Soil and groundwater contamination with gasoline and diesel oil. Assessment of subsurface hydrocarbon contamination resulting from a fuel release from an underground storage tank in Vanstad, Skåne, Sweden.

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Spills and leaks from storage tanks constitute the most common groundwater contamination source with petroleum products. Gasoline and diesel pools do not spread extensively along the water table, but dissolved constituents are transported in groundwater on relatively larger distances. Volatile hydrocarbons migrate in the vadose zone dependently on distribution and extent of the dissolved and pure phase. When influx exhausts, fuel trapped in pores at a residual saturation still remains as a potential contamination source.

Several thousand among 22 000 contaminated sites in Sweden are result of petrol stations contributing to soil and groundwater pollution. In 2003, investigations carried out by SWECO VIAK AB in the property of a former petrol station in Vanstad in Sjöbo commune in Skåne, revealed subsurface contamination with petroleum hydrocarbons and lead resulting from an underground storage tank fuel leakage. After the tank remediation it was recommended to collect water samples for oil index analysis in 2005. The property is located within a proposed water protection area. The aim of the thesis was to proceed further investigations in the vicinity of the property in order to assess overall spatial contamination and its influence on the water protection area. The investigations were carried out from April to June 2005 and included: coring, groundwater levelling, groundwater and soil sampling, oil index and volatile compounds analyses. On the basis of the field data evaluation, it is inferred that hydrocarbons in a gaseous phase can migrate upwards through all the units comprising the vadose zone, but sand and gravelly sand constitute the preferential pathways. Dissolved compounds can be transmitted northwards of the tank through silty and clayey till as well as through silty and gravelly clayey sand. Assuming the worst case scenario, the solutes are transported due to advection at the rate 5.4x10<sup>-8</sup> m/s. It was further calculated that hydrocarbons can pass in groundwater 1.7 m per year, what gives 71 m in 42 years. The "clean line" was subsequently delineated with regard to this distance. Laboratory analyses showed that groundwater is not contaminated with hydrocarbons. The oil index values are below a detection level of an instrument (50 μg/L) applied. None of BTEX is registered in a vapour headspace. N-Heptane and MTBE detection must be due to an error of the instrument applied. There is no negative impact on the proposed water protection area. Total concentrations of volatile compounds in the soil vapour (TVOC) do not exceed 20 ppm. Such low concentrations are of very marginal importance and the soil is considered as not contaminated.

It is concluded that long term, subsurface fuel releases do not necessarily result in extensive soil and groundwater contamination. The fact that contamination is not observed in the investigated area, although the distribution calculations imply so, underlines a huge role of natural attenuation as a factor limiting subsurface contamination with petroleum hydrocarbons.

Keywords: gasoline, diesel oil, contamination, underground storage tank, leakage

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Läckage och spill från cisterner utgör de vanligaste orsakerna till förorening av grundvatten med petroleum produkter. Bensin och dieselföroreningar sprids inte enbart längs grundvattenytan utan lösta beståndsdelar kan transporteras med grundvattnet relativt långa sträckor. Flyktiga kolväten förflyttar sig i den vattenmättade zonen beroende på föroreningens utbredning och fördelning.

Flera tusen av 22 000 förorenade platser i Sverige är ett resultat av att bensinstationer bidrar till mark- och grundvattenförorening. Undersökningar som gjordes av SWECO VIAK AB år 2003 på egendomen till en tidigare bensinstation i Vanstad i Sjöbo kommun i Skåne visade på föroreningar av kolväten och bly från petroleumprodukter under markytan som ett resultat av läckage från en underjordisk tank. Efter att tanken sanerats år 2005 rekommenderades att ta vattenprov för analyser av oljeindex. Egendomen ligger inom ett område vilket föreslagits som vattenskyddsområde. Syftet med arbetet har varit gå vidare med ytterligare undersökningar i omgivningarna för att bestämma föreoreningens rumsliga utbredning och påverkan på vattenskyddsområdet. Undersökningarna utfördes mellan april och juni år 2005 och innefattade borrningar, avvägning av grundvattenytan, provtagning av grundvatten och jordprover, analyser av oljeindex och flyktiga komponenter. Baserat på utvärderingen av fältdata, kan man anta att kolväten i gasfas företrädesvis kan förflytta sig upp genom alla enheterna i den luftfyllda zonen men sand och grusig sand utgör de lättaste transportvägarna. Eftersom grundvatten är ett medium i vilket lösta kolväten kan förflyttas, kommer föroreningarna att transporteras norrut med grundvattnet genom siltiga och leriga moräner såväl som genom siltig och grusig lerig sand. Under antagande om ett värsta scenario skulle lösningarna genom advektion kunna transporteras med en hastighet av 5.4x10<sup>-8</sup> m/s. Vidare gjordes beräkningen att kolväten årligen kan transporteras med grundvattnet på en sträcka av 1,7 m, vilket ger 71 m på 42 år. Den s.k. "rena linjen" avgränsandes således med avseende på detta avstånd. Laboratorieanalyser visade att grundvattnet inte är förorenat av kolväten. Värdena på oljeindex ligger under känlisghetsnivån (50 μg/L) på det instrument som användes. Inte någon av BTEX komponenterna registrerades heller i den luft som fanns ovanför vattenprovet. Spår av N-heptane och MTBE måste bero på fel i mätutrustningen. Det finns ingen påverkan inom det föreslagna vattenskyddsomårdet. Den totala koncentrationen av flyktiga ämnen i marken överstiger inte 20 ppm. Sådana låga koncentrationer är av ytterst marginell betydelse och marken betraktas som inte förorenad

Slutsatsen är att långvariga utsläpp av bränsle under mark inte nödvändigtvis leder till omfattande mark och grundvattenförorening. Det faktum att en förorening inte observerats i undersökningsområdet, även om spridningsberäkningarna antyder detta, understryker den naturliga utspädningen som en begränsande faktor av kolväten från bränsle.

Nyckelord: bensin, diesel, förorening underjordstank, läckage

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## 1. Introduction

## 1.1. Background

Petroleum products are blends of petroleum - derived chemicals (U.S. Department of Health and Human Services, 1999). Their forms vary from clear or light-coloured liquids that evaporate easily, such as gasoline, through thick dark liquids, to non evaporating semi-solids like asphalt. Many of them have a characteristic gasoline, kerosene or oily odours.

Since the huge amounts of petroleum products are utilised in transport and industry, large quantities of power fuels, oil and Stoddard solvents require utilities such as surface or underground tanks for their storage. Apart from petrol stations and industry, the tanks are owned by governmental agencies or private individuals. A leak may occur due to improper installation, loose fittings, fire fighting as well as because of age. Most tanks corrode within twenty years after installation; however, release often occurs before fifteen years of age (Chester, 1989; Oliviera et al., 1991).

Spills and leaks, as a result of inappropriate storage, constitute the most common groundwater contamination source with petroleum products (Badient et al., 1999). To give the estimate of frequency, during the survey conducted in USA in 1994, Environmental Protection Agency (EPA) found underground releases from about 12 % of the over one million storage tanks that they screened (U.S. Department of Health and Human Services, 1999). Other EPA statistics reveal leaks of motor fuel out of 35 % among 800 000 tanks (Badient et al., 1999). According to the Swedish statistics, several thousand among 22 000 contaminated sites are result of petrol stations contributing to soil and groundwater pollution.

In 1997, the Swedish Petroleum Institute (SPI) signed an agreement whereby the petroleum companies in the country accepted the obligation to remediate several thousand closed petrol stations (Naturvårdsverket & Svenska Petroleum Institutet, 1998). On commission by SPI Miljösaneringsfond AB, SWECO VIAK has remediated a number of sites so far. One of them has been chosen for further investigation for the purpose of this thesis.

The petrol station was situated in the property Vanstad 26:19, in Vanstad in Sjöbo commune in Skåne. As far as is known, the activity included sale of petrol, however, the sale of diesel has not been definitely confirmed. The storage tank had been recognised as a point source of subsurface contamination with petroleum hydrocarbons and lead; thus was remediated in 2004. Investigations carried out by SWECO VIAK AB were limited to the property of the former petrol station. The property is located within the preliminarily designated water protection area (Hansson et al., 2004).

## 1.2 Objectives

Although the influx of fuel has ceased, the contamina-

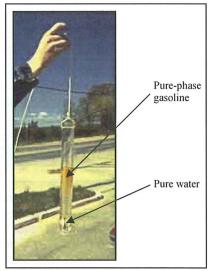
tion may be still present in the subsurface. For this reason further investigations were undertaken in the vicinity of the storage tank with the following objectives:

- (1) To define a configuration of strata comprising the framework within which the contaminants could spread;
- (2) To assess soil and groundwater contamination;
- (3) To estimate the environmental impact on the groundwater within the water protection area.

Since the assessment of contamination should begin with understanding of the subject, the investigative part of the manuscript is provided with a preface concerning subsurface releases of gasoline and diesel oil.

## 2. Contaminants

Contaminants can be defined as substances present in the groundwater or any other medium at levels greater than background values (Eliason after Andersson, 2001). Gasoline and diesel are the major contaminants originating from petrol stations; and only these are taken into account in the thesis. However, a number of other potential contaminants are commonly found at petrol stations, including brake fluids, anti-freezers, waxes, dry cleaners, etc.



**Fig. 2.1.** Pure-phase gasoline perched above the water table (Ryan, 2003).

FLUID	DENSITY at 15°C [g/mL]	KINEMATIC VISCOSITY [centipoises]
Water	0.998	1.14
Gasoline	0.729	0.62
Diesel	0.827	2.70

**Table 2.1.** Typical density and viscosity values for water, gasoline and diesel oil (Morrison et al., 1999; Oliviera et al., 1991).

