Institut für Hydrologie
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"Urban water quality-organic pollution in the city of Ramallah, West Bank"

Diplomarbeit unter der Leitung von Prof. Dr. Ch. Leibundgut
Freiburg i. Br., Januar 2006

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Table of contents

List of figures

List of tables

Table of contents of the Annex

Notation

Used symbols:

Caq = concentration of test substance in aqueous phase at equilibrium (µg. g^{-1} or µg.ml^{-1})
Csoil = concentration of test substance in soil at equilibrium (µg. g^{-1})
fa = fugacity for the air phase
fw = fugacity for the water phase
fr = reference fugacity
F = fugacity coefficient
m = total mass (kg)
mf = mole fraction of the solute in water
Pt = total pressure in Pascal.
p^o = vapour pressure of the solute at the system temperature in Pascal
V = total volume (m^3)
y = mole fraction of the solute in the air
x = amount of adsorbed test substance (µg)
γ = activity coefficient of the solute in water
ρ = object's density (kg/m^3)

Used abbreviations:

a. s. l: above sea level
ATDSR: Agency for Toxic Substances and Disease Registry
Conc.: Concentration
CPI: Carbon Preference Index
DVGW: Deutsche Vereinigung des Gas- und Wasserfaches
H: Henry's Law Constant
IDEL: Interdepartmental Equipment Laboratory
Kd: Distribution Coefficient
Kf: Freundlich Adsorption Coefficient
Koc: Soil Adsorption Constant.
Max: Maximum
MCL: Maximum Contaminant Level
MTBE: Methyl.tert.butyl ether
n.d.: no data
OECD: Organisation for Economic Cooperation and Development
PAH: Polycylic Aromatic Hydrocarbon
SVOC: Semi Volatile Organic Compound
U. S. EPA: U.S Environment Protection Agency
USGS: United States Geological Survey
VOC: Volatile Organic Compound

Summary

Volatile organic compounds (VOCs) as well as semi volatile organic compounds (SVOCs) are assessed in runoff water from four catchments located in Ramallah. Runoff is sampled from different types of urban surfaces; catchments having different percentages of impervious areas, in four stations. Three belong to a same drainage system, in the city centre, and one is located in the surroundings of the city. Additionly, the compounds are sampled from a roof station. The compounds are also measured in a spring located in the city.

First, different compounds are characterised according to their chemical families and their physical properties. This knowledge is then used to explain observed concentrations in runoff. This analysis allows drawing conclusions about the origins and the sources of these compounds. It is shown that these contaminants are mostly derived from petroleum sources and are washed out from non-point sources such as the roads for example. Urban air in Ramallah is also shown to be a non-point source. This is the case for a group of semi volatile compounds: *n*-alkanes from *n*-C$_{15}$ to *n*-C$_{28}$, that most probably originate from atmospheric fallout.

A thorough analysis of the hydrology situation that occurres on the sampling days suggests that roads are the primary source contributing to runoff.

The high concentrations measured in the spring are evidence for the influence of the city on the spring, as the aquifer in question is a karst aquifer, and allows a lot of compounds to enter and flow through it without being sorbed.
Methyl-tert- butyl ether (MTBE) is detected having a concentration of 0.1µg/L in year 2000. The concentration is comparable to MTBE's concentrations measured in German groundwater. Unfortunately it is not possible to extract a trend from the data, because of the short time period (two years).

The data comparison with 16 cities in the United States reveals significant higher concentrations for the two gasoline related compounds Total Xylene and Toluene. The Total Xylene and Toluene mean concentrations measured in Ramallah are 1.1 µg/L and 0.6µg/L respectively, and 0.4µg/L and 0.3µg/L in the United States. Nevertheless, the MTBE concentrations in Ramallah are lower than in the United States (0.1µg/L and 1.5µg/L respectively).
The Benzene and Toluene concentrations measured in Ramallah and in a parking lot in Brooklyn also show higher concentrations in Ramallah, whereas no differences are noticed on the compounds behaviour in the runoff.
Another comparison is done with a catchment in Paris. The analysis here focusses on aliphatic hydrocarbons: *n*-alkanes from *n*-C$_{15}$ to *n*-C$_{28}$, as well as on two isoprenoids: Pristane and Phytane. Here also, the concentrations measured in Ramallah are significantly higher. The total aliphatic concentration is estimated to be 128.5µg/L in Ramallah and 68.1µg/L in Paris. More than assessing significantly higher concentrations in Ramallah, the use of the Carbon Preference Index as well as the C$_{17}$/Pristane and C$_{18}$/Phytane ratios allow determining that the source of pollution is the same for both cities: traffic pollution. The significant higher concentrations measured in Ramallah compared to other cities are alarming.

