

**Tampereen teknillinen yliopisto  
Julkaisuja 411**

**Tampere University of Technology  
Publications 411**



**Sakari Halmemies**

# **Development of a Vacuum-Extraction Based Emergency Response Method and Equipment for Recovering Fuel Spills from Underground**

**Tampere 2003**

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Response Method and Equipment for Recovering Fuel  
Spills from Underground**

Thesis for the degree of Doctor of Technology to be presented with due permission for public examination and criticism in Auditorium RG202, at Tampere University of Technology, on the 21<sup>st</sup> of February 2003, at 12 o'clock noon.

**Tampere 2003**

ISBN 952-15-0974-0 (printed)  
ISBN 978-952-15-2556-8 (PDF)  
ISSN 1459-2045

## ABSTRACT

The most common type of accident is a fuel spill on the ground, which, depending on the circumstances can cause serious pollution of soil and groundwater. When fuel has seeped into the soil, there are not many effective response methods available for fire departments. The current practice mainly involves occasional pumping from ground pits, excavation and transportation of soil for treatment on landfills. Because fire departments are usually first to arrive at the scene of an accident, they could minimize the consequences of accidental fuel spills by implementing a first-responder system. A first-response remediation system should be not only effective but also relatively simple to implement and rapid.

The general objective of this study was to develop a vacuum-extraction based response method and equipment for fire departments to use in treating fresh fuel spills. The procedure developed enables volatile fuels to be recovered in both liquid and vapor forms, liquids can be separated from vapors, and vapors are destroyed by controlled incineration. The development work comprised experiments at four different scales:

1. Laboratory-scale column experiments were conducted to test the concept of the vacuum-extraction based response, the so-called Power Slurping Response (PSR), applied to fresh spill, and to provide data on the relative effects of different variables on yields when recovering fuels from different soil types.
2. Seepage and retention experiments were conducted in larger columns to determine seepage velocities of fuels in different soils and capacities of soils to retain fuels.
3. Large-scale tank experiments were to test extraction on a larger scale and to develop the response equipment.
4. Basin experiments were to test PSR at a field scale and to finalize the development of the response equipment. The main components were suction pipes with hoses, a collecting vacuum tank, an incinerator, and a temporary basin for collecting fuels as liquid.

The column experiments indicated that it was possible to recover up to 80 - 90 % of fresh fuel (diesel and gasoline) as liquids and vapors by vacuum suction, and hence to reduce fuel concentrations in soil (sand and till) to levels below its retention capacity. Increases in soil temperature, soil moisture content and air-flow rates resulted in greater recoveries. Moreover, periodic pulsing of compensation air increased fuel recoveries.

The experiments in larger columns indicated that the seepage velocity of gasoline in the vertical direction was about 5 times faster than for diesel fuel in gravely sand but only about 3 times faster than for diesel fuel in sandy till or peat. The differences can be attributed primarily to differences in viscosity. For a higher moisture content in gravely sand (twice the base value), the seepage velocity decreased by about 80 %. Seepage in the horizontal direction was over 5 times slower than in the vertical column. According to the column experiments the short-term retention capacity of gravely sand was 3.1 weight % for gasoline and 4.5 weight % for diesel fuel. Sandy till had even better short-term retention capacities: 5.8 weight % for gasoline and 6.6 weight % for diesel fuel.

The tank and basin experiment proved that vacuum extraction worked even at a larger scale. The yields varied between 55-82 % for gasoline and 30-40 % for diesel fuel from gravely sandy soil. In the basin experiments gasoline was extracted from gravely sand under both summer and winter conditions, and because of the applied vacuum, gasoline was recovered mainly as vapors. The basin experiments showed that application of a strong vacuum extraction to a fresh fuel spill for two hours immediately after leakage, makes it possible to recover the fuel that cannot be retained by the soil. In this way even groundwater pollution could be prevented, thereby avoiding the need for lengthy and expensive remediation efforts in the future. PSR is most suitable for gasoline-like fuels in permeable soils, where groundwater pollution can take place within a few hours. The SAMI response equipment was designed as a self-contained unit that can be transported readily to the accident site and which can be fully operational within approximately 15 minutes of the arrival of first response emergency services.

## **PREFACE AND ACKNOWLEDGMENTS**

The vacuum extraction based response method (PSR) and SAMI response equipment were developed during the SVE –project that was established for this purpose. The SVE –project was financially sponsored by the National Technology Agency of Finland, the Emergency Services College, the Pohjois-Savo Polytecnic, the Finnish Ministry of Environment, If Industrial Insurance Company Oy, VR-Group Oy, the Finnish Fire Prevention Fund and the Land and Water Technology Foundation Finland.

The development work was done mostly as a cooperative project between the Emergency Services College and the Pohjois-Savo Polytecnic, with additional involvement by the Geological Survey of Finland, Tampere University of Technology and Golder Associates Oy.

The experimental part of the study was carried out during 2001 – 2002 in Kuopio, at the Pohjois-Savo Polytecnic, and in the Department of Environmental Sciences in Microtecnia, at the Emergency Services College, both in the laboratory and the training field of hazardous materials, and at the landfill site in the municipality of Kuopio, managed by Jäte-Kukko Oy, in a research basin built for this purpose.

I am very grateful to my principal supervisor, Professor Tuula Tuhkanen of the Tampere University of Technology, for her advice and support during the work. She provided me with an interesting theme highly suited to applications by the emergency services. I also wish to thank Dr. John Gierke, of the Michigan Technological University, and Dr. Lauri Hietaniemi, of the Espoo-Vantaa Polytecnic, for their expert review of the final manuscript, and to Dr. Peter Sorjonen-Ward for language revision.

I would like to thank Professor Alex Mayer, of Michigan Technological University, for his expert advice on laboratory scale column experiments, and for acting as a co-author in the second article. I am very grateful to Dr. Keijo Nenonen from the Geological Survey of Finland for his versatile help during the project: soil samples, geological analyses, language checking and soil expertise. I am grateful for CEO Yrjö Lintu from Golder Associates Oy for his advice on SVE –technology, for arranging analytical services and supervision of construction of the research basin.

In addition, I want to thank Lic. Eng. Erkki Karttunen for managing the SVE –project, Mr. Ilari Seppä for giving good advice regarding response equipment, M.Sc. Anniina Määttänen for chemical analyses, Mr. Matti Pessi for assisting in building the experimental equipment, Mr. Juhani Tarhanen for analyses of fuel samples, Mr. Mikko Vuorinen for conducting laboratory scale column experiments, Mr. Mikko Parviainen for participating in the seepage and retention experiments, Lic. Eng. Risto Lautkaski for clarifying equations of vaporization, Mr. Arto Hyvönen for help during basin experiments and soil analyses, M.Sc. (eng.) Siri Gröndahl for participating in the column, tank and basin experiments and Mr. Mika Arffman for ideas in developing response equipment. Mr. Mika Tykkyläinen, Mr. Pekka Suomi and Mr. Yrjö Möttönen are to be thanked for construction of the SAMI response equipment.

Last but not least, I should like to thank my family, Kielo, Eelis, Samuel, Sofia and Linda, for their patience and encouragement during my work. Finally, thanks belong to God who has helped me in all my doings.

Sakari Halmemies

## ABBREVIATIONS

AS	Air Sparging
BTEX	Benzene, Toluene, Ethyl benzene, Xylenes
DPE	Dual-Phase Extraction
EPA	Environmental Protection Agency
ESC	Emergency Services College
GC	Gas Chromatograph
GSF	Geological Survey of Finland
ID	Inner Diameter
ISV	In-Situ Vitrification
LNAPL	Light Non-Aqueous Phase Liquid
LPG	Liquefied Petroleum Gas
LTTD	Low Temperature Thermal Desorption
MSD	Mass Selective Detector
MTBE	Methyl-Tertiary-Butyl-Ether
NAPL	Non-Aqueous Phase Liquid
OD	Outer Diameter
PCB	Polychlorinated Biphenyl
PE	Polyethylene
PHC	Petroleum Hydrocarbon
PSPT	Pohjois-Savo Polytechnic
PSR	Power Slurping Response
PVC	Polyvinyl Chloride
RIB	Rescue Information Bank
ROI	Radius of Influence
SAKU	Gasoline spill model SAKU
SAMI	SAMI response equipment
SSG	Scientific Software Group (SSG)
SVE	Soil Vapor Extraction
SVOC	Semi-Volatile Organic Compounds
TAME	Tertiary Amyl Methyl Ether
TVOC	Total Volatile Organic Compounds
USGS	U.S. Geological Survey
VOC	Volatile Organic Compounds

## LIST OF ORIGINAL PUBLICATIONS

- I Halmemies, S., Nenonen, K. and Tuhkanen, T. 2001. Development of chemical response methods for fire and rescue services. Geological Survey of Finland, Current Research 1999 – 2000. Edited by S. Autio. Special paper 31, 123 – 131, 2001.
- II Halmemies, S., Vuorinen, M, Mayer, A. and Tuhkanen, T. 2002. Vacuum based Recovery of Fresh NAPL Spills in Laboratory Scale Column Experiments. Groundwater Monitoring and Remediation, submitted 2002.
- III Halmemies, S., Gröndahl, S., Nenonen, K. and Tuhkanen, T. 2002. Estimation of the Time Periods and Processes for Penetration of Selected Spilled Oils and Fuels in Different Soils in the Laboratory. Spill Science & Technology Bulletin, submitted, 2002.
- IV Halmemies, S., Gröndahl, S., Arffman, M., Nenonen, K. and Tuhkanen, T. 2002. Power Extraction based Response Equipment for Acute Recovery of Fuel Spills from Soil. Journal of Hazardous Materials, submitted 2002.
- V Halmemies, S., Möttönen, Y. and Tuhkanen, T. 2002. Emergency Response of Accidental Fuel Spills by Power Slurping, Fire Engineering, submitted 2002.

## THE AUTHOR'S CONTRIBUTION

### Article I:

Sakari Halmemies wrote the article and is the corresponding author. He developed the concept for the emergency response method by studying the existing remediation methods. He chose vacuum extraction as a basis for response method and equipment to be developed for fire departments.

### Article II:

Sakari Halmemies wrote the article and is the corresponding author. He interpreted the results of the laboratory scale column experiments and participated in planning of the experiments.