There is not one chemical formula either for diesel or for gasoline. They are complex mixtures comprising different hydrocarbons classified into aliphatics<sup>1</sup> and aromatics<sup>2</sup> (Potter & Simmons, 1998). Gasoline consists principally of two hundred diverse compounds, mostly aliphatic hydrocarbons (alkanes), and monoaromatics; whereas diesel may contain up to five hundred chemicals among which alkanes and cycloalkanes constitute the majority (Naturvårdsverket & Svenska Petroleum Institutet, 1998; Oliviera et al., 1991). In comparison with gasoline, diesel contains smaller amounts of BTEX (benzene, toluene, ethylobenzene, total xylenes)<sup>3</sup>, but greater concentrations of Polinuclear Aromatic Hydrocarbons (PAHs)<sup>4</sup>. Additives are minor constituents of fuels. For instance methyl-tertiary-butyl-ethyl (MTBE)<sup>5</sup> is almost exclusively added to gasoline (Morrison et al., 1999).

In addition to the chemical composition, gasoline and diesel are distinguished by their physical properties. They are Light Nonaqueous Phase Liquids (LNAPLs). NAPLs do not dissolve in water, but form a visible, separate, oily phase as shown in fig. 2.1. (Morrison et al., 1999). Table 2.1. presents typical density and viscosity<sup>6</sup> values for water, gasoline, and diesel oil. By comparison, we can see that in case of any gasoline and diesel leakage from a storage tank, since they are lighter than water, gasoline will float on the top while diesel will occur as a separate phase between gasoline and water. At the same time, with lower viscosity, gasoline will move faster in a porous medium than diesel does.

## 3. Fate and transport processes

Due to the fact that gasoline and diesel are complex mixtures, prediction of their environmental fate and transport in the subsurface brings plenty difficulties and uncertainties. A NAPL pool changes its composition with time. Single constituents react within a bulk released into the ground, other separate from a mixture and migrate independently in the soil and groundwater. (U.S. Department of Health and Human Services, 1999; Potter & Simmons, 1998). Therefore, examining

the properties of the mixture as a whole is pointless; the properties of the particular components require careful investigations in order to estimate the overall fate of a fluid.

The chapter depicts a simplified transport and fate conceptual model (based on: Freeze & Cherry, 1979; Badient et al., 1999) conforming to the situation observed in the field. The model fulfils following necessary conditions:

- (1) An underground storage tank, as a point contamination source, is situated in a vadose zone.
- (2) Gasoline leaks from a tank. Continuous influx exhausts after a certain period of time.
- (3) A pool gives rise to groundwater contamination.
- (4) The following takes place so that the fuel could reach the aquifer: the release is long enough in time and the leakage volume is relatively big in relation to thickness of the vadose zone beneath the entry point.

It is further assumed that:

- (5) Migration takes place in a porous, homogeneous, not fractured medium.
- (6) Water table fluctuations are excluded.

## 3.1 Transport concerns

Fate processes are excluded in this section. Fig. 3.1. illustrates the conceptual model.

Acting under influence of gravity, gasoline primarily displaces water and gas in open pores within the vadose zone. As a result, all the pores are saturated with the fluid which forms a continuous, downward moving pool (fig. 3.1., 1). Active capillary forces give rise to lateral migration at the external part of the infiltrating body. Its extent is not significant though, and oil saturation<sup>7</sup> ceases with the capillary forces (fig. 3.1, 1a).

Subsequently, the pool reaches the water bearing zone (fig. 3.1., 2). It does not penetrate below the water table. On the contrary, gasoline spreads along the capillary fringe zone and the top portion of the saturated zone. In this stage, transport due to capillarity has superiority over gravity forces (fig. 3.1., 2a).

When the hydrocarbon influx ceases, the pool attempts to reach a stable condition (fig. 3.1., 3). With time, gasoline attains a certain degree of saturation when, having been trapped into relatively immobile condition by capillary forces, it is retained in the open pores of the soil in blobs. Water or air replaces fuel previously having filled the matrix (fig. 3.1., 3a). This is a stage of residual saturation, defined as a fraction of total pore volume occupied by NAPL under ambient condition.

## 3.2 Fate concerns

The term fate process refers to any interaction between the contaminant and physical, chemical or biological components of the subsurface. Amplifying the concep-

 $<sup>^{7}</sup>$  Oil saturation - total pore volume occupied by NAPL (Badient et al., 1999).

<sup>&</sup>lt;sup>1</sup> Hydrocarbons of chain structures; divided into classes: saturated alkanes (C<sub>n</sub>H<sub>2n+2</sub>), cycloalkanes (C<sub>n</sub>H<sub>2n</sub>), unsaturated alkenes (C<sub>n</sub>H<sub>2n</sub>) (Potter & Simmons, 1998).

<sup>&</sup>lt;sup>2</sup> Unsaturated hydrocarbons of ring structure, rings contain 6 carbon atoms linked with double bonds; the 4<sup>th</sup> bond of each carbon atom is shared throughout the ring; divided into classes: benzene, alkylbenzenes, Policyclic Aromatic Hydrocarbons (PAHs) (Potter & Simmons, 1998).

<sup>&</sup>lt;sup>3</sup> Aromatic hydrocarbons.

<sup>&</sup>lt;sup>4</sup> benzo(a)pirene, benzo(a)anthracene, benzo(b)fluoranthene, benzo (k)fluoranthene, benzo(g, h, i)perylene, chrysene, dibenzo(a, h) anthracene, ideno(1,2,3-c, d)pyrene.

<sup>&</sup>lt;sup>5</sup> MTBE is persistent in the subsurface, more mobile than BTEX. BTEX eagerly dissolves in MTBE contributing to diminished attenuation of hydrocarbons (Morrison et al., 1999).

<sup>&</sup>lt;sup>6</sup>Viscosity - property to offer internal resistance to flow, Ns/m<sup>2</sup> (Fetter, 2001).

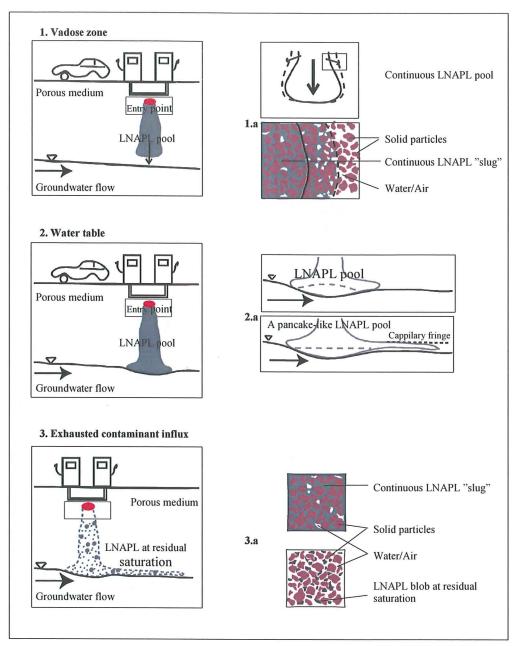


Fig. 3.1. Gasoline and diesel oil leakage from an underground storage tank. Transport conceptual model.

1. Vadose zone. The core of an infiltrating body moves downward. 1.a. Oil saturation gradually ceases at the most external parts of a pool. 2. Water table. 2.a. Fuel spreads along the capillary fringe and the top portion of saturated zone. 3. Exhausted contaminant influx. 3.a. Comparison between a continuous NAPL pool and NAPL at residual saturation.

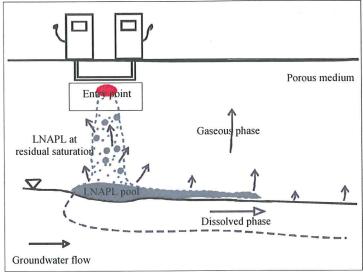
tual model presented in previous section, the gasoline released from the tank is not only actively transmitted via the porous medium but also attenuates<sup>8</sup> due to: volatilization, dissolution, in situ biodegradation and sorption.

Compounds dissolved from the gasoline pool infiltrate the saturated zone where they are subsequently transported with the groundwater flow, due to advection<sup>9</sup>. On the other hand, volatile constituents<sup>10</sup> originating from a pool, contaminated water and hydrocarbons associated to soil, when in contact with air, change into a gaseous phase and migrate upwards through open pores in the vadose zone (fig. 3.2.). Organic vapours spread independently on groundwater gradients and faster than the liquid phase. A vapour plume is transmitted in the soil matrix mostly by vapour diffu-

<sup>&</sup>lt;sup>8</sup> Natural attenuation – physical, chemical, biological processes that, under favourable conditions, act without human interaction to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater (U.S. Environmental Protection Agency, 1999).

<sup>&</sup>lt;sup>9</sup> A process by which dissolved substances are transported by the motion of flowing groundwater (Fetter, 2001).

<sup>&</sup>lt;sup>10</sup> Volatile compounds - compounds with vapour pressure greater than 1mmHg (Morrison et al., 1999).



**Fig. 3.2.** Gasoline and diesel oil leakage from an underground storage tank. Conceptual model of volatilization and dissolution.

sion<sup>11</sup> (Badient et al., 1999).

Biodegradation<sup>12</sup> commences as soon as the fuel was released into the vadose zone, on condition that sufficient concentration of oxygen and nutrients is present in the medium. NAPL pools do not biodegrade significantly. The process is, however, of importance for dissolved hydrocarbons. The beneficial aspect of this process is that the contaminant is eliminated from soil and groundwater without transport (Morrison et al., 1999). In addition, the migration can be significantly retarded<sup>13</sup> by sorption, defined as an association of a dissolved or gaseous contaminant with a solid material.

Generally speaking, aromatic hydrocarbons are more soluble in water and have less of a tendency to sorb to organic material than aliphatics (Naturvårdsverket & Svenska Petroleum Institutet, 1998). What is more, BTEX dissolve more eagerly in MTBE than in water what results in diminished retardation of gasoline originating hydrocarbons (Morrison et al., 1999).

## 4. Environmental and health concerns

Humans and animals are exposed to gasoline and diesel constituents mostly through oral exposure or inhalation. Despite the fact that an overall amount of petroleum products being released into the subsurface is rather low, and LNAPL migration is limited to a vadose zone, their impact on the groundwater quality

cannot be ignored. In the 1980's, the spill of aviation gas and fuel from an underground storage tank in Michigan state, in USA resulted in a plume more than 1.6 km long and 150 m wide, polluting about one hundred shallow municipal water wells (Badient et al., 1999). Typical fuel components such as soluble BTEX and persistent MTBE are a vital threat to municipal, industrial, and residential wells. Furthermore, BTEX and PAHs are one of the most typical organic contaminants found in groundwater. Aliphatic hydrocarbons are more volatile and may seep into basements, excavations, tunnels and the atmosphere (Badient et al., 1999; Potter & Simmons, 1998).

