each chemical substance throughout the entire system no matter where it occurs. This aggregated amount is use to compare that chemical against the threshold amounts that trigger reporting on Tier II Forms under EPCRA. The maximum amount for any unique mixture or chemical on hand that triggers a State reporting obligation is 10,000 pounds while for some counties, like Tulsa County, the reporting threshold is only 500 pounds. Separate Tier II Forms (see Section III of Appendix A) are filed for State and Local purposes. The location (AREA) and container code(s) (CONT) for each product is vital to information required on the Tier II and for profiling chemical usage by workstation within a facility.

3.2 Inputing Data

The data input process of the CMP is a per Product per MSDS operation. It is best visualized in the Product Inventory Report found in Section V of Appendix A. This report contains the basic contents of a database table called “Customdata”. This table forms the primary input
structure for 37 separate target fields for which data must be entered or calculated if available. The MSDS is the primary source of this data which is grouped into two of three major functions or categories found in the CMP: (1) Product Identification and (2) Hazard Identification

Each MSDS is identified by alpha or number or by particular facility code. The MSDS is the main source for product name, chemical constituents, CAS#, and physical state (by abbrev.). Values for estimated product weights are added as previously discussed including area and container information. The Hazard Identification function is a unique feature of the CMP. Data entry fields preceded by a "P" such as "P-FLM" are reserved for information provided by the MSDS for the product as a whole. The purpose is to provide hazard information (physical and chemical) that contrasts with the database information for each chemical or, in the absence of listed constituents, provides a default source of information for hazard assessment. In addition to physical and health hazards under 5 main EPA categories, product data for vapor number (P-VAP#), vapor pressure (VAPP), percent volatility (%VOLAT), temperature (codes for Tier II), decomposition (DECOMP), fire code (NFPA square on triangle data), personal protection equipment (PPE), and route of entry (TO for target organ) are sought in the initial scan of the Material Safety Data Sheet.
Upon completion of the Customdata table the organizational effort for MSDS’s and facility chemical inventory is largely complete. The data entry process includes all efforts required to find or extract product constituent information, discrepancies in product amounts submitted by the client, and the purging of duplicate MSDS’s or the revelation of missing documents.

3.3 Database Object Relationships

Database object relationships are briefly outlined here as representative of how data is organized from inception of the inventory process to the completed CMP manual. Tables are database objects that form the matrices for large blocks of information. Queries ask questions about information in tables in a specific manner. Queries provide the best opportunity to manipulate data in specific field and to perform calculations relative to each record that makes up a table. Reports consolidate the information created in queries and provide the best opportunity to obtain totals on number fields both for groups of related information such as a hazard category or simply to aggregate a specific chemical for its total pound weight for all products in which it occurs. Reports also provide the most flexibility for presenting data in a readable manner including the use of “unbound” cells that will accept text or numbers calculated by basic arithmetic functions built into the system. Modules add a complimentary
aspect to data management by expanding the programming capability of
the database system. In the CMP the calculation of CHEMAVG would not
be possible without expanded programming capability as commonly found
in programming languages such as Fortran or Basic. **Macros** allow
database objects such as tables, queries, and reports to be manipulated
among each other. Macros save time and make the operation of database
objects more efficient. For example, a macro can combine the printing
operation for several reports into one step. Simply run the macro like a
batch command and all the reports included in the macro set will be
opened, printed, and closed automatically. The exact structure of the
Chemical Management Program Database is not revealed in this discussion
as the structure pertains directly to the “confidentiality” of the CMP’s
commercial value and current use in fulfilling contracts.

3.4 Editing the Input

Completion of the Customdata table begins the editing function of the
CMP and is a vital process in the completion of the chemical inventory
reports. Through database applications the Customdata table is linked to
the primary data reservoir for chemical substances. A one-to-many
relationship is the foundation for the link, meaning that for every chemical
record in the database reservoir, only one primary chemical abstract number
(CAS#) exists. The Customdata table may repeat a CAS# as many times as a chemical occurs within a group of products for a facility. The editing function of this linkage is to correct both CAS# errors and chemical name errors that occur in a data input operation. In simple terms, the exact number of records entered into the Customdata table must match the output table of the linkage. That output table is the “MASTRTBL” discussed in the next section. Both the Customdata table and the Mastrtbl are open simultaneously and massaged for corrections until they agree exactly for number of records. At this point the Customdata data is saved in the code name of the facility and reserved for later use.