### Article III:

Sakari Halmemies wrote the article and is the corresponding author. He interpreted the results and participated in the seepage and retention experiments. In addition, he developed a simple computer program, Gasoline spill model SAKU, by which he studied the effects of different parameters on the fate of gasoline spill on ground.

### Article IV:

Sakari Halmemies wrote the article and is the corresponding author. He interpreted the results and planned and conducted the tank and basin experiments where fuels were extracted from different soils. He participated in planning the key components of the emergency response equipment, namely a collecting vacuum tank and an incinerator.

### Article V:

Sakari Halmemies wrote the article and is the corresponding author. Based on the results of basin experiments, he drew up instruction procedures for fire departments to use when responding to accidental ground fuel spills. In addition, he participated in the planning and construction of the final SAMI response equipment.

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# 1. SUMMARY OF THE THESIS

## 1.1 Introduction

According to federal survey by the Finnish Ministry of the Environment, the largest proportion of accidents that impact adversely on the environment is due to industry (47 %), while the next most common cause is road and railway transportation (20 %) Väättäinen *et al.* (1995). In 1997 a total of 53.6 million tons of hazardous materials were transported in Finland. This amount is divided among the different modes of transportation as follows: 9.6 million tons by road, 8.4 million tons by rail, 34.2 million tons by sea and 1.4 million tons by air. Flammable liquids are the most commonly transported hazardous materials with a share of 75 % (LM 1999).

Typical transportation accidents are where a tanker overturns either on a road or on rails, resulting in a spill of fuel or other liquid. Most accidents occur during transportation of oil products, such as heavy fuel oil, diesel fuel, and gasoline (LM 1997). For example, fire departments responded to 440 chemical accidents in Finland during 1988-1992, and in 110 cases, fuel spills were involved (Emergency Services College 1996).

Because the current response measures of fire departments are mainly concerned with preventing the spread of chemicals and recovering the spilled chemicals, it is vitally important to develop methods by which fuels can be recovered from soil. Otherwise, light fuels such as gasoline can very easily penetrate into the soil and cause serious environmental pollution, especially if they contaminate groundwater. The more traditional oil products (diesel fuel and fuel oil) are only slightly water-soluble. The greatest threat to groundwater comes from unleaded gasoline with a partially water-soluble additive MTBE (methyl-tertiary-butyl-ether). Finnish unleaded gasoline can include up to 15 volume per cent of MTBE. Even at low concentrations, MTBE can make water undrinkable, and it can actually penetrate to the water table at a faster rate than the oil product itself. Therefore, MTBE poses a real danger to the typically shallow Finnish soils, where the water table is normally 2-4 meters below the ground surface (Airaksinen 1978).

Because fire departments/services take on average 15 minutes to arrive at the scene of an accident, they potentially could implement rapidly a suitable response action and thus minimize environmental consequences and even prevent pollution of the groundwater. Soil vapor extraction (SVE) has traditionally been used for remediation of soils polluted with fuels. It would, therefore, be very useful to develop an aggressive vacuum-extraction based emergency response method enabling fire departments to recover fresh volatile compounds (VOC) from soil. Such response methods and equipment are not currently available to emergency services, and so fuel spills are not addressed until after environmental effects have already become severe or extensive. In the most susceptible sandy soil types, gasoline can reach the groundwater in a few hours, during which time there are normally only fire fighters on the site. From a remediation perspective, these first hours following the spill are nevertheless the most critical for minimizing environmental impacts.

In-situ treatment technologies are important components of subsurface remediation efforts. However, the following necessary steps in the development are needed to lead them to accepted use: research and technology development, controlled field experiments, large-scale site trials, and accepted use (Gierke *et al.* 1997).

For PSR-method and SAMI response equipment, research and technology development was conducted during the laboratory-scale column experiments and the tank experiments. The research basin experiments corresponded to controlled field experiments, during which a lot of data and experience was acquired. The fact that we knew the fuel amount in the soil in the beginning of the extraction helped us to calculate the recoveries of fuel in the basin experiments; in most cases an amount of pollutant has to be estimated. In our case, when an emergency response method and equipment is to be

developed, large-scale site trials are impossible to arrange; the response method and equipment become tested at this scale first, when responding to an accidental fuel spill. The experience acquired from a real emergency response gives guidelines for further development of PSR-method and SAMI response equipment. Already now, PSR-method and SAMI response equipment can be considered suitable for emergency response of accidental fuel spills by fire departments, and its commercial application is in progress.

## **1.2 Objectives and structure of the thesis**

The general objective of this study was to develop an emergency response method and equipment to enable fire departments to recover volatile fuels from soils. The first phase of the study involved reviewing the literature to identify possible remediation technologies that could be utilized in an emergency response. In the experimental stage of the project, the most suitable remediation technology – vacuum extraction – was first tested in laboratory scale column experiments and then at larger scales in a tank and a research basin. The specific aims of the present work were to:

1. Review the existing remediation methods for polluted soils to determine which technology could be adopted and utilized in an emergency response method.
2. Determine the applicability of vacuum extraction for recovering fresh fuels from different soils, so that fuel is recovered in both liquid and vapor form and to document the effect of different parameters (soil type, soil temperature, airflow rate and soil moisture content) on recovery efficiencies of the different fuels.
3. Measure seepage velocities and short-term retention capacities of gasoline and diesel fuel in different soil. Develop a simple computer-aided gasoline spill model (SAKU) to estimate vertical transport (vaporization, retention and groundwater pollution) of gasoline spill on the ground.
4. Develop a strong vacuum-extraction based emergency response method. As a result, the Power Slurping Response (PSR) was developed and tested both in tank and basin experiments, where fuel yields were determined under varying conditions.
5. Develop and test full-scale response equipment (SAMI) for emergency use by fire departments. Its main components are perforated suction pipes, a collecting vacuum tank, and an incinerator. Operating procedures for SAMI response equipment were developed to obtain optimum efficiency, and to consider safety aspects when dealing with flammability and explosion risks.

The results are published in a compendium of five articles referred to in the text by the Roman numerals (I-V). Part 1 of the thesis summarizes the content of the compendium. Part 2 reviews the literature concerning existing response methods and physical remediation technologies, with particular emphasis on methods where the use of vacuum extraction has been studied in detail.

Two diploma students at the Tampere University of Technology and two engineering students at Pohjois-Savo Polytechnic, Kuopio, also participated in this research; some of the results of this work have been reported in the theses of Mikko Vuorinen and Siri Gröndahl of the Tampere University of Technology, and Mikko Parviainen and Mika Arffman of Pohjois-Savo Polytechnic, Kuopio.

## **1.3 Materials and methods**

### **1.3.1 Review of remediation methods**

Information on existing remediation methods was found through an internet search using the keywords *soil remediation* and *soil vapor extraction*. On the web pages of the United States Environmental Protection Agency (U.S. EPA) there was an exhaustive description of the different remediation methods and their respective advantages and disadvantages (U.S. EPA 1993a, U.S. EPA *et al.* 1993b,

U.S. EPA 1995 a-c, U.S. EPA 1996 a-b). Reports based on actual remediation projects done were also used. (Envirocon 1993, Buzzelli *et al.* 1997). EPA's VISITT –database includes both vendor information (204 pcs) and descriptions of the cleaning techniques (325 pcs), as well as information on treatment costs (U.S. EPA 1997). Finnish publications on environmental technology were also used (Jeltsch 1990, LaGrega *et al.* 1994, Mroueh *et al.* 1996, RIB 1999, Veriö 1991, YM 1994).

### 1.3.2 Soil and fuel types used

The column, tank and basin experiments were conducted with gravely sand and sandy till. The sandy till was chosen since it is the most common soil type on Finnish roadsides (Keijo Nenonen, Geological Survey of Finland, personal communication, 29 Oct 2001). Geotechnical analyses of soil samples were made by the assistance of GSF and concerned the following: dry bulk densities were determined by the Proctor method (GSF 2000), grading curves by sieving and by Sedigraph equipment (Rantamäki *et al.* 1997), hydraulic conductivities by a constant pressure method (GSF 2000), and moisture contents by a heating cabin (GTK, 2000). Dry bulk density and hydraulic conductivity of the gravely sand were 2.04 g/cm<sup>3</sup> and 2.60(10)<sup>-5</sup> m/s, respectively, and for the sandy till they were 2.16 g/cm<sup>3</sup> and 6.36(10)<sup>-7</sup> m/s, respectively. Residual moisture contents of the soil samples were 6.3 weight-% for gravely sand and 8.3 weight-% for sandy till.

In addition to gravely sand and sandy till, seepage and retention experiments in peat was also performed. For peat, the dry bulk density was 0.326 g/cm<sup>3</sup>, the moisture content was 150 weight-% and hydraulic conductivity of 3.6(10)<sup>-5</sup> m/h. The soil was packed into the columns to 90 % of the maximum dry bulk densities of the soils in order to correspond to the natural tightness (gravely sand and sandy till 1.64 kg/dm<sup>3</sup> and 0.29 kg/dm<sup>3</sup> for peat).

The fuels used were 98 Octane gasoline containing MTBE and diesel oil (winter type) produced by a well-known Finnish oil company. These fuels were analyzed before use by a GC, so as to enable monitoring changes in concentrations of some water-soluble compounds.

### 1.3.3 Laboratory scale column experiments

Two identical columns were used in parallel for the laboratory-scale PSR experiments. The columns were manufactured of PVC-plastic (length 150 mm and internal diameter (ID) of 44.5 mm) fitted with a perforated aluminum suction pipe (ID of 4.2 mm), positioned upright in the center of the column. The soil was saturated with a fuel (26 – 46 g) by the aid of a vacuum of 97 kPa (Nenonen 1980), after which a vacuum pump was started to recover fuel both as liquid and vapor form. Liquid was first trapped by a glass bottle and hydrocarbon vapors after that by another trapping bottle including hexane. The liquid recovery bottle was weighed and sampled periodically in order to determine the mass of liquids recovered with time. In the same way, a sample was taken periodically from the trapping liquid for analysis. The duration of each experiment was two hours. Each experiment was repeated, so that the number of replicate runs was four.