It must be underlined that even if an influx is exhausted, blobs trapped in pores, in the vadose zone, remain as a potential contamination source because water, passing through, dissolves hydrocarbons and transfers them towards the underlying aquifer (Badient et al., 1999).

The health effects depend upon the compound, exposure time, and the amount of chemicals one is exposed to. Skin irritation, damage to the central nervous system, and cancer are only a few of the implications. Most of the compounds are accreted with urine during exhalation (U.S. Department of Health and Human Services, 1999).

National Chemicals Inspectorate in Sweden (KemI) has classified chemical substances regarding their toxicity. According to this, gasoline and diesel oil are along with aromatic hydrocarbons considered to be very hazardous, whereas benzene and PAHs as extremely hazardous. Aliphatics indicate moderate toxicity (Naturvårdsverket, 2002).

In 1998, Naturvådsverket & Svenska Petroleum Institutet established guideline values for compounds released at petrol stations. The term guideline values stands for concentrations in soil and groundwater which, when exceeded, may lead to undesirable effects on human health and/or to the environment (Naturvådsverket & Svenska Petroleum Institutet, 1998). A new, unofficial proposal of the guideline values for groundwater contaminants at petrol stations has been recently suggested on commission by the Swedish Petroleum Institute (Elert, 2004) and these are commonly used in practice.

## 5. Study area

## 5.1. Contamination source

An underground storage tank was recognised as a source of groundwater and soil contamination with petroleum hydrocarbons.

#### 5.2. Location

The storage tank, pointed out in the site map, Appendix 1, is situated in the property Vanstad 26:19, in Vanstad, Sjöbo commune, Skåne County. The prop-

<sup>&</sup>lt;sup>11</sup> Vapour diffusion – spreading due to partial pressure gradient of gaseous component in a gaseous mixture; from an area of higher to an area of lower pressure (Morrison et al., 1999).

<sup>&</sup>lt;sup>12</sup> Biodegradation – complete conversion of a contaminant to mineralized end products such as carbon dioxide and water through metabolism by living organisms (Badient et al., 1999).

<sup>13</sup> Retardation – decrease in average velocity of a contaminant mass in relation to the average groundwater velocity (Morrison et al., 1999).

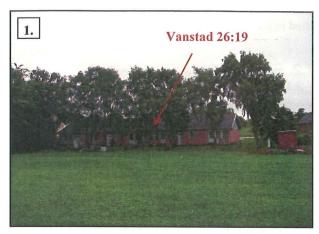




Fig. 5.1. Vanstad (Głowacka, 2005).

1. Investigated area. Picture taken from the north. 2. Underground storage tank. Picture taken from the south.

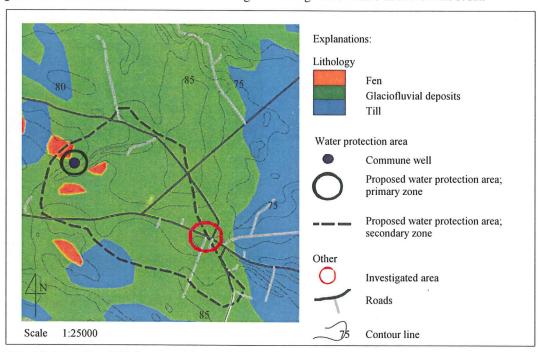


Fig. 5.2. Map of surficial deposits and water protection area, Vanstad (modified after SWECO VIAK AB,

erty lies in a hummocky area, in a topographic low trending from south-east to north-west.

The term "investigated area", used in the following chapters, applies to a land covering 12 800 m<sup>2</sup> in the immediate vicinity of the premises, where detailed fieldwork was conducted. The area lies at average elevation 79 m.a.s.l. A hill, 89.9 m.a.s.l., forms its northern boundary (Hansson et al., 2003; Pettersson & Ohlsson, 1984; field observations).

## 5.3. Spatial planning and water supply

The investigated area is depicted in fig 5.1. According to Naturvårdsverket & Svenska Petroleum Institutet (1998) the premises are classified as a land with sensitive use (KM). Nowadays, the property Vanstad 26:19 is used for housing. A row of semi-detached houses is surrounded by lawns, slab and asphalt covered surfaces. There is a pump station for wastewater on the

northern side of the property. Fields and more houses are located in the proximity.

Most inhabitants in Vanstad are connected to the commune water supply net. The 9 m deep well is situated approximately 1 km north-west of the investigated area. Private wells are rarely used in Vanstad. There is none in the property 26:19 (Hansson et al., 2003; field observations).

No detailed plan for Vanstad exists at the moment; however, the investigated area is situated within a proposed secondary zone of a water protection area<sup>14</sup> (fig. 5.2.).

<sup>&</sup>lt;sup>14</sup> Water protection area - a protected land or water area established by the county administrative board or a municipality for the purpose of protecting surface water or groundwater supplies, that are, or are likely to be, used as water catchments (Miljöbalken, 2000).

## 6. Previous activities

As far as is known, the petrol station was established in 1963 and closed in 1972. The activity included sale of gasoline; diesel is not well confirmed. The petrol station had an underground storage tank and a garage (Hansson et al., 2003).

In 2003, on commission by SPIMFAB, SWECO VIAK AB made an environmental, technical investigation of the soil and groundwater in the property Vanstad 26:19. The results were as follows. A contamination with petroleum hydrocarbons was detected on the northern and southern sides of the buildings. Oil index<sup>15</sup> in the groundwater exceeded a guideline value at three out of six sampling points; one of them (307) is pointed out in Appendix 1. Low concentration of lead was detected too. Determination of volatile compounds in the soil samples indicated values below 25 ppm. The indoor air was not infected (Hansson, et al., 2003).

Further technical activities undertaken in 2004 revealed that the 6 m³ tank contained 0.5 m³ of gasoline. A remediation was performed immediately, including cleaning and filling the tank with sand. Soils, with VOC content above 30 ppm were replaced and sent to a certified plant for oil-polluted soil.

Below the tank, at the depth of 2.60 m, carcinogenic PAHs were registered in the soil at concentrations exceeding a guideline value applied to a sensitive land use (0.6 ppm) for analyzed soils, and 0.3 for guideline values (Naturvårdsverket & Svenska Petroleum Institutet, 1998).

In a report published in 2004, after the tank remediation, it was recommended to collect two rounds of water samples in the year 2005, and to analyze them for the oil index (Hansson, et al. 2004).

## 7. Methodology

The investigations were carried out from April to June 2005 with a surmise that groundwater and soil contamination may occur in the investigated area.

## 7.1. Literature studies

General information about the site and previous activities were obtained from SWECO VIAK AB reports (Hansson et al., 2003; Hansson et al., 2004; SWECO VIAK AB, 2004). Geology data were gathered from: Daniel (1986), Erlström (2004), Gustaffson (1970) Jordartskartorna 2D Tomelilla SO/2E Simrishamn SV, Ser. Ae no 65. The Guideline values were taken from Naturvådsverket & Svenska Petroleum Institutet (1998) and Elert (2004). Other sources, like maps and handbooks were used to evaluate field data and are

 $^{15}$  Hydrocarbon oil index; HI – total amount of hydrocarbon compounds ( $10 \le EC \le 40$ , where EC stands for range of equivalent carbon number) that can be extracted from water and soil samples (Facchetti & Cadippi, 2005).

cited in the text.

## 7.2. Fieldwork

### 7.2.1. Coring

Ten coring sites were chosen altogether. The locations are pointed out in the site map (Appendix 1). Coring protocols are shown in Appendix 2. Corings no 1, 2, 3, and 5 were chosen to determine groundwater flow conditions. Sampling point no 4 was set to define "background" concentrations of volatile compounds. Five additional sample points (no 6, 7, 8, 9 and 10) were located on a rough grid pattern within a "clean line" (chapter 10) to asses subsurface contamination with petroleum hydrocarbons.

The corings were carried to the first groundwater met or to a maximum depth of 5 m. Apart from a hand-auger, a motor powered equipment attached to a vehicle was used. The methods do not generate cuttings through which the contaminants can escape; hence, allows collecting high-quality soil samples (Gregg Drilling & Testing, Inc. 2002/2003).

## 7.2.2. Levelling

The coring sites were levelled with one of the following devices: Kernlevel produced by LEICA or WILD NAKI by WILD HEERBRUGG. Reference points, marked in Appendix 1, were obtained from Sjöbo commune.

#### 7.2.3. Groundwater levelling

Groundwater table readings were essential to estimate flow conditions and the contaminants' distribution. Levelling was conducted with a water level meter produced by EL-WA, type PLA 30 box. The readings were taken in 11 wells, a piezometer installed by SWECO VIAK AB, and coring sites no 3, 5, 7, 8, and 9. Prior to taking the readings, inert PCV tubes ended with a screen (fig. 7.1.) were emplaced in the coring points. The wells along with the piezometers were subsequently levelled with the WILD NAKI instru-



**Fig. 7.1.** Ending of the piezometer used during the field investigations. The key used for scale. (Glowacka, 2005).

ment.

### 7.2.4. Sampling

During the coring, the soil samples were collected continuously with screened intervals of one meter unless the lithology has changed. In order to analyze volatile compounds in the soil, additional samples were collected within the investigated area into special sample bags with tight-fitting clips.

The water sampling was conducted in the investigated area with a stainless, steel foot valve pump attached to a PCV tube (fig. 7.2.). The material of this tube is inert to hydrocarbons. In order to obtain representative groundwater samples, stagnant water was first removed from the piezometers. The equipment was cleaned prior to use and between the sampling points. Water was collected into Teflon-lined bottles with screw caps, ordered from the Analytica laboratory.