The following work shows that runoff water in Ramallah has a higher organic pollution compared to other cities. This urban stormwater would most effectively be protected by

controlling land surface sources. An increase of the public environmental awareness is also necessary.

Zusammenfassung

Abflüsse von vier verschiedenen Einzugsgebieten in Ramallah (West Bank) wurden auf flüchtige und halbflüchtige organische Verbindungen (VOCs bzw. SVOCs) untersucht.
Abflüsse verschiedener urbaner Oberflächen wurden beprobt; die jeweiligen Einzugsgebiete weisen unterschiedliche Versieglungsgrade auf.
Insgesamt wurden Proben an vier Abflussmessstationen genommen, von denen drei Stationen zu dem gleichen Kanalsystem im Stadtzentrum gehören und eine am südwestlichen Stadtrand gelegen ist. Zusätzlich wurde der Niederschlag, der auf einem Dach gesammelt wurde, beprobt. Die Schadstoffanalyse wurde ebenfalls für eine Quelle in die Stadt durchgeführt.

Zunächst werden anhand der chemischen Familie und der physikalischen Eigenschaften die verschiedenen Verbindungen charakterisiert. Mit den hieraus gewonnenen Erkenntnissen werden die in den Abflüssen beobachteten Konzentrationen interpretiert, um Schlussfolgerungen über die Stoffe und deren Herkunft ziehen zu können. Es wird gezeigt, dass diese Schadstoffe hauptsächlich aus ölhaltigen Quellen stammen und diffus eingetragen wurden, beispielsweise von Straßen. Zu diesen diffusen Quellen kann auch die städtische Luft in Ramallah gezählt werden. Dies kann besonderes an den halb flüchtige Verbindungen den *n*-Alkane von *n*-C15 bis *n*-C28 gezeigt werden, die hauptsächlich aus atmosphärische Deposition stammen.

Eine gründliche Analyse der hydrologischen Situation während des Beprobungszeitraums weißt darauf hin, dass die Straßen die primären abflussbeitragenden Flächen sind.

Die hohen Konzentrationen, die in der beprobten Quelle gemessen wurden, liefern einen Beweis für den Einfluss der Stadt auf die Quelle, da der in Frage kommende Aquifer ein Karstsystem darstellt, der von vielen Komponenten sorptionsfrei durchflossen werden kann.
Methyl-tert Butyl Ether (MTBE) wurde im Jahr 2000 mit einer Konzentration von 0.1µg/L nachgewiesen, die vergleichbar ist mit Konzentrationen in Grundwässern in Deutschland. Aufgrund der zu kurzen Datenreihe (zwei Jahre) ist es leider nicht möglich eine Trendanalyse durchzuführen.

Der Vergleich der gemessenen Daten mit 16 Städten in den USA zeigt signifikant höhere Konzentrationen der beiden Benzininhaltsstoffe Total Xylol und Toluol in Ramallah. Die mittleren Konzentrationen von Total Xylol und Toluol betragen in Ramallah 1.1 µg/L bzw. 0.6µg/L und 0.4µg/L bzw. 0.3µg/L in den Vereinigten Staaten. Die gemessenen MTBE-Konzentrationen sind niedriger als in den Vereinigten Staaten (Ramallah: 0.1µg/L; USA: 1.5µg/L).
Die Benzol- und Toluol-Konzentrationen in Ramallah sind ebenfalls höher als in Brooklyn, USA. Das Verhalten der beiden Komponenten im Oberflächenabfluss ist in beiden Städten gleich.
Ein weiterer Vergleich mit einem Pariser Einzugsgebiet stellt die aliphatischen Kohlenstoffe in den Mittelpunkt (*n*-Alkane von *n*-C15 bis *n*-C28 und zwei Isoprenoide Pristane und Phytane). Auch hier sind die Konzentrationen in Ramallah signifikant höher: 68.1µg/L in Paris und 128.5µg/L in Ramallah. Der *Carbon Preference Index* und die C17/Pristane- und C18/Phytane- Verhältnisse weisen hin auf die Quelle der Verschmutzung, die in beiden Städten dieselbe ist, nämlich der Straßenverkehr.

Die folgende Arbeit zeigt, dass der Oberflächenabfluss in Ramallah eine stärkere organische Verschmutzung als andere Städte aufweist. Um die Reinhaltung des städtischen Oberflächenabflusses zu gewährleisten, sollten versiegelten Flächen stärkeren Kontrollen unterliegen. Ein weiterer Schritt wäre die Steigerung des öffentlichen Umweltbewusstseins.