A water bath was used to control the temperature of the column between 7 – 50 °C (± 2 °C) and the column inlet was connected to a moisturizer to maintain a stable moisture content. The air flow rate was adjusted by needle valves and flow meters with an accuracy of ± 10 ml/min. Polyurethane was mainly used as tubing material. Fuel type (gasoline and diesel oil), soil type (gravely sand and sandy till), soil temperature (7, 25 and 50 °C), soil moisture content (6 and 12 weight-%) and air flow rate (500, 1000 and 2000 ml/min) were used as variables. The highest temperature of 50 °C was used to study an effect of possible soil heating to recoveries.

#### **1.3.4 Seepage and retention experiments in pilot scale columns**

Seepage velocities and short-term (2 h) retention capacities were determined using a PVC transparent pipe with an ID of 10 cm and a length of 0.9 m as a column. The column was aligned and kept in the vertical position. One liter of fuel colored with an indicator (Oil Red EGN, Aldrich Cat. No. 23,411-7) was poured into the top of the vertical column and seepage penetration depths were registered as a function of time, utilizing a measuring tape fixed outside the column wall. Seepage velocities resulting from spills were then determined on the basis of these data. Retention capacities of soils were determined during the first two hours.

Additional column experiments were conducted to study spreading of gasoline, both in the vertical and the horizontal directions, in 1.5-m long columns (ID 10 cm) packed with gravely sand. Seepage velocities and penetration times were determined, where a constant layer of gasoline (thickness of 1.5 cm) was maintained over the top level of the column.

The wall effect on seepage rate in the columns was minimized by covering the inner walls of the columns with a silicone wax (Hochvakuumfettmittel, Wacker-Chemie GmbH). The parameters measured were fuel type (gasoline and diesel fuel), soil type (gravely sand, sandy till and peat), and also soil moisture content (6 and 12 weight-%) for gasoline in gravely sand. The results were compared with studies available from the literature.

Preferential flow is a term used to describe soil systems where water flows through a fraction of the available wetted area. Gravity-driven preferential ('fingered') flow can occur even in relatively homogenous soils (Wojick *et al.* 1998). Hillel and Baker (1988) proposed that flow fingers developed when water is supplied to the surface of a highly-conductive soil at a rate less than the conductivity of the soil at the water-entry suction. In a case of accidental fuel spill, conditions differ from this so much (i.e. the application rate is so much higher than the fluid conductivity) that preferential flow could be unimportant (John Gierke, personal communication, 10 Jan, 2003).

#### **1.3.5 Gasoline spill model SAKU**

The advective transport process was studied more thoroughly, because it seems to be dominant (Looney *et al.* 2000, LaGrega *et al.* 1994) in vulnerable sandy soils during accidental spills. By combining equations of advection (Weaver, 2001), retention (Eiling *et al.* 1994) and vaporization (Yellow Book 1979, Johnson *et al.* 1990a), a simple calculation model was developed to predict seepage velocities for gasoline spills in permeable soils. This Excel-based calculation model (SAKU) was developed as a tool to estimate the effects of changing weather and geological conditions on the advective transport of gasoline in permeable soils as a result of accidental fuel leaks. The purpose of this model is to simulate worst case scenarios for emergency fuel spills by assuming only vertical spreading (gradient equals one). On the basis of initial values for the size of the spill (volume of gasoline and pool diameter), weather conditions (atmospheric temperature, wind speed) and geological values (hydraulic conductivity, hydraulic gradient, distance to groundwater) the model can estimate the progress and fate of the gasoline spill in three parts: vaporization, retention of the soil, and groundwater pollution. In addition, the model can inform fire departments of the approximate time they have available to prevent pollution of the groundwater.

The results have been compared with the data from a Swedish spreading model available to the Emergency Response Services (RIB 2001) and with the On Site formulas used by the EPA (Weaver, 2001).

#### **1.3.6 Tank experiments**

The development of the vacuum-extraction based response equipment started with the tank experiments, where the existing response equipment of Emergency Services College (ESC) were

partially utilized (a peristaltic vacuum pump, a vacuum barrel, and anti-static hoses). The main function of this equipment combination was to suck spilt chemicals from the ground surface to a recovery container (barrel) with the aid of a vacuum generated by a peristaltic pump. This concept provided the basis for developing of a vacuum-extraction based response equipment for subsurface recover of volatile hydrocarbons. In addition to the equipment mentioned above, a perforated pipe (OD of 34 mm) was sunk into the soil in the tank experiments.

The stainless steel tank was filled and packed with 500 l of gravely sand. There was a valve at the bottom of the tank by which a possible penetration of water or fuel through the soil could be checked. Water (30 l) or fuel (10 l) was poured onto the soil and allowed to seep for 5-15 minutes before starting vacuum-based extraction. Tank experiments were to give information on how parameters, such as soil moisture, water or fuel type, use of compensation air, immersion depth and covering of soil will effect recovery of water or fuels from the soil. The first four experiments concerned water, and the next four experiments concerned fuels, gasoline and diesel fuel. At the end of the fuel extractions (duration 50-120 minutes) soil samples of 100 g were taken for analysis from different depths (10, 25 and 40 cm) and at different radial distances.

### **1.3.7 Basin experiments**

To be able to simulate extraction for larger fuel spills and to avoid wall effects, a large concrete research basin (9 m x 9 m x 3 m, 243 m<sup>3</sup>) was built at a landfill site in the municipality of Kuopio. The basin was divided into two equal parts, the first of which was filled and packed totally with sandy till (2.8 meters depth). The second part was filled firstly with 1.5 meters of sandy till and overlain by 1.3 meter of layer of gravely sand as far as the surface. Soils were packed with a shaker in an attempt to achieve natural porosity conditions. The parameters were soil type, fuel type and ambient temperature. The basin was divided into four equal partitions (4.5 x 4.5 m), into three of which 100 l of fuel was poured.

The response equipment used in the research basin differed from that used during the tank experiments (a new collecting vacuum tank, a new incinerator, and new perforated pipes). In fact, it was actually developed as experience was gained during the course of the tank experiments. The recovery container was constructed from a steel tank and included inlets that made it possible, if needed, to both fill and discharge the container during extraction. The loss of vacuum during discharge of the container was to be prevented by maintaining a certain level of liquid. The container was filled from the top by a perforated spiral pipe that channelled liquid to the bottom of the container. To prevent excess vaporization of recovered liquid, extracted vapors were able to escape from holes of spiral before entering the bottom of the container.

The other equipment developed for the basin experiments was a burner, a barrel (filled partially with water and possessing a clear plastic pipe level indicator), and a torch nozzle equipped with a “flame arrester” (flame retardant material). Vapors had to penetrate the water layer and filter of non-combustible material before reaching the atmosphere for burning. Hence, there was a three-stage security system to prevent flame burning backwards to the vacuum container: water, flame arrester, and overpressure. The burner was equipped with a bunsen burner for ignition of combustible vapors.

At the beginning, 100 litres of fuel (98 octane gasoline or diesel fuel) was poured onto the soil over an area of about 1m<sup>2</sup>, where it formed a pool. The pool was allowed to seep and vaporize during 15 minutes, after which recovery commenced. If there was any liquid remaining in the pool, it was first recovered by pumping, prior to starting the vacuum-based extraction from the soil. Before commencing the fuel extraction, the spill area was covered with extinguishing powder to prevent the possibility of ignition. After that the perforated suction pipe was sunk into the soil by aid of a combustion engine driven shaker (Cobra mk 1, Atlas Copco). Two compensation air pipes were already in place, having been earlier sunk diagonally at the distance of 1.3 m from the suction pipe, to

a depth of 0.8 m. To extend the suction effect, the spill area was covered with polyethylene plastic sheeting.

After all connections were made, including grounding of the equipment, extraction was started by switching the vacuum pump on. A vacuum in the recovery container varied between 10 – 40 kPa. Fuel was extracted with the aid of vacuum into the recovery container and vapors were released into the atmosphere or trapped by the burner. The burner was used only for gasoline. In the gasoline experiments, concentration and volume of gasoline vapors were measured during extraction. In addition, the dispersion of gasoline through the soil was monitored by taking soil vapor samples. After all experiments, soil samples were taken and analyzed to determine yields and efficiencies of the response actions. Four different extraction experiments were made: three in summer and one under winter conditions. Recovery of gasoline and diesel oil from gravely sand was studied under summer conditions, but two other experiments were conducted for gasoline: recovery from sandy till under summer conditions and recovery from gravely sand under winter conditions.

### **1.3.8 Analytical and measuring methods**

Before commencing the column experiments, both the gasoline and diesel oil were analyzed by a gas chromatograph. During laboratory scale column experiments, liquid samples were taken to analyze BTEX- compounds and to some extent MTBE. The same compounds were analyzed at the end of the experiment from soil. Compositions of fuels were analyzed by a gas chromatograph (Hewlett Packard 6890) connected to a mass selective detector MSD (Hewlett Packard 5973).

At the end of the tank experiments, residual fuel concentrations in the soil were determined by samples analyzed by a gas chromatograph (Shimadzu GC-17A, FID detector), though without analyzing the different components of the fuels. Concentrations of gasoline vapors were monitored by an explosimeter (combustible gas indicator, Auer Ex-Ox-Meter II).

In basin experiments concentrations of BTEX (benzene, ethyl benzene, toluene, xylenes), MTBE (methyl tertiary butyl ether), TAME (tertiary amyl methyl ether) and TVOC (total volatile organic compounds) of gasoline were analyzed from retrieved vapors and soil samples after extractions by a gas chromatograph (HNU-311), following procedures and standards based on EPA requirements (U.S. EPA 1990). Soil samples were analyzed according to standards EPA-5021, EPA-8015B, EPA-8021B and ISO-11423-1. The analysis was based on gas chromatography with double columns and head space technology (HSGC-FID). Vapors of gasoline were also monitored by an explosimeter (combustible gas indicator, Auer Ex-Ox-Meter II) parallel with GC.

## **1.4 Results**

### **1.4.1 General**

The development phase of the project began with designing an emergency response method based on existing remediation and response methods. After building the response equipment based on the design, experiments were conducted at four different scales to test the effectiveness of the equipment and response procedure. To facilitate comparisons between the different extraction experiments, boundary conditions were kept as constant as possible. The soil types and their tightness were the same in all the column and tank experiments. However, in the basin experiments, the type of gravely sand (hydraulic conductivity  $1.2(10)^{-7}$  m/s) and sandy till (hydraulic conductivity  $8.2(10)^{-8}$  m/s) differed from the types used earlier ( $2.60(10)^{-5}$  m/s for the sand and  $6.36(10)^{-7}$  m/s for the till). The same types of fuels were used both in column and basin experiments.