**Fig. 7.2.** Water sampling device. Foot valve pump attached to a PCV tube. The tea spoon used for scale (Głowacka, 2005).

## 7.3. Analyses 7.3.1. Soil analyses

Grain size analysis was performed on 50 soil samples in order to define lateral and vertical configuration of strata comprising the framework within which hydrocarbons could spread. The analysis followed the procedure depicted in Talme & Almen (1975). After the sieving, 15 representative samples were selected for hydrometer analysis, on the basis of visual examination in the field, grain size distribution and sorting.

26 soil samples collected in locations 4, 6, 7, 8, 9 and 10 were examined for total volatile compounds. Photoionization Detector (PID), described in Appendix 4, was chosen as the most suitable method. The analyses were carried out, with assistance in the SWECO VIAK AB laboratory in Malmö with Voyager Portable Digital Gas Chromatograph produced by PE Photovac. The data were processed thereafter with software Site Chart II. This analysis technique pro-

vides an accurate response in the range from 10 to 150 ppm.

The samples were refrigerated prior to the analyses.

## 7.3.2. Water analyses

In case of groundwater, the samples were screened for oil index and specific volatile compounds. Two gas chromatography techniques, GC-FID and GC-PID<sup>16</sup> were chosen to analyze the water samples. The methods' depiction is given in Appendix 4.

Total Petroleum Hydrocarbons (TPH) is one of the primary applications of the FID and was employed to detect hydrocarbon oil index, conventionally used to express the level of pollution. Sampling point no 3 was chosen in order to ensure that contamination is limited to the "clean line", whereas sites no 7 and 10 are located on the southernmost and northernmost parts of the area suspected to be contaminated. The groundwater samples were sent to an accredited laboratory in Täby (Analytica). A quantification level of the GC-FID is 50  $\mu$ g/L (Analytica AB, 2001).

In order to detect Benzene, Toluene, Ethylene and Xylenes present in vapour headspace, the GC-PID technique was utilized on six groundwater samples (site no 3, 6, 7, 8, 9 and 10). The analyses were carried out, with assistance, in the SWECO VIAK AB laboratory in Malmö with the Voyager Portable Digital Gas Chromatograph. The instrument is able to detect a concentration as low as 5 ppb.

The samples examined for organic vapour were refrigerated prior to the analysis. Since the oil index does not include volatile compounds, it was sufficient to keep the samples in the dark. The samples were transported to the laboratories within 24 hours of collection.

## 8. Geology

The bedrock around Vanstad is mainly composed of sedimentary rocks, where Paleozoic sandstones and shale overlie Precambrian gneisses. In the Late Cretaceous, due to uplift, the younger mezozoic rocks were eroded and the structural unit Colonus Shale Trough was formed. The trough is separated from Linderödsåsen Horst on the north-east and from Vomb Through on the south-west by faults of regional scale. The thickness of the sedimentary bedrock does not exceed 2000 m (Erlström et al. 1985).

Fig. 5.2. presents a map of surficial Quaternary deposits occurring in the proximity of Vanstad. The village lies in an area of glaciofluvial deposits consisting of eskers and hills. The underlying till rests on the bedrock. Its thickness does not exceed 5 m.

The Lövestad esker is the largest esker in the area and comprises vast amounts of glaciofluvial

<sup>&</sup>lt;sup>16</sup> Gas Chromatography with Flame Ionization Detector and Gas Chromatography with Photo-Ionization Detector, respectively.

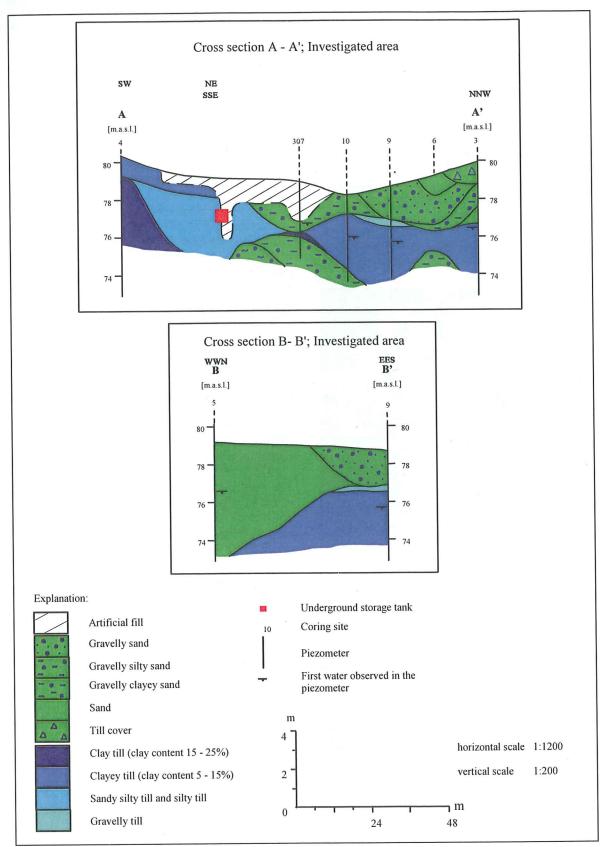


Fig. 8.1. Cross sections through the investigated area.

gravel along with gravelly sand ranging in thickness from about 0.5 to 20 m. The central parts of the form, at least partially, rest on the bedrock (Daniel, 1986; Gustafsson, 1970; Gustafsson, 1984; SGU, 1985).

The stratigraphy is complex. The bedrock was not reached during the coring, that is until 5 m.b.g.s. Appendix 2 presents detailed logs (corings no 302, 303, 307 were made by SWECO VIAK AB in 2003 (Hansson et al., 2003)), whereas fig. 8.1. shows the two-dimensional interpretation in a cross section form. The cross section lines are pointed out in Appendix 1.

In the property Vanstad 26:19 there is a filling consisting of sandy soil and till to the approximate depth 1-2 m, but the thickness of artificial material exceeds 3 m in the place where the tank is located. These deposits rest on gravelly clayey sand and till (Hansson et al., 2003). The till ranges from clay and clayey to sandy silty and silty till. Sand layers are observed in the silty till (site no 302, 303). In places (sites no 303, 307), the till overlies gravelly silty sand or gravelly clayey sand.

Northwards from the property, diverse superficial sandy deposits rest on clayey till (with clay content of between 5 and 15 %) and gravely till. These are medium sand, also not completely sorted gravelly clayey sand and gravelly sand. Their overall thickness ranges from 1 to 4 m. At a few sites (no 3, 6, and 10) gravelly clayey sand is a bottommost unit and underlies the till. While at location no 3 clayey till forms also a superficial part, at sites no 5 and 7 no till is observed at all, but medium sand. In the latter the sand is overlain with gravelly clayey and gravelly sand.

On the south-west from the property (site no 4), a one meter thick layer of clayey till rests on a clay till with clay content above 15 %.

## 9. Hydrogeology

### 9.1. Limitations

The data were collected during the first rainy afternoon after at least one week of sunny weather. Since infiltration of rain water, through the zone of aeration to the zone of saturation, is retarded in time (Pazdro, 1977), it is assumed that precipitation did not manage to reach the water table and cause any rise. Rather the opposite situation is expected, that is the observations may relate to a temporary lowering of the water table after the dry period.

The readings at the sites 3 - 10 were taken a few hours after the coring. This is considered long enough to fill the piezometers and ensure a representative measurement for sandy deposits. However, for clayey units observed in the investigated area it might be too short (Jeppsson, 2005). No signs of clogging were observed. The wells were lidded and are not used for water supply anymore.

It is inferred that the readings taken in the wells and piezometer installed by SWECO VIAK AB (site no 307) do indicate the static water level. Also meas-

urements taken in medium sand (sites no 5 and 7) indicate representative values, whereas at sites no 3, 8, 9 and 10, the water table elevation is not so reliable.

The piezometers are installed in the saturated zone at various depths. In topographic lows, the deeper piezometer is installed in an unconfined and homogenous aquifer, the higher hydraulic heads it encounters. Hence, unless the piezometer was emplaced at the depth of the water table, measured hydraulic head would be higher than the one adjacent to the well (Domenico & Schwartz, 1990).

This phenomenon is omitted further in the manuscript. Locations no 5 and 7 have almost the same elevation; the piezometers were installed at both sites app. 2 m below the water table. The measured readings are comparable even though they are increased. The reading taken in piezometer no 307 is adjacent to the well.

## 9.2. Water table

The groundwater levelling was carried out on the 13<sup>th</sup> June 2005. All water table readings are shown in a table attached to Appendix 3. Some of them are also repeated in the coring protocols, Appendix 2. Contour lines were designated based on the data interpolation. In the water table map (Appendix 3) only these locations are marked which were used to construct the map.

Within the investigated area only sites 5, 7 and 307 were taken into account because these readings are undoubtedly representative.

Measurements taken in wells no W2 and W11 indicate 76.25 and 76.12 m.a.s.l. but were omitted during interpretation. This is due to the fact that a topography controlled flow pattern can be expected, yet the data interpolation (wells W1, W2 and W5, W10, W11) implies flow inconsistent with surface topography.

No groundwater was found in the clay till, site no 4. The extent of this unit is unknown, as well as its influence on the level of the water table. It may underlie an aquifer or it may form local lateral boundary of a water-bearing unit. Thereby, the observation is marked with dotted contour in the water table map.

At locations no 1 and 2, the water table is not observed until 5 m (the depth of the coring).

In the southern part of Vanstad the level of the water table decreases northwards (82-77 m.a.s.l.).

### 9.3. Groundwater flow

Following were taken into account during evaluation of the section: field observations (hydraulic head readings along with presence of surface water), and topography. A graphic interpretation is presented in the water table map, Appendix 3.

Because of the lack of the water table data north of the storage tank, assuming that topography controls the flow pattern, the flow lines were drawn in

	Medium sand, sorted	Gravelly clayey sand, sorted to not completely sorted	Clayey till, not sorted
Gravel content [%]	11 – 15	20 – 24	22 - 37
Sand content [%]	75 – 81	58 – 60	44 – 55
Silt & clay content [%]	6 – 10	19 – 22	16 – 26
Sorting [-]	1.9 - 2.0	3.0 - 3.3	3.6 - 5.5

**Table 9.1.** Fraction contents and sorting of sand, gravely clayey sand and clayey till sampled below the groundwater table in sites no 4, 6, 7, 8, 9, 10 & 11. Results of grain size analysis.