3.5 The “MASTRTBL”

The Mastrtbl, the source table for all queries and reports in the CMP, is the product of the linking of the Customdata table built on facility MSDS’s and other information and the chemical based primary data reservoir. It includes a complete alpha product listing with all descriptive field data, each chemical constituent, and all the hazard information available on that chemical. MSDS’s are assigned alpha or alpha-numeric values (A, B, C, D, etc.) in order to group tabs. This method of sorting allow reports such as the Product Index Report (Section 5 of Appendix A) to contain clear associations between the products listed and the MSDS of
origin. The Product Index Report is also placed in the front of each master
MSDS book(s) as a means of maintaining order in the MSDS system and
as a checkpoint for exact product-MSDS association.

The Masrtrtbble is also copied and recorded in the name of the facility for
which it was constructed as a permanent record of that inventory effort
for the year, and as the source of Tier II information provided to State and
local authorities. Both the Customdata and Masrtrtbble tables are cleared of
content after each inventory project to retain uniformity in the data input
process.

3.6 Printing Reports

The reports included in the CMP manual are supported by over 33
independent queries that manipulate information contained in the Masrtrtbl.
The finished product of the CMP contains reports in Sections III-VI of the
client manual. Reports are dedicated to the Tier II reporting function, the
chemical listing, product listing, and EPCRA Form R candidate report,
functions of the CMP. The “10,000 Pound Tier II Report”, the EHS Tier II
Report”, the “EHS Tier II Solid Qualifier” and the “500 Pound Tier II”,
reports list the chemicals selected in the CMP process for EPCRA threshold
reporting responsibilities. Thus, each Tier II form submitted to the State
and County has a source list for the chemicals reports. The Tier II forms allow submission of estimated chemical weights in wide ranges by code. The reports mentioned above give the exact amounts estimated in pounds including the number of times the chemical occurs. Chemicals are also qualified for a “solid” or article exemption. This exemption for chemicals or products that present no physical hazard because of the physical state, is applied with great scrutiny and generally applies only to products bought and resold by a company or permanent fixtures and improvements to a facility. The chemical and product reports are discussed in section 4.0 of this text.

3.7 Reporting Functions to Agencies

A primary function of the CMP is to provide Tier II reports to respective agencies in the name of a facility required by law to comply with the Emergency Planning and Community Right-To-Know Act (EPCRA) of 1986 also known as the nested Sara Title III Act under CERCLA. This is accomplished with the information compiled in the Aggregate Chemical Inventory Report, the supportive Tier II reports mentioned in Section 3.6 of this text, and through the Expanded Aggregate Chemical Inventory Report. The State Emergency Response Commission, the Local Emergency Planning Committee, and the Fire Department each get a Tier II form (form approved
by the Office of Management and Budget No. 2050-0072, revised EPA 1990). The local Fire Department and LEPC also receive a copy of the Aggregate Chemical Inventory Report to comply with the Chemical Listing requirement of EPCRA. A list of all the chemicals in a facility, a facility layout, and the Tier II Form are provided. At the State level, only the Tier II Form for chemicals at the 10,000 pound threshold are provided plus a "Emergency and Hazardous Chemical Inventory Coversheet". The coversheet gives facility identification information, NFPA placard codes, type alarm system, EPA Hazardous Waste ID# if applicable, and 1st and 2nd Emergency contact at the facility. The reporting obligation under EPCRA is due by March 1 for inventories in the previous year. According to EPCRA, facilities with on-site inventories that exceed the State or County thresholds for Emergency Planning are encouraged to implement programs of source reduction especially in the case of Extremely Hazardous Substances (section 302 of EPCRA), the 189 AIR Toxics under Section 313, or the set of Water Priority Pollutants targeted under the Storm Water Pollution Prevention initiative.

3.8 Finished CMP Manual

Appendix A contains a sample of a completed Chemical Management Program document. It is self contained with a Preface, Contents in Brief,
Introduction and a full set of reports and instructional material allocated to different sections of the manual. A permanent copy is provided for each client’s inter-facility use and as a record of compliance available for review by any visiting representative of a State or Federal Environmental Agency.
4.0 APPLYING THE OUTPUT

4.1 The Aggregate Chemical Inventory Report and Summaries

This report lists all chemicals reported by the facility or extracted from MSDS’s. It identifies each chemical by name and CAS#, lists it only once, and prints its aggregated weight in pounds on hand at any given time. It provides sample container and location codes for the chemical although some variation in those values is lost in the aggregation process. The complete information for container and location are provided in the Expanded Aggregate Chemical Inventory Report. Each reported chemical is identified for EHS or CERCLA status with a numerical value that describes the spill reporting threshold applicable to that chemical. The aggregate amount for the chemical can be easily compared with the thresholds under EHS or CERCLA columns. If the CHEMWT AGGREGATED meets or exceeds a threshold, an Emergency Planning Requirement is triggered.