The results are grouped into five categories: a) design and development of response method b) efficiencies of fuel recovery in three different scales c) seepage velocities and retention capacities d) gasoline spill model SAKU, and e) a vacuum extraction based response method (Power Slurping Response) and equipment (SAMI response equipment) suitable for fire departments., which was the ultimate goal of the development work.

#### **1.4.2 Design and development of a response method (Article I)**

Based on the existing remediation procedures, various physical methods were considered most likely to be capable of emergency response. Biological methods were rejected as too slow and chemical methods as too complicated to implement and expensive. Amongst the physical methods, vacuum extraction and a controlled burning were chosen for further development, because both are potentially appropriate for response actions by fire departments. A traditional vacuum extraction (SVE) is, however, too slow for emergency response and incapable of rapidly removing high concentrations and volumes associated with a fresh fuel spill, which is why the traditional SVE process needed significant modification for deployment as an emergency response. The primary modification was a dramatic increase in the extraction rate so as to flush the contaminated zone with more air and simultaneously using a high vacuum so as to enhance the volatilization of the contaminant. In addition, free-product recovery was included because applying a strong vacuum and air flow rate to a fresh spill would likely lead to recovery of liquid phase contamination.

#### **1.4.3 Efficiencies of fuel recoveries (Article II, and IV)**

##### *Article II*

The results of the laboratory-scale column experiments showed that the concept of using vacuum extraction for fresh volatile hydrocarbons works very well. Unlike in traditional SVE, fuels can be recovered both in liquid and vapor forms. The column experiments indicated that by vacuum it was possible to recover 80-90 % of fresh fuel as liquids and vapors, and so to decrease the initial fuel concentrations of the soil on an average from 14 -15 weight-% down to 2.0 weight-% and 3.7 weight-% for gasoline and diesel oil, respectively. This means that by a strong vacuum applied to a fresh fuel spill it is possible to recover enough fuel that the amount left behind is less than the retention capacity of the soil (determined in retention experiments). Gasoline is recovered more easily than diesel because it is more volatile and less viscous than diesel. Because of the vacuums (20-50 kPa) formed in the till, gasoline was mainly vaporized and liquid recoveries were accordingly much smaller than for diesel. Despite this, total recoveries of gasoline were still in excess of 90 %, even from till. Increases in soil temperature, soil moisture content, and air flow rate will also improve fuel yields. Moreover, it was found that compensation air given as pulses improved recoveries of fuels slightly (maximum 10 %) irrespective of fuel and soil type (Kirtland *et al.* 2000).

##### *Article IV*

In the tank experiments, extraction was tested in a larger scale. The first experiments were conducted with water and no contamination. The best recoveries were 20 %. Estimated amount of vaporization at a vacuum of 40 kPa was 10 %. The best estimated recoveries of fuels were 70 % for gasoline and 40 % for diesel fuel. Maximum liquid recoveries were only 24 % for gasoline and 19 % for diesel. Because of the presence of a vacuum, gasoline was recovered mainly as vapors; the highest gasoline concentration measured by an explosimeter was 9 volume-%. Air flow rates were not measured, but on the basis of residual fuel concentrations (0.2-1.5 weight-%) analyzed from soil samples after the extraction, the total recovery of gasoline was estimated to 70 %.

The gasoline was mainly recovered in vapor form due to its high volatility at ambient temperatures. The vapor pressure curve of gasoline indicates that at 15 °C and at an absolute pressure of 60 kPa (40 kPa of vacuum), as was the case in the tank experiment, 50 % of the gasoline occurs as vapors. The increase in vaporization is due to the increase in air flow caused by the vacuum. The same conclusions

were reached as before: fuel recovery is enhanced where soils have higher moisture contents, the moisture preventing the penetration of the contaminant into the soil. In addition, an important outcome of the tank experiments were the development of a vacuum collecting tank and an incinerator that were to be used in the basin experiments.

In the basin experiments allowed field scale testing of the PSR –method. Experiments mainly involved gasoline, which was recovered from gravely sand under both winter and summer conditions. For summer conditions, the total estimated recovery was about 82 % and for winter conditions about 55 %. The gasoline recovery from sandy till was only 40 %, but because of vaporization, only 30 % of the initial amount of gasoline remained in the sandy till. Gasoline recoveries were calculated in two ways: firstly, on the basis of the liquid and vapor recoveries, and secondly, on the basis of the measured residual gasoline concentrations of the soil (0.6 – 1.5 weight-%) and the assumption that the remainder of the original amount of gasoline was recovered. The proportion of gasoline recovered as vapors was determined by multiplying about 50 % of the air flow rates, 300 - 500 m<sup>3</sup>/h (air flow velocities, 9-14 m/s, measured by a Pitot –pipe) with gasoline concentration, 2 – 6 volume-% (measured by an explosimeter and a gas chromatograph). Diesel fuel spill was extracted only under summer conditions from the gravely sand, and then only 30 % was recovered, mainly as liquid directly from a pool. This again demonstrated that it is much easier to recover the less viscous and more volatile gasoline than diesel fuel.

Compensation air pipes were used when extracting gasoline, which seemed to improve the suction effect. In the gasoline experiments, soil concentrations could be lowered below short-term retention capacities of the soil (3.1 weight-% for gravely sand and 5.8 weight-% for sandy till). In this way it was possible, during the first two hours, to stop spreading of gasoline and to prevent pollution of groundwater, thus providing time for further remediation of polluted soil in order to attain acceptable levels of contamination (0.08 weight-% for gasoline and 0.5 weight-% for oils, Moen *et al.* 1986). In addition, on the basis of basin experiments, both the collecting vacuum tank and incinerator were reconstructed for the final SAMI response equipment.

#### **1.4.4 Seepage velocities and retention capacities (Article III)**

Seepage velocities were determined in vertical soil columns and showed that the highest velocities occurred for gasoline in gravely sand with a moisture content of 6 weight-% (13 m/h). When the soil moisture content was doubled (12 weight-%), the seepage velocity was reduced by a factor of four to 3 m/h. The seepage velocity of gasoline was about 5 times faster than for diesel fuel in gravely sand (2.8 m/h), but about 3 times faster than for diesel fuel in sandy till or peat. The difference can be attributed largely to differences in viscosity. Experiments conducted with a longer sand column indicated that seepage of gasoline in the horizontal direction is over 5 times slower than vertically.

Retention capacities were measured for two hours (short-term retention). Sandy till had a retention capacity 1.5 – 2 times greater than gravely sand. Peat (absorbent) had the best retention capacity of the soils tested, retaining up to 62 – 90 weight-% of its own mass or 24 – 32 volume-% of its gasoline and diesel content, respectively. The change of moisture content from 6 to 12weight-% had only a minor effect on retention, but a great effect on seepage, as noted earlier. Gravely sand and peat can hold about 30 – 45 % more diesel fuel than gasoline, but in sandy till the difference is only about 10 %. Sandy till and peat were able to retain the total amount of fuel. The short-term retention capacities determined here are from 2-6 times greater than long-term retention values reported in the literature (LaGrega *et al.* 1994; Nikkarinen 1995).

#### **1.4.5 Gasoline spill model SAKU (Article III)**

The Excel-based calculation model is easy to use for rough estimation of the transport of gasoline spills in permeable soils. The model was also used to study the effects of varying different parameters

on vaporization, seepage velocities, retention and the time for an acute response to prevent pollution of groundwater. Case studies presented in the article III illustrate the use of the model.

Vaporization rates increase exponentially with ambient temperature (the vapor pressure curve of gasoline was determined for the temperature range  $-40$  to  $+40$  °C). The vaporization rate from the gasoline pool is about 6 times greater at a wind speed of 10 m/s than at a wind speed of 1 m/s. A doubling in diameter of the gasoline pool will increase the vaporization rate nearly fourfold. The longer the time that gasoline remains ponded at the ground surface without seepage, the more of it will vaporize, even all of it in ideal cases. The degree of vaporization will therefore be inversely proportional to hydraulic conductivity. Hence, when hydraulic conductivity decreases by an order of magnitude, the amount of gasoline vaporized increases ten fold. In soils with a hydraulic conductivity smaller than 1 darcy ( $1 \cdot 10^{-5}$  m/s) most of the gasoline pool can vaporize.

Seepage velocities are directly proportional to the hydraulic gradient and conductivity, e.g., when either decreases by a factor of ten, the seepage velocity of gasoline decreases accordingly by an order of magnitude. The greater the diameter of a pool, the greater will be the retention capacity of the spill zone, for example, if the pool diameter exceeds 25 m, a gasoline spill of 20 m<sup>3</sup> on the ground will be totally retained, providing that the water table is at least 3 m below the ground surface. Depending on the hydraulic gradient, coarse sandy soils with a hydraulic conductivity over 10 darcies may require very rapid response measures. Fine sands, silts and clays are not as susceptible to permeation of spilled fluids and can in most cases resist gasoline seepage. The time frame for an acute response to prevent pollution of groundwater could be as little as few hours for typical Finnish shallow soils.

#### **1.4.6 A vacuum extraction based response method (Power Slurping Response) and equipment (SAMI response equipment) suitable for fire departments (Article V)**

Based on the results of different experiments, a vacuum extraction based response method (Power Slurping Response, PSR) and equipment (SAMI response equipment) was developed for fire department emergency use, since existing SVE –equipment and incinerators were not designed specifically for circumstances prevailing in an emergency situation. The idea of extracting freshly spilt fuel from permeable soils in both liquid and vapor form, with the aid of a high vacuum, separating them, and destroying the vapors by controlled incineration, has turned out to be a practical response method for adoption by emergency services.

SAMI response equipment extracts volatile hydrocarbons using a partial vacuum (even at pressures of 0.8 bar) via perforated steel suction pipes (OD of 25 mm) into a collecting tank, where vapors and liquids are separated by a special cyclone principle. Vapors are drawn from the top of the collecting tank by a vacuum pump into an incinerator for a controlled combustion, whereas entrained liquid and solid particles are discharged from the bottom of the collecting tank to a temporary basin. Power slurping is to be continued for as long as the vapors are burning (about  $> 1$  volume-%). After that, extraction will be continued from other suction pipes. Several suction pipes (usually about 6) are sunk into the soil by means of an auger and hammer. In order to maximize a yield, it is useful, by lifting perforated pipes in holes, to find the right depth for pipes for the extraction (a yield of each suction pipe could be determined by using explosimeter to measure the fuel concentration of vapors from a sample valve of the incinerator). The generation of vacuum peaks, by throttling a valve between a suction pipe and the collecting tank for several minutes, has been found to keep holes clear in the suction pipes and to improve the yield.