Soil classi-	Site desig-	Depth	Gravel	Sand	Silt	Clay	Sorting
fication	nation	[m. b. g. l.]		-			
	3	3,30 - 4,00	26.3	52.4	14.1	7.2	3.8
	3	5.00 - 6.00	25.7	52.6	2	1.7	3.7
	6	3.00 - 3.20	22.7	54.6	22.7		3.9
	8	2.30 - 3.00	30.1	47.6	15.9	6.4	5.2
~: '''	8	3.00 - 4.00	35.1	45.8	12.1	7.0	4.4
Clayey till	8	4.00 - 5.00	31.6	49.0	19.4		4.0
	9	3.00 - 4.00	34.7	48.8	16.5		3.8
	9	4.00 - 5.00	35.3	47.9	9.6	7.2	3.6
	10	2.00 - 3.00	22.2	52.5	15.6	9.7	55
	10	3.00 - 4.00	37.5	44.4	18.1		4.0

**Table 9.2.** Fraction contents and sorting of clayey till sampled below the groundwater table in the investigated area, Vanstad. Results of grain size analyses.

accordance with the topography as reflected in a topographic map in scale 1: 100 000 (Pettersson & Ohlsson, 1984).

In the north-eastern part of Vanstad, there is a side stream of Tolångaån River which in turn is situated more to the north of the village. The Tolångaån forms a gaining stream (Hansson et al., 2003). Groundwater also discharges into two pools situated close to the esker (app. 1 km north-west of the tank) and into an artificial pond (app. 400 m to the south-east of the tank).

The hills constitute recharge areas. Groundwater flows downhill in all directions from the northern "knoll" and a few water divides could be designated there. As interpreted in the water table map, groundwater flows from northern and southern directions into the elongated topographic low, where the investigated area is located. The groundwater passing through the property Vanstad 26:19 is transmitted northwards (hydraulic gradient<sup>17</sup>,  $i = 1.4 \times 10^{-2}$ ) and in the valley changes the direction to the north-west (where continues towards the commune well situated further to the west).

where: i – hydraulic gradient,  $\partial h$  – difference in elevation;  $\partial l$  – distance; the negative sign indicates that flow is in the direction of decreasing hydraulic head (Domenico & Schwartz, 1990).

## 9.4. Heterogeneity of the saturated zone

The saturated zone extends over diverse units, that is silty till, clayey till, gravelly clayey sand and medium sand (fig 8.1.).

Discussing grain size distribution and sorting of particular units (table 9.1.), sandy units indicate low variables in gravel, sand, silt and clay contents, whereas the same values of clayey till vary considerably. A few similarities are noticed from table 9.2. where relevant values of till samples are marked. For instance, grain size distribution at sites no 3 and 6 is rather uniform, and the samples collected from the depth above 3 m (sites no 8, 10) are less sorted. Also, apart from location 10 (9.7 %), clay content is relatively invariable (6.4 – 7.2 %). Nonetheless, there is no general spatial pattern in the clayey till of the saturated zone which would constitute preferential pathways for the groundwater flow.

Water flow across sandy units seems to be independent on their physical properties, yet, anisotropy may be to some extent of importance in case of nonuniform clayey till. Sandy layers observed in the silty till (sites no 302, 303) may constitute preferential flow pathways.

## 9.5. Hydraulic conductivity

As seen in table 9.3. various values of hydraulic conductivity of till, clayey and silty sand as well as of medium sand can be found in the literature. Neverthe-

 $i = -\frac{\partial h}{\partial t}$ 

Reference	Till	Clayey sand	Silty sand	Medium sand
Badient et al. (1999) / Domenico & Schwartz (1990)	$2x10^{-6} - 1x10^{-12}$	-	-	5x10 <sup>-4</sup> – 9x10 <sup>-7</sup>
Fetter (2001)	$10^{-6} - 10^{-8}$	$10^{-6} - 10^{-8}$	$10^{-5} - 10^{-7}$	-
Pisarczyk (2001)	$1.5 \times 10^{-8} - 1.5 \times 10^{-10}$	-	$1.5 \times 10^{-6} - 1.5 \times 10^{-7}$	-
Pazdro (1977)	$10^{-6} - 10^{-8}$	-	$10^{-5} - 10^{-6}$	$10^{-3} - 10^{-4}$
Average range	$1 \times 10^{-6} - 5 \times 10^{-9}$	$10^{-6} - 10^{-8}$	$7x10^{-6} - 4x10^{-7}$	$7x10^{-4} - 5x10^{-5}$

Table 9.3. Representative values of hydraulic conductivity (k; m/s) for materials observed in the investigated area below the ground water table.

Lithology	Site	Depth (m.b.g.s.)	(-)	k (m/s)
Madina	5	1.50 - 3.00	8	1.6x10 <sup>-4</sup>
Medium sand	5	4.00 - 5.00	4	3.2x10 <sup>-4</sup>
Sanu	5 .	5.00 - 6.00	6	1.6x10 <sup>-4</sup>
Clayey till	3	4.00 - 5.00	11	(7.2x10 <sup>-5</sup> )*

Table. 9.4. Hydraulic conductivity of medium sand and clayey till calculated from the Hazen formula, Vanstad.

d<sub>60</sub>/d<sub>10</sub> - ratio between 60 % and 10 % of the finest grains in a sample; k – hydraulic conductivity

less, the ranges of magnitude are similar for particular deposits. Medium sand has values between  $10^{-4}-10^{-5}$  m/s and is the most permeable. Clayey sand and silty sand have less good hydraulic properties and values of hydraulic conductivity do not exceed  $10^{-6}$  m/s. The largest differences in the parameter have been calculated for till. It forms aquifuges with conductivity even as low as  $10^{-12}$  m/s. This might be the case of the claytill observed in the investigated area. But when till indicates filtration coefficient of  $10^{-6}$  m/s<sup>18</sup> it may store and transmit water (aquitard)<sup>19</sup>.

There was an attempt to calculate hydraulic conductivity from the field data. In practice, three methods are employed to determine the parameter: field tests, laboratory tests and empirical methods. While outcomes of laboratory tests refer to particular samples, not to a bulk of a stratum, slug tests provide more reliable results, since they characterize conditions over a larger area of the aquifer. Due to logistic reasons, field methods could not be employed. The empirical correlation method<sup>20</sup> was finally used here as the simplest and commonly used during preliminary hydrogeological investigations (Domenico & Schwartz, 1990; Fetter,

Hazen formula has been proven to be reliable correlation method for sandy sediments in Sweden, used to determine general seepage conditions (Jeppsson, 2005). Thus, it was employed as expressed in fig 9.1. The formula is valid on the condition that the ratio between 60 % and 10 % of the finest grains in a sample,  $(d_{60}/d_{10})$ , in millimetres, does not exceed 5 (Craig, 1997).

$$k = 10^{-2} (d_{10})^2$$
, where (Fig. 9.1.)

k – hydraulic conductivity, in m/s;  $d_{10}$  – effective grain size defined as value where 10 % of the particles are finer and 90 % coarser, in millimetres (Craig, 1997).

Hydraulic conductivity has been calculated for three samples of medium sand and one sample of clayey till, collected in the investigated area (Table 9.4). The method confirms good hydraulic properties of the sand, where  $10^{-4}$  m/s is a typical value for the aquifers. Although the ratio  $(d_{60}/d_{10})$  slightly exceeds 5 in two samples, it does not influence the results much. It looks differently in the case of the till. On the basis

<sup>\*</sup> hydraulic conductivity value is not representative

<sup>2001;</sup> Badient et al., 1999; Pazdro, 1977).

 $<sup>^{18}</sup>$  Geologic units with hydraulic conductivity below  $10^{-7}$  m/s (arbitrary limit) are typical for aquifers, whereas units indicating higher values are called confining layers (Fetter, 2001).

<sup>&</sup>lt;sup>19</sup> The flow in an aquitard is significantly retarded in comparison to an aquifer (Bates & Jackson, 1987; World Meteorological Organisation & UNESCO, 1992).

<sup>&</sup>lt;sup>20</sup> Empirical correlations enable to determine conductivity through comparison with various properties of a porous medium, for instance granulometry. They are simple methods which do not concern natural properties of an aquifer, for instance packing of grains, which have a definite impact on filtration. Therefore, they provide rough calculations of the coefficient (Pazdro, 1977).

of the Hazen formula, clayey till is medium permeable ( $k = 10^{-5}$  m/s). In fact, for many collected till samples, the ratio ( $d_{60}/d_{10}$ ) is much higher than 5 (calculated in hundreds) and the formula can not be applied. Therefore,  $k = 10^{-5}$  m/s is not the representative value for the clayey till observed in the investigated area. Worse hydraulic properties are expected, but permeability of the till cannot be lower than  $10^{-8}$  m/s which is a bottom limiting magnitude required to transmit water through a porous material (Kleczkowski & Różkowski, 1997).

In conclusion, medium sand have the best hydraulic properties ( $k = 10^{-4}$  m/s) and forms the unconfined aquifer. The filtration coefficient of silty sand, gravelly clayey sand and clayey till are typical for aquitards and range between  $10^{-6}$  and  $10^{-8}$  m/s. The silty till is a leaky confining unit too, but it can transmit relatively bigger amounts of groundwater through sandy layers. Field observations imply that the clay till constitutes an important barrier to the groundwater flow (a potentiometric surface is observed at site no 307).

## 9.6. Seepage velocity

Darcy's law, stating linear relationship between velocity, hydraulic conductivity and hydraulic gradient, was employed to determine seepage velocity. It is valid for granular materials and expresses laminar velocity through pore openings by the equation given in fig. 9.2. (Domenico & Schwartz, 1990).

$$V = \frac{ki}{n_e}$$
 , where (Fig. 9.2.)