Each listed chemical is reported for physical and health hazard information, NFPA code for pure chemicals, and demarcated by an “x” for regulation by six Acts of Congress. This report is found in Section IV. of Appendix A and functions as the basic support document for use by the local Fire Department and the LEPC in determining the chemicals stored, used or otherwise processed within a facility under their jurisdiction. At the end of Aggregate Chemical Inventory Report are two Summary reports
that provide summary totals for Groups of Hazards and for Regulatory Acts of Congress. The first report is the Facility Hazard and Regulatory Group Summary. Each row of values for a particular subject item gives a group aggregate total, and average percent composition among products, the number of times the hazard appears as a chemical, the maximum aggregate value for any member in the group, and the total annual weight for the group over the course of a year. In many cases the aggregate amounts for hazards of concern can be startlingly high and may encourage steps toward source reduction, or at least the reassessment of the role of each hazard in facility health and safety. In addition to the hazard and regulatory categories, the bottom of the report contains an aggregated amount in pounds for percent volatility among all chemicals in the facility. This amount may have important bearing on the predictions of air quality emissions or the probability of employee exposure to hazardous vapors.

The Second summary report is a Table of “Chemicals With Highest Totals in Hazard Groups”. This report isolates the chemical within each Hazard Group with the largest aggregated amount in pounds. This amount is shown as a percentage of the total Group Hazard Weight. In some cases as with the report sample in Appendix A, a certain chemical or compound may appear as the predominant hazard in more than one group. This particular reporting function of the CMP meets a primary goal in the
chemical management process of providing at-a-glance hazard identification information for preemptive planning purposes.

4.2 The Expanded Aggregate Chemical Inventory Report

This report was designed to provide maximum chemical information as it pertains to the activity of a chemical within the entire facility. Thus, each chemical is followed by a list of the products in which it occurs with the percentage of composition and other pertinent information including Tier II information for reporting purposes. At the bottom of each chemical section is a set of three True-False (-1 = True : 0 = False) values identifying a reporting requirement for an EHS, County, or State reporting threshold. EHS’s are reportable for any chemical identified as an EHS and whose aggregate amount on hand exceeds 500# or the chemicals reporting threshold, which ever comes first. County Tier II thresholds may be as low as Tulsa County’s 500# limit, or may not exist at all. The State level for Oklahoma is set at the Federal Limit of 10,000 pounds on hand any given time. The State can lower that threshold if it wishes.

The EHS and CERCLA emergency planning columns on the Aggregate Chemical Inventory Report are carried over in the right hand corner of each chemical section to alert facility management of emergency preparedness.
responsibilities. This report is found in Section IV.1 of Appendix A, immediately following the Aggregate Chemical Inventory Report.

4.3 The Product Index Report

This report as previously discussed is used as an index in the front of master MSDS file books required for maintenance by each facility and for access to all employees. It makes a particular product easy to locate and provides basic identification information, physical state-container-location information, and four physical parameters for spot hazard analysis. This report can assure that in each reporting year, existing MSDS’s are properly filed and recorded, and that new products introduced to a facility will be logically named and filed for updating the next year. This report preceeds the Product Inventory Report in Section V of Appendix A.

4.4 The Product Inventory Report

The Product Inventory Report is a condensed mirror image of information retrieved from the Material Safety Data Sheet. It identifies the product, profiles it by physical and health hazard, lists its constituents and the hazard information for each chemical provided by the master chemical database. The contrast of a product profile and a constituent(s) profile
reveals the content and quality of the information provided on the MSDS and subsequently narrows the margin of error in assessing the degree of risk associated with the products use in facility activities. In the event a product is a Trade Secret, has no listed constituents, or is a common mixture such as oil, or carbohydrate it will still have a hazard profile be it benign or otherwise.