The Finnish Emergency Services College will commence training of SAMI response equipment during 2003. Production of SAMI response equipment by a Finnish company also commenced during 2003.

## 1.5 Discussion

### 1.5.1 Fuel extraction

In the laboratory scale column experiments, the maximum recovery of NAPL as liquid occurred within the first 10 minutes of extraction. Even if, because of the vacuum used, gasoline yields in basin experiments were recorded mainly as vapors, the highest vapor concentrations (27 volume-%) was almost halved during the first hour. This indicates that the most the mobile phases in gasoline can be rapidly recovered to prevent spreading, thereby providing additional time for further remediation. In an emergency response, this kind of rapid lowering of fuel concentrations to values below the retention capacity of the soil is essential for minimizing the consequences of acute fuel spills.

The column experiments indicated that NAPL recovery was better at elevated temperatures (50 °C), when even water condensate was collected. At a large-scale extraction, fuel recovery could be improved for example, by pumping compressed super heated steam into the soil through pipes similar to the suction pipes. Heating will both increase vapor pressures and lower the viscosity, thus enhancing recover, even of heavier hydrocarbons, such as diesel fuel and fuel oils. The increased recovery is greater than the effect reducing the viscosity has on propensity for vertical migration. Because there is less pore space available for the NAPL in wet soil than in dry soil, fuel recovery is better when extracting from wet soil. In addition, as noticed during the column experiments, vacuum pressures were higher when recovering from soil with a high moisture content, which resulted in a better yield. Compensation air was fed in pulses into the columns to generate vacuum, and this was also found to increase NAPL recovery. In the basin experiments, the same effect was achieved by causing vacuum peaks (even 80 kPa) in the collecting tank by throttling the closing valve between a suction pipe and the tank. This pulsing also helped to keep the holes of the suction pipe open.

### 1.5.2 Seepage velocities and retention capacity

Because of the back pressure caused by saturated soil, natural seepage velocities are much slower than those determined in the column experiments, where fuel was discharged directly at ambient room pressure. Even though silicone wax was used to prevent wall effects, wall effects could not be totally eliminated. In addition, soil types in nature are never so homogenous as was the case in our column experiments. In heterogeneous soils, as is the case in reality, seepage velocities are much lower. In addition, vertical and horizontal spreading occurs simultaneously in nature, which effectively reduces vertical seepage velocities. Therefore, even in situations that potentially present the highest risks, such as a gasoline spill on shallow sandy Finnish soils, fire departments have at least a few hours to prevent pollution of the groundwater. Because of the slow seepage velocities of fuels in sandy till and peat, accidental fuel leaks in these environments do not constitute such critical hazards to groundwater. However, water soluble compounds including BTEX and specially MTBE can reach the groundwater via infiltration of capillary water, even if no gasoline itself reaches the groundwater (Fetter, 1999).

The retention capacities determined in this work primarily concern the first two hours (short-term), after which changes are very slow. Long-term retention could be 5-6 times smaller, but a rapid reduction in fuel concentration of the soil below its short-term retention capacity will stop further spreading of fuel through the soil and provide extra time for applying recover measures, which is the main purpose of an emergency response. The basin experiments indicated that the highest residual concentrations of fuel after the two-hour extraction period were about 50% of the values for long-term retention. Acceptable residual concentrations could still be 5-10 times smaller than long-term retention values (0.08 weight-% for gasoline and 0.5 weight-% for oils); the same type of method (PSR) and equipment (SAMI) could be utilized in this remediation phase as well (Moen *et al.* 1986).

Comparison of seepage velocities and retention capacities with values reported in the literature is very problematic, because in most cases detailed data on soil type is lacking. For example, a soil type classified as sand can have a hydraulic conductivity that varies by up to two orders of magnitude.

However, both the seepage velocities and the retention capacities determined are very useful when comparing different soil types, because the circumstances of the column experiments were kept as constant as possible.

### **1.5.3 Gasoline spill model SAKU**

The gasoline spill model SAKU was developed as a simple tool for roughly estimating the progress and the transport of a gasoline spill on ground under a worst-case scenario. It does not however, consider the potential effect of varying soil moisture content. Vaporization from a pool can be significant for gasoline-like volatile liquids, much more than vaporization from the soil. On the other hand, extensive vaporization takes place only so long as the pool stays on the ground surface without seepage. The model accordingly calculated a time for vaporization on the basis of a theoretical thickness of gasoline layer on the ground and the seepage velocity. In most cases the theoretical thickness is greater than in reality because spilt gasoline makes a pool with a typical thickness of 1.5 cm (Yellow Book 1979).

In one accident case scenario, the model gave results similar to those based on a spreading model used by Swedish fire departments (RIB) and the U.S. EPA. In fact, there are not many models capable of estimating spreading when tens of cubic meters of fuel has been spilt. Most models simulate small-scale incidents that take place as a result of leakage in underground fuel tanks. Swedish fire departments and rescue organizations use RIB for a rough estimate in emergency cases. The EPA provided only a set of equations. The validity of the SAKU model is highly dependent on the initial values, their reliability and other assumptions made. Changes to values for hydraulic gradient and conductivity have a very great effect on seepage velocity.

### **1.5.4 Results of basin experiments**

The greatest uncertainty concerns recovery of gasoline vapors, their concentrations and especially their flow rates. There were differences in concentrations measured by different instruments, but except for the winter test, only concentrations measured by the gas chromatograph were used. Only a few soil samples from different depths could be taken for analysis, and the residual gasoline concentrations were estimated on this basis. Recovery of gasoline vapors was estimated in two ways: by measuring vapor concentrations and air flow rates, and by measuring residual gasoline concentrations in the soil after extractions. Despite some uncertainties in the recovery results, this does not detract from the usefulness of the PSR-equipment and its potential in emergency responses.

MTBE is a very volatile compound and vaporizes from gasoline very easily. On the other hand, MTBE has the greatest water solubility of the compounds analyzed (ca. 4 weight-% at 20 °C) and its water solubility increases when temperature decreases; at 0 °C it is ca. 8 weight-% (OVA-instructions 1999). In wet soils, and especially in Finnish-like shallow soils, it is possible that MTBE may contaminate groundwater via infiltration of capillary water through a zone of residual gasoline, even if no liquid gasoline reaches the water table (Fetter, 1999).

### **1.5.5 Comparison of SVE and PSR**

There are some factors that make recovery with PSR much more effective than traditional soil vapor extraction. First, a fuel spill is normally weathered when using SVE, but PSR can be applied to a fresh spill, so that fuel is recovered both in vapor and liquid form. Also note that the recovery capacity of SVE is about 5-8 times more effective for a fresh spill than for a spill that has been in the soil for a longer time (Johnson *et al.* 1990b). Vacuums used during PSR (even at 80 kPa) are several times higher than typical vacuums during SVE (20 kPa). High recoveries of PSR (even 100-200 l/h) are short-term values that decrease very rapidly after most of the free phase has been extracted.

Application of PSR will not remove the need for further remediation (for example by SVE), but it will shorten it and make it easier, so that benefits are environmental and economical. Moreover, PSR-equipment can also be used after an emergency response phase during the remediation phase, as even weak vapors, less than the lower explosive limits, can be burned by LPG, if needed.

## 1.6 Conclusions

Of the remediation technologies studied at the beginning of this development project, a vacuum extraction based method appears best suited for acute emergency response by fire departments when recovering fresh fuel spills from the soil. On the other hand, hydrocarbon vapors are most easily destroyed by a controlled incineration.

The laboratory-scale column experiments indicated that vacuum extraction is suitable for recovering fresh fuels from different soils, yielding both liquid and vapors. An elevated soil temperature was observed to increase fuel recovery, but this factor was not explicitly incorporated in the design or development of the response equipment. The influence of air flow rate on recovery has, however, been optimized by maximizing the vacuum used. In addition, the positive effect of vacuum peaks on recovery was utilized in the vacuum extraction based response method by periodic valve throttling.

The seepage velocities determined are useful when comparing migration of fuels in different soil types. A vacuum-extraction can be considered effective, because in most cases the residual fuel concentration of the soil was below the corresponding two-hour retention capacity. A simple gasoline spill model SAKU is suitable for a fast and cursory estimate of the fate of a gasoline spill on the ground in terms of vaporization, retention and groundwater pollution.

A strong vacuum-extraction based emergency response method, termed Power Slurping Response (PSR), was developed and tested in both tank and basin experiments, where it turned out to be useful. The PSR-method is best suited for the recovery of gasoline-like volatile hydrocarbons from permeable sandy soils. Its application to more viscous and less volatile liquids, such as diesel fuels, is more limited, but could be improved by combining the PSR-method with soil heating and pumping compressed air into the soil. The SAMI response equipment was developed for emergency use of fire departments. It utilizes a high vacuum based extraction procedure combined with controlled burning in an incinerator. The SAMI response equipment is self-contained and can be set up and operational in approximately 15 minutes. It can be easily transported to an accident site, for example, by towing behind a standard 4WD vehicle or a fire engine. The PSR-method will be added to the operational guidelines of fire departments for responding to chemical accidents. The Finnish Emergency Services College begins training with SAMI response equipment during 2003.

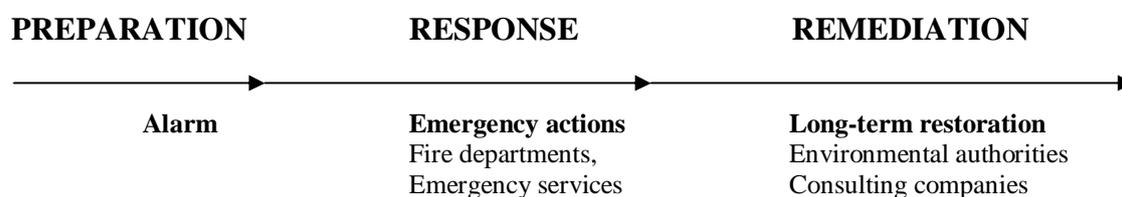
The SAMI response equipment was developed specifically and is most suited for emergency responses of acute fuel spills from the soil. As a future project, PSR-method could be enhanced by hydrogen peroxide or ozone treatment of the soil, carried out immediately after the extraction. This kind of oxidization treatment, typical at a remediation sites, could significantly reduce residual fuel concentrations in the soil and accelerate the recovery of a soil contaminated by accidental fuel spills.