V - velocity [m/s],

k - hydraulic conductivity [m/s],

n<sub>e</sub> - effective porosity [dimensionless],

i – hydraulic gradient [dimensionless]

Determination of the effective porosity with laboratory methods is complex and requires knowledge of the bulk density. Considering the fact that velocity calculations are not very sensitive to errors in this parameter (hydraulic gradient and hydraulic conductivity values are the decisive parameters), porosity representative values were used instead (from Badient et al., 1999). This does not change the magnitude of the calculated velocity values; however they are lower

in comparison to those which could be calculated for the effective flow.

The hydraulic gradient and hydraulic conductivity values are taken, as described in sections 9.3. and 9.5. Mean permeability ranges are employed for clayey till, clayey sand and silty sand, whereas conductivity of medium sand was calculated from the Hazen formula.

The data and results of the velocity calculations are shown in table 9.5. Due to limited field data, the results can only be considered as approximations of the velocity. The main factor influencing the groundwater flow velocity is the filtration coefficient of the various stratigraphic units. By analogy, the fastest flow takes place through medium sand (10<sup>-6</sup> m/s). The velocity in clayey and silty materials is similar, with magnitudes between 10<sup>-8</sup> and 10<sup>-10</sup> m/s.

## 10. "Clean line" delineation

A term "clean line" stands for a boundary of an area supposed to be contaminated with hydrocarbons. As has been previously explained (chapter 3), the dissolved phase is transported larger distances than the pure-phase fuel; as well as that migration of volatile hydrocarbons in the vadose zone strictly depends on spatial distribution of the dissolved and pure phase. Hence, it was essential to calculate what distance solutes could have been transported from the storage tank, prior to the "clean line" delineation. On the basis of the field data evaluation (chapter 8, 9), it is assumed that:

- Hydrocarbons in a gaseous phase can migrate upwards through all the units comprising the vadose zone (impervious deposits do not occur in the vadose zone), yet sand and gravelly sand constitute the preferential pathways.
- (2) Groundwater flow is a medium transmitting dissolved hydrocarbons. Contaminants are transported to the north through silty and clayey till as well as through silty and gravelly clayey sand. Sand layers can constitute preferential flow pathways in silty sand.
- (3) Groundwater flow velocity refers to a rate of the solutes' transport. Assuming the worst case scenario, the contamination could spread in the saturated at the rate 5.4x10<sup>-8</sup> m/s.

Parameter	Clayey till		Clayey sand		Silty sand		Medium sand
n; -	0.31		0.39 0.39		0.39		0.39
i; -	1.4x	(10 <sup>-2</sup>	1.4x10 <sup>-2</sup>		1.4x	10-2	1.4x10 <sup>-2</sup>
k; m/s	10 <sup>-6</sup>	10-8	10 <sup>-6</sup>	10-8	10 <sup>-6</sup>	10 <sup>-7</sup>	10-4
V; m/s	4.3x10 <sup>-8</sup>	4.3x10 <sup>-10</sup>	5.4x10 <sup>-8</sup>	5.4x10 <sup>-10</sup>	5.4x10 <sup>-8</sup>	5.4x10 <sup>-9</sup>	5.4x10 <sup>-6</sup>
	max	min	max	min	max	min	

**Table 9.5.** Velocity evaluation for materials comprising the saturated zone in the investigated area. n - porosity; i - hydraulic gradient; k - hydraulic gradient g

(4) In the worst case scenario, the gasoline influx started in 1963 (when the petrol station was established). A period between 1963 and 2005 is taken into account to calculate seepage velocity, since this is the longest period when dissolved contaminants can be distributed in the subsurface.

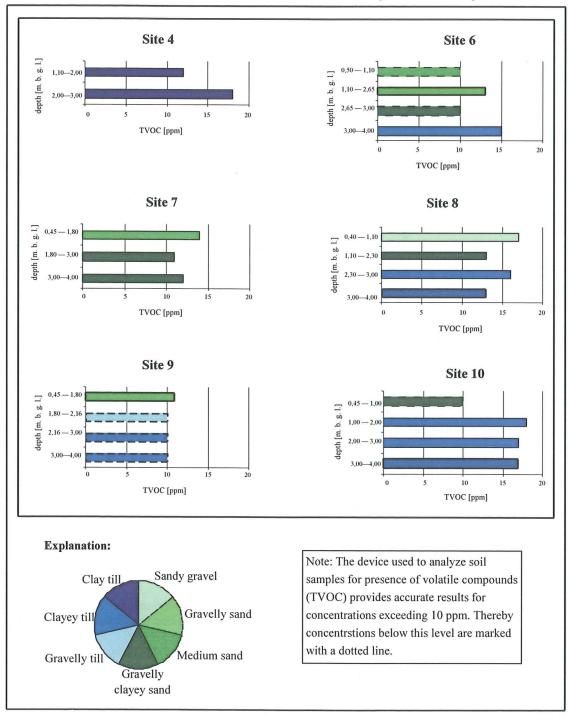
From above, it is calculated that, hydrocarbons pass in groundwater 1.7 m per year, what gives approximately 71 m in 42 years. The "clean line" was subsequently delineated with regard to this distance. The area as-

sumed to be contaminated is marked in the water table map (Appendix 3). Its northern end trends slightly towards north-west because of changing groundwater flow direction.

## 11. Groundwater and soil contamination. Results

### 11.1. Groundwater

Results of the groundwater analyses with GC-PID and



**Fig. 11.1.** TVOC concentrations in soil vapour in the investigated area. PID results. Bar charts show TCOC contents in relation to the depth and lithology.

GC-FID are presented in Appendix 4.

In all analysed samples oil index values do not exceed 50  $\mu$ g, which is the detection level of the instrument.

Analyses of vapour headspace in the groundwater do not indicate presence of Benzene, Toluene, Ethylbenzene, or Xylenes. Some other compounds are, however, registered. In all samples, unidentified compounds are detected, except for those collected at sites no 6 and 10, but the detector response is weak. At locations no 3 and 6 n-Heptane is registered at concentrations of 0.07 and 0.11 ppb. MTBE is identified at location no 7 (1.52 ppb).

#### 11.2. Soil

During the fieldwork a smell of gasoline was not noticed in the soil.

The PID results are shown in fig. 11.1.

Downgradient from the tank, total concentrations of volatile compounds in the soil vapour (TVOC) do not exceed 20 ppm. Indication of 28 % of the samples is lower than the accuracy level of the instrument (10 ppm). This is observed independently of lithology, depth and a distance from the storage tank. Among the results above 10 ppm, relatively higher values were documented in the clayey till (> 15 ppm), but a concentration of 17 ppm was also observed in sandy gravel (site no 8). There is no decreasing, neither increasing relation between distribution of TVOC and depth. For instance at location no 10 the outcomes are very similar for samples collected below and above the water table (-2.13 m); at location no 8 larger concentration is observed at the water surface (-2.46 m), whereas at site no 7 (water table is at -2.80 m) lower concentration is registered above the water table. Further, at sites no 7, 8 and 9 the largest TVOC amounts occur in the uppermost units (gravelly sand and sandy gravel).

At site no 4, situated upgradient from the source of contamination (hence the soil can not be influenced by the leakage from the tank), values documented in clay till indicate an slight increase with depth: 12 and 18 ppm.

## 12. Contamination assessment

## 12.1. Groundwater

The oil index values do not exceed the guideline value for non-polar aliphatic hydrocarbons  $^{21},\ 100\ \mu g/L.$  None of the BTEX compounds, which could be detected in vapour headspace, is documented in the groundwater. Other compounds detected by PID show concentrations lower than the detection level of the

<sup>21</sup>Neither The Swedish Environmental Protection Agency nor The Swedish Petroleum Institute has officially established a guideline value for oil index. The one for non-polar aliphatic hydrocarbons is commonly used in practice (Naturvådsverket & Svenska Petroleum Institutet, 1998; Elert, 2004).

instrument, i.e. 5 ppb. Furthermore, MTBE cannot be detected with chosen settings of the instrument settings and the substance was not used as a gasoline additive in the 60's and 70's. It is inferred that n-Heptane and MTBE values must be due to a measurement error.

In conclusion, the groundwater in the investigated area is not contaminated with hydrocarbons originating from subsurface gasoline release in the property Vanstad 26:19. Hence, there is no negative impact on the proposed water protection area. Neither n-Heptane nor MTBE constitute any threat for groundwater quality.

### 12.2. Soil

Migration of volatile compounds may be retarded in till deposits.

If a pure phase-gasoline was present along the water table, and dissolved hydrocarbons contributed to groundwater contamination, the biggest TVOC amounts would be observed close to the water table. It does not refer to the discussed situation. Furthermore, the groundwater is not contaminated with petroleum hydrocarbons. Hence, gasoline derived compounds (resulting from the leakage of the underground storage tank) are not expected to occur in the soil vapour<sup>22</sup>. This is also sustained by the fact that TVOC concentrations measured upstream and downstream from the storage tank are similar.

Naturvådsverket has not established any guideline or reference values for volatile compounds present in the soil (Naturvådsverket, 2002). In practice, concentrations exceeding 100 ppm are considered to be very high (Vanek, 2005). During the remediation procedures in the property Vanstad 26:19, soils with a VOC level below 30 ppm were classified as not contaminated<sup>23</sup> (Hansson et al., 2004). Hence, TVOC detected in the soil in the investigated area is of very marginal importance.

## 13. Future investigations

- (1) In order to define an extent of contamination from a known contamination source it is advised to do field investigations according to the following steps:
  - 1. Define geology and groundwater flow direction,
  - 2. Define seepage velocity,
  - 3. Emplace piezometers downgradient, in order to define the length of a plume, and collect the samples,
  - 4. Emplace piezometers on a transverse line, in order to define the plume width, and collect the samples,
  - 5. Define plume thickness.

<sup>&</sup>lt;sup>22</sup>Stored fuels constitute not the only possible source of contamination with VOC. Volatile compounds may originate also from automotive and household products, cleansers and disinfectants etc. (U. S. Environmental Protection Agency, last updated on the 6<sup>th</sup> Oct. 2005).