4.5 The “Form R” Report

Section 313 of EPCRA is controlled by a requirement for annual completion of a toxic chemical release form for a list of toxic chemicals contained in subsection (c) of the Act. The Form R Report in Section VII of Appendix A is an evaluation of all chemicals identified as 313 candidates within the inventory of the facility. The report lists each chemical candidate or Group Compound such as Glycol Ethers, and further evaluates it for aggregate amounts that exceed the 25,000 pound threshold for chemicals manufactured or processed and the 10,000 pound threshold for chemicals otherwise used. Chemicals are exempted from aggregation if the De Minimis percentages are below 1% or .1% as provided with the list of 313 chemicals. The final aggregate amount for a Form R chemical candidate is then subject to engineering evaluation for the chemical(s) fate in facility process streams. Section 313 provides examples and
instructional material for completing the nine page Form R report and for estimating the fate of a chemical in process and waste streams using mass balance equations. The CMP cannot affirm the actual outcome of a toxic candidate but has been used in engineering evaluation procedures to reduce time and effort in elimination of candidates. This example exemplifies the unique value of the aggregating and identification functions of the Chemical Management Program.

4.6 Applications Beyond the Scope of the CMP

Sections 2.5 and 2.6 of this text discussed the relevance of chemical inventory information derived from the Chemical Management Program to aspects of health, safety and environmental considerations. The discussion emphasized simple relationships between weight-volume and volume-volume relationships of chemicals aggregated in pounds, identified for physical state, and characterized for the ability to change state and present a lung or skin absorption hazard. Those chemicals identified as toxic emission candidates under section 313 also become Clean Air Act candidates and can be preliminarily assessed in emission inventory projects. The limits of applying CMP data to other facility safety and health priorities reinforces the need of most facilities to incorporate other factors of exposure into the long term plans for health and safety assessment. On
the environmental side, the CMP is an indicator of the chemical points of
terest important to source reduction or pollution prevention initiatives in a
facility.

One of the main limitations to expanding the CMP may be an economic
barrier. It is common knowledge that approximately 80% of the economic
activity of the United States is generated by medium to small business
concerns. The budget for environmental compliance projects is usually
small and managed by personnel not completely trained in the finer areas of
chemical management and industrial hygiene. Though willing, the average
firm takes a step-by-step approach to compliance. The CMP’s role in
complying with EPCRA provides a level of comprehensive chemical
management that is still affordable to most companies. To extend its
capacities for inventory to the level of comprehensive health and safety
analysis at the “actual” release or exposure level, enters into another realm
of financial and time restraints. It is prudent to retain those applications of
the CMP as additions to its current scope of work with the idea that
facilities will graduate to higher and higher levels of environmental
compliance initiatives.
5.0 CONCLUSION

The Chemical Management Program is a logical framework for completing one of the most comprehensive set of environmental compliance standards promulgated by the Environmental Protection Agency. The CMP was designed to fulfill its compliance mission through an object oriented database with reproducible results for a host of manufacturing and non-manufacturing concerns that handle hazardous chemicals as a regular part of the business plan. The finished CMP document present in Appendix A and currently in use for the completion of Tier II reporting requirements under EPCRA is the fulfillment of that objective. Concurrent applications of the CMP have been discussed for actual value as a complimentary tool in the completion of "Form R" reporting requirements and in the completion of emissions inventories under the Clean Air Act. The CMP earns this role by virtue of its aggregating function for chemical weights, its identification of chemical relationships to multiple Acts of Congress, and the input of chemical physical and hazard information during the inventory process.

The CMP concept is a reflection of the sciences of Toxicology and Industrial Hygiene. It borrows from the sciences of information systems, chemistry, physics, environmental science, and environmental law while seeking to incorporate the value of research in human factors engineering.
and ergonomics into a better product to serve the community. It is
designed to be competitive by virtue of the economic benefit of the
information it provides in terms of the reducing the chemical research
efforts required under Section 313 of EPCRA or emission inventory
requirements under the Clean Air Act. In its completed state the CMP
produces a maximum amount of information for an initial compliance
effort, reducing or eliminating duplication of hazardous chemical inventories
common to numerous regulatory entities. The goal of providing source
documentation for multiple compliance requirements, is realized, at least in
part, and complimented by a flexible database design, capable of meeting
the challenges of extended health and safety applications.
REFERENCES


APPENDIX A

Appendix A to the Chemical Management Program (CMP) for the Emergency Planning and Community Right-To-Know Act has been deemed confidential and subject to review under the express written consent and supervision of the author. To review Appendix A to the CMP as a finished commercial product used in facility compliance, please write to the following address:

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