## 2. REVIEW OF THE LITERATURE

### 2.1 Response of chemical accidents

#### 2.1.1 General

The time needed to deal with chemical accidents by emergency services can be divided into three phases (Figure 1): *preparation*, *response*, and *remediation* (Statens forurensningstilsyn 1991). The preparation stage starts when an accident occurs and ends when a fire department arrives at the accident site ready for commencing response actions. The total time of preparation is thus the sum of the time it takes to alarm the fire department, for the fire department to arrive at the scene of the accident and get ready to implement response actions. The response time is the time it takes for the fire department to take the necessary response actions that do not involve the remediation: rescuing of victims, stabilization of the situation and elimination of the major hazards (explosion, flammability, and toxicity). The remediation time is the time needed to remove contamination to a level that minimizes immediate risk to the environment and restore the accident site to its former state. Depending of the nature of contamination, this stage can take years.



**Figure 1.** The different phases of response to a chemical accident

The aim of this study is to eliminate the time lag between response and remediation by expanding the traditional response actions of fire departments to the remediation side, while at the same time maintaining or enhancing their capabilities.

There are two basic methods for mitigation of hazardous material incidents: physical and chemical. Physical methods of control involve any of several processes or procedures to reduce the area and volume of the spill, leak, or other release mechanism (Tokle 1992).

#### 2.1.2 Physical methods of response

Physical methods of hazard mitigation include: a) absorption, b) covering, c) dikes, dams, diversion, and retention, d) dilution, e) overpacking, f) plug and patch, g) transfer, h) vacuuming, i) vapor dispersion, j) vapor suppression (blanketing), and k) venting (Tokle 1992). *Absorption* is the process by which materials hold liquids through the process of wetting. *Covering* refers to a temporary form of mitigation for radioactive, biological, and some chemical substances. *Dikes, dams, diversion, and retention* refer to the use of physical barriers to prevent or reduce the quantity of liquid flowing into the environment. *Dilution* refers to the application of water to water-miscible hazardous materials to reduce concentrations. *Overpacking* is most commonly implemented by using an oversized container. *Plug and patch* are used to reduce or temporarily stop the flow of materials from small holes, rips, tears, or gashes in containers. *Transfer* refers to the process of moving a liquid, gas, or some forms of solids, either manually, or by pump, or by pressure transfer, from a leaking or damaged container or tank. *Vacuuming* refers to recovery of hazardous materials by utilizing a vacuum. *Vapor dispersion* is used to disperse or move vapors from certain materials. *Vapor suppression or blanketing* refers to the reduction or elimination of vapors emanating from a spilled or released material through the most

efficient method or application of specially designed agents (for example an aqueous foam blanket). *Venting* is a process that is used to deal with liquids or liquefied compressed gases where the risk of explosion or mechanical rupture of the container or vessel is considered likely (Tokle 1992).

### **2.1.3 Chemical methods of response**

Chemical methods of mitigation include: a) adsorption, b) controlled burning, c) dispersion, surface active agents, and biological additives, d) flaring, e) gelation, e) neutralization, f) polymerization, g) solidification, h) vapor suppression, and i) venting and burning (Tokle 1992). *Adsorption* is a process in which a sorbate (hazardous liquid) chemically adheres to a solid sorbent surface. *Controlled burning* or controlled combustion is considered a chemical method of control. *Dispersion, surface active agents, and biological additives* are certain chemical and biological agents that are used to disperse or break up the materials involved in liquid spills. *Flaring* is a process that is used with high-vapor-pressure liquids or liquefied compressed gases for the safe disposal of the product. *Gelation* is a process of forming a gel of a hazardous material. *Neutralization* is a process of applying acids or bases to a spill to form a neutral salt. *Polymerization* is a process in which a hazardous material is reacted in the presence of a catalyst, of heat or light, or with itself or another material to form a polymeric system. *Solidification* is the process whereby a hazardous liquid is treated chemically so that a solid material results. *Vapor suppression* can be achieved with the use of solid activated materials to treat hazardous materials so as to effect suppression of volatilization. *Venting and burning* involves the use of shaped charges to vent the high vapor pressure at the top of the container and then with additional charges to release and burn the remaining liquid in the container in a controlled fashion (Tokle 1992).

### **2.1.4 A summary of the existing response methods**

In a case of fuel spill on the ground – the most common type of chemical accident, fire departments normally use response methods to prevent spreading of fuel on the ground or on water. Suitable physical response methods could be blanketing, pumping from pools, absorbing, dams, and plugging of a sewage network. From chemical response methods, a controlled burning could be useful, if risks for fire spreading can be eliminated. However, an effect of burning is restricted to fuel on the ground, not to fuel deeper in the soil, because there is insufficient oxygen at depth. When fuel has seeped into the soil, there are not many effective response methods available, because they all concentrate on mitigation at the ground surface, but not below ground. There could be occasional pumping from ground pits, but because fire departments lack response methods suitable for recovering fuels from soils, remediation methods are applied by service companies at a later stage, by which time contamination may have spread significantly (Helsingin Sanomat 1999; Rescue 1999; Karlsson *et al.* 1999). According to current practice, it often means expensive excavation and transportation of polluted soil for treatment on landfills.

## **2.2 Remediation methods for polluted soils and groundwater**

There are many innovative treatment technologies for cleanup of soil and groundwater contaminated with hazardous materials or petroleum waste. For example, VISITT is a database developed by the Technology Innovation Office (TIO) within the Office of Solid Waste and Emergency Response of the United States EPA and lists 325 different technologies (U.S. EPA 1997). Remediation methods can be divided into four classes: a) chemical, b) physical, c) thermal, and d) bioremediation.

From an emergency point of view physical and thermal methods could be utilized as an acute response. That is why they are studied in more detail. Chemical methods are too expensive and complicated. Chemical methods requiring matching of treatment agent with the contaminant, careful control of the delivery and recovery, and maybe even permitting. Bioremediation methods are too slow for emergency use, not to mention the detailed characterization work that is required to optimize

the conditions for microorganism growth and substrate utilization. Ideally, a recovery method should require no characterization work and readily use materials likely to found at the site.

### **2.2.1 Physical methods of remediation**

Physical methods of remediation include: a) soil vapor extraction, b) air sparging, c) dual-phase extraction, and d) physical cleanup of the groundwater.

#### *Soil Vapor Extraction (SVE)*

Soil vapor extraction, also known as soil venting or vacuum extraction, is an in-situ remedial technology that reduces concentrations of volatile constituents in petroleum products adsorbed to soils in the unsaturated (vadose) zone. This technology relies on applying a vacuum to the soil matrix to create a negative pressure gradient that causes movement of vapors toward extraction wells. Volatile constituents are readily removed from the subsurface through the extraction wells. The extracted vapors are then treated, as necessary, and discharged to the atmosphere or re-injected to the subsurface, where permissible (U.S. EPA 2002).

#### *Air Sparging (AS)*

Air sparging is an *in situ* remedial technology that reduces concentrations of volatile constituents in petroleum products that are adsorbed onto soils and dissolved in groundwater. This technology, which is also known as in-situ air stripping and in-situ volatilization, involves the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapor phase. The air is then vented through the unsaturated zone. Air sparging is most commonly used together with soil vapor extraction (SVE), but it can also be used with other remedial technologies. When air sparging is combined with SVE, the SVE system creates a negative pressure in the unsaturated zone through a series of extraction wells to control the vapor plume migration. This combined system is called AS/SVE (U.S. EPA 2002).

#### *Dual-Phase Extraction (DPE)*

Dual-phase extraction, also known as multi-phase extraction, vacuum-enhanced extraction, and bioslurping, is an in-situ technology that uses pumps to remove various combinations of contaminated groundwater, separate-phase petroleum product, and hydrocarbon vapor from the subsurface. Extracted liquids and vapor are treated and collected for disposal, or re-injected to the subsurface (where permissible). Dual-phase extraction systems can be effective in removing separate-phase product from the subsurface, thereby reducing concentrations of petroleum hydrocarbons in both the saturated and unsaturated zones of the subsurface. Dual-phase extraction systems are typically designed to maximize extraction rates; however, the technology also stimulates biodegradation of petroleum constituents in the unsaturated zone by increasing the supply of oxygen, in a manner similar to bioventing (U.S. EPA 2002).

#### *Physical cleanup of the groundwater*

Polluted groundwater can be purified with traditional methods used by water treatment plants, including oil separation, precipitation, flotation, sedimentation, the use of hydrocyclone, filtering and membrane technologies (Childs 1985; Jeltsch 1990).

### **2.2.2 Thermal methods of remediation**

Thermal methods of remediation include: a) low-temperature thermal desorption, b) incineration, c) vitrification, and d) steam stripping.

#### *Low temperature thermal desorption (LTTD)*

Low-temperature thermal desorption (also known as low-temperature thermal volatilization, thermal stripping, and soil roasting, is an ex-situ remedial technology that uses heat to physically separate

petroleum hydrocarbons from excavated soils. Thermal desorbers are designed to heat soils to temperatures sufficient to cause constituents to volatilize and desorb (physically separate) from the soil. Although they are not designed to decompose organic constituents, thermal desorbers can, depending upon the specific organics present and the temperature of the desorber system, cause some of the constituents to completely or partially decompose. The vaporized hydrocarbons are generally treated in a secondary treatment unit (e.g., an afterburner, catalytic oxidation chamber, condenser, or carbon adsorption unit) prior to discharge to the atmosphere. Afterburners and oxidizers destroy the organic constituents. Condensers and carbon adsorption units trap organic compounds for subsequent treatment or disposal. (U.S. EPA 2002)

#### *Incineration*

Incineration is normally carried out as an ex-situ method, where polluted soil is excavated and fed into an oven. Most organic compounds, including halogenated hydrocarbons, are decomposed at temperatures above 1300-1400 °C to carbon dioxides, water, and acid vapors (U.S. EPA 1993a). An in-situ method of incineration is controlled burning, which has been used by fire departments for destroying flammable liquids spilt on the ground on remote districts (Helsingin Sanomat 1992).