<sup>&</sup>lt;sup>23</sup>During remediation the level of contamination was detected with a field instrument which is less accurate than laboratory methods.

- Laboratory analyses should be conducted where it is appropriate.
- (2) In order to obtain representative groundwater table readings in the piezometers, it is recommended to take the measurements twice (close after the coring and after longer period of time). The filter should be installed at the water table depth.
- (3) In order to obtain a more accurate seepage velocity value, hydraulic conductivity should be estimated from slug tests rather than from empirical correlations and effective porosity should also be calculated.

## 14. Conclusions

- (1) Long term, subsurface fuel releases do not necessarily result in extensive soil and groundwater contamination (as in the Vanstad example: in 42 years only 71 m).
- (2) The fact that contamination is not observed in the investigated area, although the distribution calculations imply so, underlines the huge role of natural attenuation as a factor limiting subsurface contamination with petroleum hydrocarbons.

## **Acknowledgments**

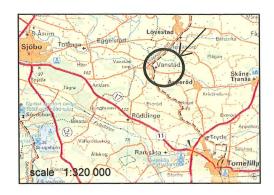
Above all, I am very grateful to my supervisors, prof. Per Sandgren, and Hans Jeppsson from SWECO VIAK AB for constructive discussions and assistance during the preparation of the manuscript. I would like to thank Vladimir Vanek for his assistance in the SWECO VIAK AB laboratory and Esbjörn Tagesson from the same company who rendered the reports of Vanstad 26:19 accessible. I also wish to thank my ERASMUS friends, especially to Ernesto Beltrame and Marton Megyeri for their patience and help during the fieldwork.

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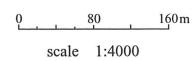
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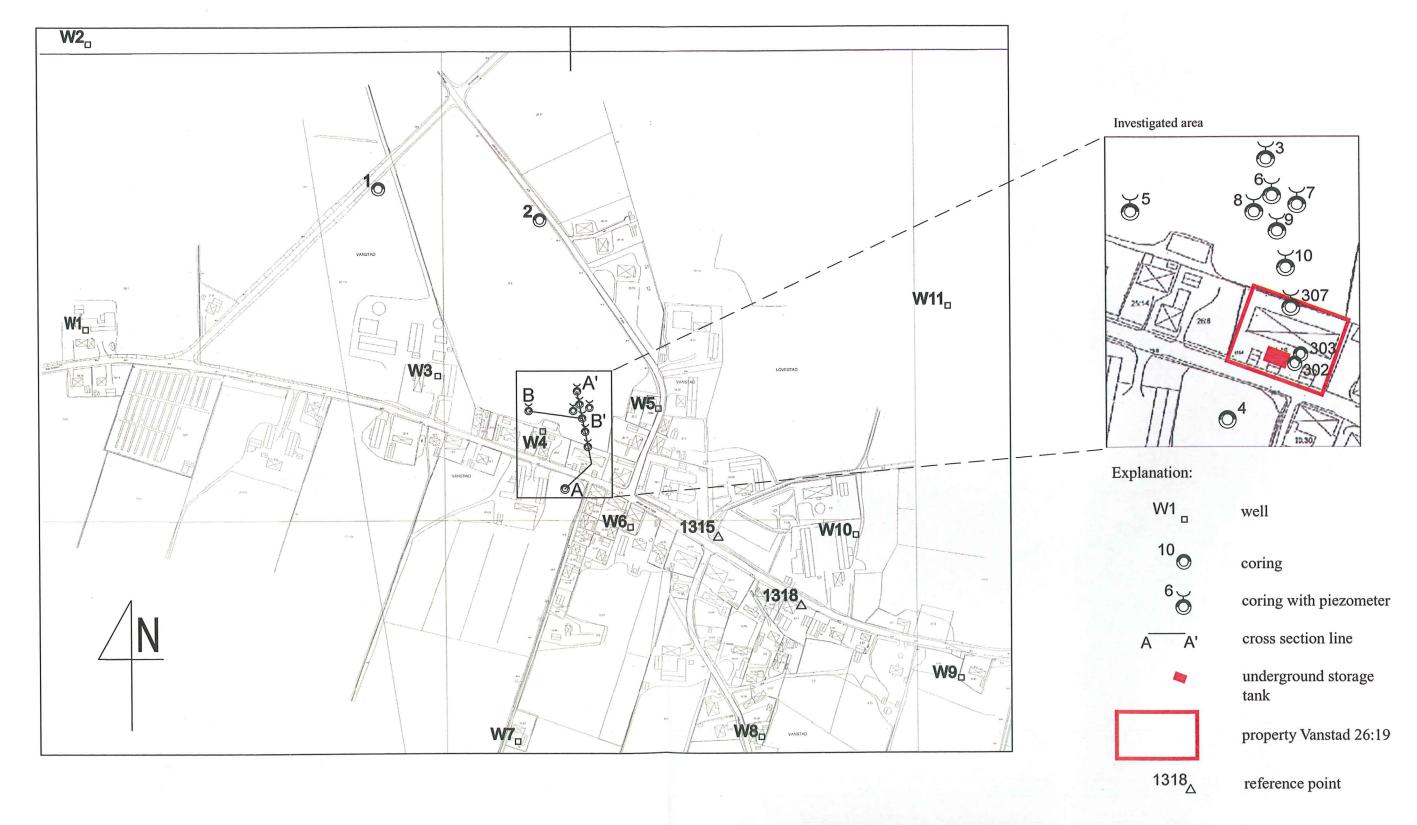
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## Site Map





**Note:** The device used to analyze soil samples for presence of volatile compounds (TVOC) provides accurate results for concentrations exceeding 10 ppm. Thereby, concentrations below this level are marked with "< 10".

Site designation:	Ground surface elevation: 86,22 m.a.s.l.		Groundwater table observations		
			Elevation [m.b.g.l./m.a.s.l.]:		Date:
Completion date: 3 <sup>rd</sup> June 2005	Drilling method: hand-auger / truck mounted direct push rig	Pipe diar	neter: -	Top	of casing elevation:

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,50	topsoil				
0,50 – 1,20	sand	brown, dry	0,50 – 1,20		
1,20 – 1,50	gravelly sand	brown, dry	1,20 – 1,50		
1,50 – 3,00	sand	brown, dry	1,80 – 2,80		
3,00 – 4,00	gravelly sand	brown, dry	3,00 – 4,00		
4,00 – 5,00	clayey till	grey, moist	4,00 – 5,00		

Site designation:	signation: Ground surface elevation: 79,93 m.a.s.l.			Groundwater table observations		
			Elevation [m.b.g.l./m.a.s.l.]: 3,43 / 76,50		Date: 3 <sup>rd</sup> June 2005	
Completion date: 3 <sup>rd</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe diar	neter: 63 / 57 mm	Top	of casing elevation: 80,18 m.a.s.l.	

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 - 0,55	topsoil				
0,55 – 1,20	clay till	brown, dry, no odour	0,55 – 1,20		
1,20 – 2,40	gravelly clayey sand	grey, dry, no odour	1,20 – 2,40		
2,40 – 3,30	sand	brown, dry, no odour	2,40 – 3,30		х
3,30 – 6,00	clayey till	grey, moist, no odour	3,30 - 4,00 4,00 - 5,00 5,00 - 6,00		

Site designation: Ground surface elevation: 80,31 m.a.s.l.			Groundwater table observations			
				Elevation [m.b.g.l./m.a.s.l.]:		Date:
Completion da 3 <sup>rd</sup> June 2		Drilling method: truck mounted direct push rig	Pipe dia	meter:	Top	o of casing elevation:

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,45	topsoil			_	
0,45 – 1,10	clayey till	grey, dry, no odour	0,45 – 1,10		
1,10 – 4,50	clay till	brown, dry, no odour	1,10 - 2,00 2,00 - 3,00 3,00 - 4,50	12 18	þ

Site designation:	Ground surface elevation: 79,15 m.a.s.l.	Groundwater table observations			ole observations
			Elevation [m.b.g.l./m.a.s.l.]: 2,57 / 76,58		Date 3 <sup>rd</sup> June 2005
Completion date: 3 <sup>rd</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe diar	neter: 25 / 21 mm	Top	o of casing elevation: 79,74 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,60 0,60 – 6,00	topsoil sand	brown, dry to wet, no odour	0,60 - 1,50 1,50 - 3,50 4,00 - 5,00 5,00 - 6,00		x

Site designation:	Ground surface elevation: 79,29 m.a.s.l.		Groundwater table observations		ble observations
			Elevation [m.b.g.l./m.a.s.l.]:		Date: 13 <sup>th</sup> June 2005
Completion date: 13 <sup>th</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe diar	meter: 25 / 21 mm	Top	o of casing elevation: 79,44 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 - 0,50	topsoil				
0,50 – 1,10	sand	brown, dry, no odour	0,50 - 1,10	< 10	
1,10 – 2,65	gravelly sand	brown, dry, no odour	1,10 – 2,30	13	
2,65 – 3,00	gravelly clayey sand	grey, moist, no odour	2,65 – 3,00	< 10	х
3,00 -4,00	clayey till	grey, wet, no odour	3,00 – 4,00	15	
4,00 - 5,00	gravelly clayey sand	grey, soaked, no odour	4,00 – 5,00		

Site designation:	Ground surface elevation: 79,19 m.a.s.l.	Groundwater table observations		
		4	Elevation [m.b.g.l./m.a.s.l.]: 2,80 / 76,39	Date: 13 <sup>th</sup> June 2005
Completion date: 13 <sup>th</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe diar	neter: 25 / 21 mm	Top of casing elevation: 79,33 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,45	topsoil				
0,45 – 1,80	gravelly sand	brown, dry, no odour	0,45 – 1,80	14	
1,80 – 4,00	gravelly clayey sand	grey, moist, no odour	1,80 – 3,00 3,00 – 4,00	11 12	x
4,00 – 5,00	sand	brown, wet, no odour	4,00 - 5,00		

Site designation: 8	Ground surface elevation: 78,85 m.a.s.l.	Groundwater table observations			
			Elevation [m.b.g.l./m.a.s.l.]: 2.46 / 76.39		Date:
Completion date: 13 <sup>th</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe di	ameter: 25/21 mm	Top	p of casing elevation: 79,05 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 - 0,40	topsoil				
0,40 – 1,10	sandy gravel	brown, dry, no odour	0,40 – 1,10	17	-
1,10 – 2,30	gravelly clayey sand	grey, moist, no odour	1,10 – 2,30	13	x
2,30 – 5,00	clayey till	grey, wet to soaked, no odour	2,30 – 3,00 3,00 – 4,00 4,00 – 5,00	16 13	, == = =

Site designation:	Ground surface elevation: 78,68 m.a.s.l.		Groundwater table observations	
			Elevation [m.b.g.l./m.a.s.l.]: 2,95 / 75,73	Date: 13 <sup>th</sup> June 2005
Completion date: 13 <sup>th</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe dia	ameter: 25 / 21 mm	Top of casing elevation: 78,78 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,45	topsoil	7			
0,45 – 1,80	gravelly sand	brown, dry, no odour	0,60 – 1,80	11	
1,80 – 2,16	gravelly till	grey, moist, no odour	1,80 – 2,16	< 10	x
2,16 – 5,00	clayey till	grey, wet, no odour	2,16 - 3,00 3,00 - 4,00 4,00 - 5,00	< 10 < 10	

Site designation: 10	Ground surface elevation: 78,25 m.a.s.l.	Groundwater table observations		
			Elevation [m.b.g.l./m.a.s.l.]: 2,13 / 76,12	Date: 13 <sup>th</sup> June 2005
Completion date: 13 <sup>th</sup> June 2005	Drilling method: truck mounted direct push rig	Pipe d	iameter: 25 / 21 mm	Top of casing elevation: 78,60 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,45	topsoil				
0,45 – 1,00	gravelly clayey sand	brown, dry, no odour	0,45 – 1,00	< 10	
1,00 – 4,00	clayey till	grey, moist to soaked at 3-4m, no odour	1,00 - 2,00 2,00 - 3,00 3,00 - 4,00	18 17 17	х
4,00 -5,00	gravelly clayey sand	grey, wet, no odour	4,00 – 5,00		

Site designation:	Completion date:	Drilling method:
302	25 <sup>th</sup> Sept 2003	Screw drill with help of truck mounted rig

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 3,40	Artificial fill: silty sand rich in humus	At the depth 1,80 – 3,40 m.b.g.l. brown and moist			- 1
3,40 – 5,00	Silty till with thin sand layers	Grey, moist - wet			

Site designation:	Completion date:	Drilling method:
303	25 <sup>th</sup> Sept 2003	Screw drill with help of truck mounted rig

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 - 1,20	Artificial fill: gravelly sand				
1,20 – 2,20	Sandy silty till	Greyish-black			
2,20 – 3,40	Silty till with thin sand layers	Black, moist		100	
3,40 – 5,00	Gravelly silty sand	Grey, wet			

Site designation: Ground surface elevation: 78,94 m.a.s.l.		Groundwater table observations		
			Elevation [m.b.g.l./m.a.s.l.]: 2,2 / 76,74	Date: 13 <sup>th</sup> June 2005
Completion date: 25 <sup>th</sup> Sept 2003	Drilling method: Screw drill with help of truck mounted rig	Pipe d	iameter: 50	Top of casing elevation: 79,54 m.a.s.l.

Depth [m. b. g. l.]	Soil classification	Observations	Soil sample withdrawal	TVOC [ppm]	Groundwater analyze
0,00 – 0,50	Artificial fill: sandy silty soil with humus	Brownish-black			
0,50 – 2,15	Artificial fill: silty till rich in humus	Grey			
2,15 – 2,70	Sandy clayey soil with humus	Brownish-black, moist			
2,70 - 3,00	Sandy clay till	Grey, moist		= 1	
3,00 -4,50	Gravelly clayey sand with clay layers	Grey, wet			

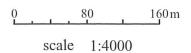
Date:

13.06.05.

13.00.0	J.		
Site	Groundwater	Ground surface	Depth to the water
designation	elevation	elevation	table
	[m.a.s.l.]	[m.a.s.l.]	[m]
W1	76.25	79.26	3.01
W2	75.31	82.13	6.82
W3	76.45	79.54	3.09
W4	76.65	78.35	1.70
W5	76.54	79.47	2.93
W6	78.91	80.69	1.78
W7	87.10	88.25	1.15
W8	86.76	87.99	1.23
W9	80.97	83.11	2.14
W10	78.45	80.01	1.56
W11	75.04	77.62	2.58
3	76.50	79.93	3.43
5	76.58	79.15	2.57
7	76,39	79,19	2.80
8	76,39	78,85	2.46
9	75,73	78,68	2,95
10	76,12	78,25	2,13
307	76,74	78,94	2,20

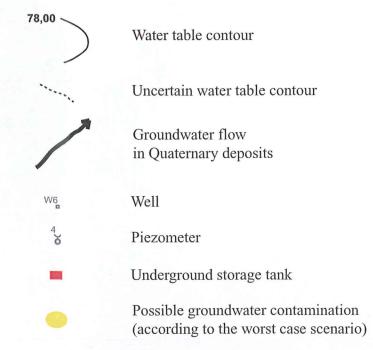
Table. Groundwater levelling results.

## Water table map of Vanstad





## Explanation:



#### Gas chromatography. Method description.

On a gas chromatograph, sample components first become separated from one another in a separating column. The components are retained afterwards for a different length of time, and elute into a detector at a retention time, characteristic for each a compound. The detector responds as each component flows through the detector cell. If the detector response is displayed against the elapsed time, then a series of peaks separated in time is seen. The retention time of the tip of each peak indicates the component, while the area of the peak it's concentration. Since the gas chromatograph is a comparative technique, reported outcomes are based on the retention times and peak sizes of previously analyzed standards. If they match, the peak is identified as the corresponding library compound. So as to calculate the concentration, the peak area is divided by the library sensitivity for the compound<sup>1</sup>. In total volatile compounds mode a sample is carried directly to the detector, and the separating columns are bypassed. Therefore, the detector response is a single pick representing the composite of all detectable compounds in the sample.

Library retention times and sensitivities were updated automatically before the analysis, as set out in the table below.

Compound	Retention time [sec]		
Benzene	226		
Toluene	394		
Ethylobenzene	699		
p-xylene	705		
m-xylene	741		
o-xylene	950		

Retention times of library components of interest detectable by the photoionization detector (PID) in a column applicable for mid-range compounds. Voyager Portable Digital Gas Chromatograph (Vanek, 2005).

The basic difference between FID and PID is that, respectively, a hydrogen/air flame or ultra-violet light which caries 10,6 eV of energy is directed at the eluting molecules, to produce ions. The carrier gas and the sample matrix (argon, carbon dioxide, nitrogen, oxygen, water vapour, etc.) have relatively higher Ionization Potential (IP) than the energy of light in FID; thus, cannot be ionized. The ionized molecules, collected by electrodes, generate a current proportional to analyte concentration, which is further converted to a digital signal.

PID is applied only to air analysis. Hence in case of water samples a vapour headspace is screened (PE Photovac, 1997; School of Chemistry & Physics, The University of Adelaide).

#### Oil Index values. GC-FID.2

From: Analytica AB, Nytorpsvägen 16, 183 25 Täby. Tfn: 08/52 77 52 00. Fax: 08/768 3423. Email: taby@e [per.sandgren@geol.lu.se] To: Lunds Universitet Ref: Per Sandgren Program: VATTEN Ordernumber: T0503490 Report created: 2005-07-05 by tommy SAMPLE V4 21,06.05 13.05 V8 21,06.05 12.45 V11 21,06.05 13.25 ELEMENT ia ia dekantering ja oljeindex >C10-C40 µg/l < 50 < 50 < 50

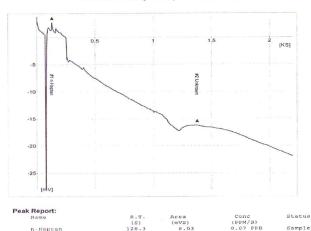
<sup>&</sup>lt;sup>1</sup> the response (peak area) to concentration ratio, [mVS/ppm] (PE Photovac, 1997).

<sup>&</sup>lt;sup>2</sup> The groundwater samples refer to following sites: V4 – Site 3; V8 – Site 7; V11 – Site 10



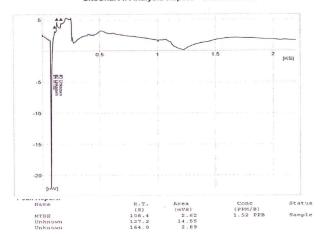
Site 3

#### SiteChart II Analysis Report - B5062000.PID



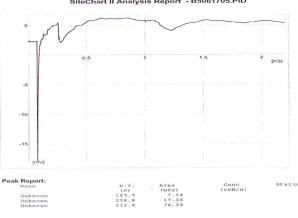
Site 7

#### SiteChart II Analysis Report - B5061709.PID



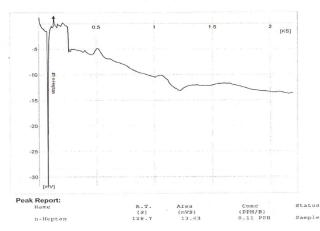
Site 9

#### SiteChart II Analysis Report - B5061705.PID



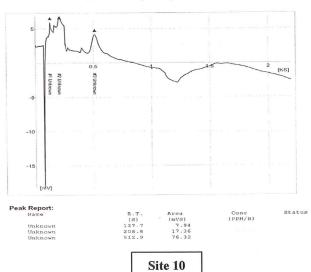
Site 6

## SiteChart II Analysis Report - B5062001.PID

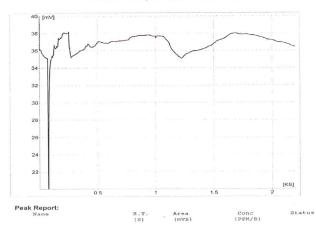


Site 8

#### SiteChart II Analysis Report - B5062002.PID



SiteChart II Analysis Report - B5061702.PID



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