#### *Vitrification*

An in-situ vitrification (ISV) technology is designed to treat soils, sludges, sediments and mine tailings contaminated with organic and inorganic (metals and radionuclides) compounds by destroying organic and immobilizing the inorganics. This process uses electrical current to heat (melt) and vitrify the soil in place. Organic contaminants are decomposed by the extreme heat into simple gases, which then rise through and escape from the molten soil. Inorganic contaminants are trapped within the molten soil, which cools and solidifies into a glassy monolith (Richardson 1995). This is a very expensive technique and could cause explosion hazards for explosive materials like gasoline.

#### *Steam treatment*

Steam treatment or stripping is an in-situ method, used to improve the efficiency of soil vapor extraction. Hot steam (130-180°C) is injected into polluted soil to remove volatile organic compounds (Hilberts *et al* 1986). By steam injection it is possible to conduct much more heat energy than by using water or air (Udell 1996).

### **2.2.3 Remediation methods suitable for an emergency use**

There are a number of essential requirements for response methods and equipment suitable for fire departments. First, response equipment must be readily available. Second, both the response method and equipment chosen must be simple enough and rapid to use. Third, the response has to be an in-situ method. Forth, the response method and equipment have to be suitable to dealing with a potentially large volume of contaminant both above and below ground.

SVE has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum products, and its principle is useful for an acute response where the vadose zone has been polluted with volatile hydrocarbons, such as gasoline. However, the traditional form of SVE is too slow and complicated for standard emergency use. On the other hand, circumstances in an acute response of fresh fuel spill differ considerably from those when extracting a weathered spill from the soil. Concentrations of hydrocarbon vapors are so high (even exceeding 20 %) that they cannot be treated traditionally: by activated carbon beds or a catalytic oxidation. Carbon can be used to treat almost any kind of vapor stream but is only economical for very low emission rates (< 100 g/d). Catalytic oxidation units have good destruction efficiencies (typically 93-96 %), but they are only appropriate for vapor concentrations less than 0.8 %. More concentrated vapors can cause catalyst bed excursions and melt-down. Vapor combustion units are suitable for an emergency use, because they have both good destruction efficiencies (> 95 %) and can accept high vapor concentrations. In fact, they become less economical only, when vapor

concentrations decrease below 1 %, in which case burning will not take place without the use of an additional fuel such as propane (U.S. EPA 1993a).

Both AP, DPE and physical clean-up techniques for groundwater are used in situations where groundwater is already polluted. The main premise for an emergency response is to prevent groundwater pollution by a strong vacuum-based extraction. The idea of using DPE to pump both liquid and vapors, and to use high vacuums is useful for an emergency response. However, in the power slurping response (PSR) – the emergency response method to be developed, fresh fuel is extracted from vadose zone both as liquid and vapors. In the worst case, when the fuel has already reached the groundwater, suction pipes could be sunk down to the level of the groundwater, in which case the response method would in fact resemble DPE.

LTTD is an ex-situ method and not suitable for an emergency use, because it needs an excavation of polluted soils. Moreover, the equipment is too complicated and relatively difficult to obtain. Incineration can be considered as the best way to destroy hydrocarbon vapors, providing that the incinerator is mobile and easy to use. As long as there is no risk for fire spreading, the controlled burning of flammable liquids on ground is a good way to decrease pollution of soils. Gasoline fires will burn at about 30 cm/h; a spill of 3 mm deep burns in about 37 seconds (Peterson 2001). However, burning will only take place on the ground level and the subsurface must be treated by other means.

ISV needs a very special knowhow and equipment which makes it impossible to be utilized by fire departments. Heating of the soil by steam treatment has been considered as beyond the scope of the PSR –method. However, a steam heating could be suitable to be added to PSR –method, so that even diesel-like less volatile hydrocarbons could be recovered.

#### 2.2.4 Remediation costs

Excavation and treatment is a rather common way to remediate soil polluted as a result of fuel spill. Another common way is to use in-situ or ex-situ SVE, weeks or even months after the spill. Below are summaries of four cases where remediation costs were provided for chemical accidents that happened in the Northern countries.

(1) About 30 t of hexane-heptane leaked into the soil on a railway yard. Thousands of tons of polluted soil was excavated and transported away. In-situ SVE was used for the contaminated soil that was left after excavation. The remediation costs totaled over 120 000 euros (Väätäinen *et al.* 1995).

(2) Seven railway tankers derailed and got fire. About 80 tons of raw oil leaked into the soil. About 7500 m<sup>3</sup> of polluted soil was excavated and treated by the following means: SVE, stabilization and compost piles. The remediation costs totaled over 1 million euros (Helsingin Sanomat 1999; Rescue 1999).

(3) As a result of a turnover of a tanker with a trailer 19 m<sup>3</sup> of gasoline leaked into a gravelly sand soil. A total of 270 t of polluted soil was excavated and transported away for treatment. Also the groundwater was polluted to some extent. The remediation costs were totally 200 000 – 400 000 euros (Räddningsverket 1999).

(4) In an industrial area 10 m<sup>3</sup> of MTBE leaked into the soil. The polluted soil had to be excavated away manually. The remediation costs were totally 83 000 euros (Väätäinen *et al.* 1995).

Table 1 gives average costs of the most typical remediation methods.

**Table 1.** Average costs of typical remediation methods (U.S. EPA 1997; Mroueh *et al.* 1996; YM 1994) .

Remediation method	Remediation costs	
Excavation and transportation (50 km)	10	euros/ m <sup>3</sup>
Compost piles	104	euros/ m <sup>3</sup> of soil
Soil vapor extraction	21	euros/ m <sup>3</sup> of soil
Incineration	42	euros / m <sup>3</sup> of soil
Physical purification of groundwater	50	euros / m <sup>3</sup> of water

### A hypothetical example on remediation costs

A total of 30 m<sup>3</sup> of gasoline leaks into sandy soil and spreads on an area with forms a pool with a radius of 10 m. The distance to the groundwater is 3 meters. The hydraulic conductivity is 1 darcy (similar to a silty of fine sand). It is summer and the air temperature is 20 °C and there is a steady breeze (wind speed of 5 m/s). According to gasoline spill model SAKU, 24 % of the gasoline will vaporize, 71 % will be retained in the unsaturated zone, and about 5 % (1500 liters) is continuing its way towards the groundwater.

#### A. Excavation and ex-situ treatment (incineration)

##### Scope of pollution

Amount of polluted soil:  $(\pi \times r^2 \times h) = (\pi \times 10^2 \times 3) \text{ m}^3$  942 m<sup>3</sup>

Amount of undrinkable groundwater, if only 100 liters of unleaded gasoline reach the groundwater:

- content of MTBE 11 %
- water solubility of MTBE at groundwater 6,5 %
- EPA's taste limit 20 ppb of MTBE  $(0.1 \times 0.11 \times 0.065 / 20 \times 10^{-9}) \text{ m}^3$  35 750 m<sup>3</sup>

##### Remediation costs

Polluted soil : (942 x 52 ) euros 48 984 euros  
 Polluted water: (35 750 x 50) euros 1 787 500 euros  
**Totally 1 836 484 euros**

#### B. PSR (Power Slurping Response)

By a rapid response started within an hour after the spill, pollution of the groundwater can be prevented, because it takes over 15 hours before gasoline reach the groundwater (gasoline spill model SAKU). It means that the amount of gasoline (1500 l) that is not retained can be recovered by PSR - method. It is probable that because of an effective vacuum extraction a spreading of gasoline can be restricted to a depth of 1 m.

##### Scope of pollution

Amount of polluted soil:  $(1/3 \times \pi \times r^2 \times h \times \rho) = (1/3 \times \pi \times 10^2 \times 3 \times 1.64) \text{ m}^3$  515 t  
 Amount of polluted water: none

##### Remediation costs

PSR by a fire department (8 hours) 3 333 euros  
 The final remediation could be completed by SVE  
 Polluted soil: (314 x 21) euros 6 594 euros  
**Totally 9 927 euros**

In our hypothetical example, the remediation costs of polluted soil decreased to about 1/5, which complies with the concept that mere SVE is about 5 – 8 times more effective for a fresh spill than for a weathered one. Because pollution of the groundwater was prevented, the total remediation costs decreased to less than 1 % otherwise. With good reason can be claimed that, in a case of accidental fuel spill described above, PSR -method carried out by SAMI response equipment repays its investment cost (about 40 000 euros) very fast, maybe even in one incident, and decreases remediation costs in most cases to only a tenth or less of what it would cost to clean the soil that has been contaminated for a longer time. It is worth mentioning that the PSR-method is not so superior compared to conventional techniques, but a recovery of fresh fuel is so much more effective than recovering in a case of weathered spill.

## 2.3 Soil vapor extraction (SVE)

### 2.3.1 General

Because PSR represents an application of traditional soil vapor extraction, SVE is described in greater detail, in order to clarify the requirements and limitations of the technology.

### 2.3.2 Factors affecting on SVE

There are three main factors that control the performance of a venting operation: a) vapor flow rates through the unsaturated zone b) the chemical composition of the contaminant and c) the flow path of carrier vapors relative to the location of the contaminants (Johnson *et al.* 1990b).

#### *Vapor flow rate*

A vapor flow towards a single well in an unsaturated zone of uniform thickness (assuming homogenous, isotopic properties and steady flow), impermeable on the top, can be calculated mathematically by Equation 1 (Johnson *et al.* 1990b).

$$\frac{Q}{H} = \pi \cdot \frac{k}{\mu} \cdot \frac{[1 - (P_{atm} / P_w)^2]}{\ln(R_w / R_I)} \quad (1)$$

where,

- Q/H = flow rate per unit thickness of well screen [cm<sup>3</sup> /s]
- k = soil permeability to air flow [cm<sup>2</sup>] or [darcy]
- μ = viscosity of air = 1.8 x 10<sup>-4</sup> [g/cm-s] or 0.018 [cP]
- P<sub>w</sub> = absolute pressure at extraction well [g/cm-s<sup>2</sup>]
- P<sub>atm</sub> = absolute ambient pressure ≅ 1.01 x 10<sup>6</sup> [g/cm-s<sup>2</sup>]
- R<sub>w</sub> = radius of vapor extraction well [cm]
- P<sub>I</sub> = radius of influence of vapor extraction well [cm]

The largest uncertainty in flow rate calculations will be die to the air permeability value k, which can vary by one to three orders of magnitude (Johnson *et al.* 1990b). Wet soils are not as permeable as dry soils, which is why the performance of SVE is reduced. Stratification of the soil, in general, has a great effect on vapor flow rates. Table 2 shows typical values of different soil types.

**Table 2.** Grain size, porosity, permeability and conductivity of different soil types (Facta 2001, Lojander 1985, Johnson *et al.* 1990b)

Soil type	Grain size	Porosity	Air permeability		Hydraulic conductivity	
	[mm]		n [%]	k [cm <sup>2</sup> ]	K [cm/s]	& k <sub>f</sub> [Darcy]
gravel	2 - 20	25 - 40		10 <sup>-6</sup> - 10 <sup>-3</sup>	10 <sup>-1</sup> - 10 <sup>2</sup>	10 <sup>2</sup> - 10 <sup>5</sup>
sand	0,2 - 2	30 - 40		10 <sup>-9</sup> - 10 <sup>-5</sup>	10 <sup>-4</sup> - 1	10 <sup>-1</sup> - 10 <sup>3</sup>
fine sand	0,02 - 0,2	40 - 50		10 <sup>-10</sup> - 10 <sup>-6</sup>	10 <sup>-5</sup> - 10 <sup>-1</sup>	10 <sup>-2</sup> - 10 <sup>2</sup>
clayey sand	0,002 - 0,02	40 - 60		10 <sup>-12</sup> - 10 <sup>-9</sup>	10 <sup>-7</sup> - 10 <sup>-4</sup>	10 <sup>-4</sup> - 10 <sup>-1</sup>
clay	< 0,002	60 - 75		< 10 <sup>-12</sup>	< 10 <sup>-7</sup>	< 10 <sup>-4</sup>

It may be noted that vapor flow rate increases by 15 % when the diameter of an extraction well increases from 10 to 20 cm (Johnson *et al.* 1990b). Radius of influence (ROI) of single extraction wells can vary from 6 to 45 m (Hiller *et al.* 1989). For a 10 cm diameter vacuum well, the vapor flow rate prediction decreases by 20 % when ROI increased from 15 to 61 m. (Johnson *et al.* 1990a). The most commonly used vacuums are 23 kPa, corresponding to a vapor flow rate of 5 600 l/min (Goldfarb *et al.* 1994).

#### *Chemical composition of the contaminant*

The maximum vapor concentration of any compound (mixture) in extracted vapors is its equilibrium or “saturated” vapor concentration, which can be calculated from knowledge of the molecular weight of the compound (or mixture), vapor pressure for the relevant soil temperature, residual soil contaminant composition, and Raoult’s law and ideal gas law according to Equation 2 (Johnson *et al.* 1990b).

$$C_{est} = \sum_i \frac{x_i P_i^v M_{w,i}}{RT} \quad (2)$$

where,

- C<sub>est</sub> = estimate of contaminant vapor concentration [mg/l]
- x<sub>i</sub> = mole fraction of component i in liquid-phase residual (x<sub>i</sub> = 1 for single compound)
- P<sub>i</sub><sup>v</sup> = pure component vapor pressure at temperature T [Pa]
- M<sub>w,i</sub> = molecular weight of component i [mg/mole]
- R = gas constant = 8.314 [J/ (K mole)]
- T = absolute temperature of residual [K]

When using Equation 2 it is assumed that the total vapor concentration exceeds 200 mg/kg (200 ppm). If a site is chosen for remediation, the hydrocarbon content in soil typically exceed 500 mg/kg (Johnson *et al.* 1990b). Table 3 compares fresh and weathered gasoline.

**Table 3.** Comparison of fresh and weathered gasoline (Johnson *et al.* 1990b)

Type of gasoline	Mole weight (g/mole)	Vapor pressure, 20 C (kPa)	Vapor concentration (mg/l)
fresh	95	34	1300
weathered	111	5	220

The vapor pressure of each component at the operating temperature is calculated from values of the vapor pressure at 20 °C and the boiling point at 100 kPa (T<sub>B</sub>). Assuming that the vapor behaves as an ideal gas with a relatively constant enthalpy of vaporization over the temperature range between T<sub>B</sub> –

20 °C, the Claussius-Clapeyron equation (Barrow 1961) predicts the vapor pressure dependence on the temperature T (Johnson *et al.* 1990a):

$$P_i^v(T) = P_i^v(T_R) \exp\left[\left(\frac{T_B T_R}{T_B - T_R}\right)\left(\frac{1}{T} - \frac{1}{T_R}\right) \ln(P_i^v(T_R)/P_B)\right] \quad (3)$$

where,

- $P_i^v$  = pure component vapor pressure at temperature T [Pa]
- $T_R$  = the reference temperature at which the vapor pressure is known, normally 20°C = 293 K [K]
- $T_B$  = the boiling point at normal atmospheric pressure, 100 kPa [K]
- T = the absolute temperature of at which the vapor pressure is to be calculated [K]
- $P_B$  = the pressure at which the boiling point ( $T_B$ ) is measured [Pa]

*Flow path of carrier vapors relative to the location of the contaminants*

Maximum removal rates are achieved when the induced vapor flow travels only through the zone of contamination and no mass-transfer limitations are encountered. In reality, this is not always the case. It is possible that a part of the vapor flows through uncontaminated soil, or that the vapor flows parallel to, but not through, the zone of contamination (a layer of liquid hydrocarbon resting on the top of an impermeable strata of the water table). The situation in which vapor flows primary past, rather than through the contaminated soil zone, might occur when a contaminated clay lens is surrounded by sandy soils. In this case vapor phase diffusion through the clay to the flowing vapor limits the removal rate. It has been pointed out that vapor concentrations recovered by SVE are 10-50 % of the saturated vapor concentrations, and that is why vapor flow rates have to be multiplied by 0.1-0.5 to correspond operating efficiencies of 10 – 50 % (Johnson *et al.* 1990b).

**2.3.3 Requirements for SVE**

SVE is a useful remediation method in the unsaturated zone, but is generally not appropriate for sites with a groundwater table located less than 1 m below the land surface. Ground-water pumping might be necessary in cases where the groundwater table is located less than 3 m below the land surface (U.S. EPA, 1995a). The soil must be permeable enough to allow penetration by soil vapors, which essentially means sandy and gravelly soils. In addition, the best result is achieved in homogenous soil, where different soil types have not mixed with each other. (Lindmark 1994). On the other hand, the soil must be dry enough and shall not include too much organic matter. The removal of chemicals from the soil is more efficient when more volatile compounds are involved. The volatility or vapor pressure also depends on atmospheric temperature. For example, 90 % of gasoline can be recovered by SVE at a temperature of 20 °C, but only 56 % at a temperature of -20 °C. SVE will not remove heavy oils, metals other than mercury, PCBs (polychlorinated biphenyl), or dioxins (Goldfarb *et al.* 1994). Table 4 summarizes the requirements of SVE.

**Table 4.** Requirements of SVE (U.S. EPA, 1996b)

Soil layer	Unsaturated zone (above the groundwater)
Soil permeability	> 10 <sup>-6</sup> cm <sup>2</sup> (>10 <sup>-1</sup> cm/s)
Soil moisture content	< 50 %
Soil/air filled porosity	< 40 %
Organic carbon of the soil	low content (not much peat or humus)
VOC vapor pressure	> 66 Pa
Dimensionless Henry's constant <sup>1</sup>	> 0.01 <sup>2</sup>

<sup>1</sup> The Henry's constant of volatile hydrocarbons increases approximately threefold for a 10 °C increase in temperature (LaGrega *et al.* 1994; Kavanaugh *et al.* 1980)

<sup>2</sup> It has been stated that SVE is effective already then when a dimensionless Henry's constant is greater than 0.001 at 10 °C (Goldfarb *et al.* 1994)

### **2.3.4 Items to be considered when using SVE**

During a venting operation the vacuum, or reduced pressure in the soil, will cause a rise, or "upwelling", in the water table. The rise will be equivalent to the change in pressure (max. 10 m) and that is why many soil venting operations include a ground-water pumping well to keep the ground-water level below the region of contamination (Johnson *et al.* 1990a).

The rate of gasoline removal rapidly decreases over a period of few days. On the other hand, gasoline contains 10 % to 20 % of relatively non-volatile compounds ( $>C_{10}$ ), which are not removed rapidly by soil venting. (Johnson *et al.* 1990a)

An effect of SVE can be improved by increasing  $R_f$  by covering the contaminated area by a plastic film, asphalt, cement or clay. Even a 90-m of  $R_f$  has been achieved by covering the ground (Hiller *et al.* 1989) Covering has the maximum effect when extracting from less than 5-m below the ground surface (Johnson *et al.* 1990b). In addition, SVE can be combined with soil heating by injecting steam into the soil. Only the injection of uncontaminated air will improve an effect of extraction.

A cost estimation model for SVE has been developed based on models of contaminant removal, air flow and cost estimation algorithms (Depaoli *et al.* 1990).

## **2.4 Modeling subsurface transport of petroleum hydrocarbons**

There are many mathematical models available to simulate the fate and transport of subsurface spills of petroleum hydrocarbons. Hydrocarbon Spill Screening Model (HSSM) is an EPA model which simulates subsurface releases of light nonaqueous phase liquids (LNAPLs). (Weaver 2002) MT3D model simulates contaminant migration in the groundwater. (Fetter 1999, Chiang *et al.* 2001) R-Unsat is a computer model designed for quantifying rates of volatilization and biodegradation of organic compounds near the water table. R-Unsat was developed and documented by U.S. Geological Survey (USGS). (USGS 2002)

There are special Soil Vapor Extraction Models available from the The Scientific Software Group (SSG). It lists altogether over 140 environmental software programs (SSG 2002).

Most NAPL-spreading programs handle underground spills and they cannot be used for accidental spills of petroleum hydrocarbons on the ground. On the other hands, those programs that could be suitable for accidental fuel spills on the ground are too complicated and slow for an emergency use. That is why a simplified gasoline spill model was developed by the author to help fire departments to estimate an urgency of response actions. (See the chapter 1.4.5)

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