1. Introduction

Although people have lived in cities for thousands of years, urban development has significantly accelerated over the past century. In 1900, only 10% of the world's population lived in cities. Today, more than half is currently living in urban areas and these areas are expected to accommodate most of the projected increases in population for both developed and developing countries (United Nations, 1991).

The growing urbanisation and the increase of anthropic activities that arises from it, have provoked great concern about urban runoff principally for two reasons: First, because of its quantity (floods), and secondly because of its quality (pollution).

In undeveloped areas, the runoff undergoes long surface travel times and the drainage pattern is formed by natural flow paths. Here, the soil type, the presence of vegetation and the topography play very important roles in the runoff response to rainfall. The infiltration of the water is possible and attenuates its response to rainfall.

The expansion of cities is usually associated with changes in their natural hydrological balance. The infiltration capacity is reduced because of the occurrence of impervious areas, followed by an increase of runoff. Also the absence of vegetation and the less existing topography consequently enhances the runoff quantity. Additionally, the drainage systems present in cities intensify the rates of runoff. These reasons illustrate the runoff quantity problems in urban areas (Osman Akan, 2003; Johnson, 1997).

Urban areas can be divided into main roads (including parking lots and airports), roofs, residential, commercial and industrial areas, lawns and open areas (Asaf, 2004).

A great mixture of pollutants from cars, leaking storage tanks and gas stations, for example, are washed out from these urban areas and then carried by urban stormwater. The pollutants that are studied in this work are all hydrocarbons, more precisely volatile organic compounds and semi volatile organic compounds.

Volatile organic compounds (VOCs) have chemical and physical properties that allow the compounds to move freely between the water and the air phases of the environment. These compounds generally have low molecular weights, high vapour pressures, and medium water solubilities (Rathbun, 1998). Semi volatile organic compounds (SVOCs) are only considered as "semi" volatile as they are characterised by higher molecular weights, lower vapour pressures and are practically all insoluble in water.

VOCs are widely used in urban areas and were identified as potential contaminants in 38% of community water systems in the United States (U. S. Environmental Protection Agency, 1997). These compounds occur in various products including fuels, solvents, paints, adhesives, deodorants and refrigerants (Smith, 1988; Bloemen, 1993).

SVOCs are found in fuel and solvents as well, and in food derivates.

Because of the mobility and the toxicity (health hazard for humans) of these compounds, they are often the focus of water quality investigations. Consequently, a good understating of these compounds' behaviour and a good knowledge of their sources of emission is necessary. Their sources of emission can be classified as point sources (e.g.: gas station) or non-point sources. In the case of a non-point source, the pollution is emitted from multiple small sources spread over a considerable area (Moilleron, 2002). Urban air for example can be considered as a non-point source.

Knowing that Ramallah City has the highest rates of urbanisation in Palestine, and that the undeveloped city drainage network only allows direct connections to the road or the drainage network for modern houses, whereas the traditional houses drain their water to the gardens, an investigation on the water quality in Ramallah is from great importance.

For this purpose, the concentrations of over 30 VOCs and over 50 SVOCs have been measured in the urban stormwater (in Ramallah and its surroundings) and in a spring located in the north-west of the city centre. The runoff samples are taken in the year 2000 for the VOCs and in the years 2000 and 2001 for the SVOCs.

The objective of the analysis described in this study is to assess the level of organic pollution in Ramallah. The relative importance of land surfaces is determined, as together with air, it is the only possible non-point source (Lopes, 1998).

The compounds are also described accordingly to their physical properties (e.g.: Soil Adsorption Constant, Henry's Law Constant, Vapour pressure) as these influence the behaviour of the compounds in the hydrological system.

At last, a comparison of the measured concentrations is carried out between Ramallah and other cities, in Europe and the United States, in order to obtain a relative insight of the degree of exposure in Ramallah.

2. Chemical and physical properties of organic compounds

2.1 Chemical families:

In order to get familiar with the basic terminology of organic chemistry, this chapter is intended to summarise the main chemical families and their corresponding nomenclature. Because of the high number of compounds that has been measured in Ramallah, they are divided in different chemical families, which make the analyses that are made in following chapters easier. The five major chemical families are described here.

2.1.1 Aliphatic hydrocarbons

In the aliphatic hydrocarbon group, carbons are linked in a linear fashion, without forming rings or cycles. The saturated compounds (containing only hydrogen and carbon) are known as alkanes and possess the following empirical formula C_nH_{2n+2}. Alkanes that have four or more carbon atoms can exist in both straight-chain and branched-chain isomers. Those compounds containing one double bond and possessing the general empirical formula C_nH_{2n} are called alkenes. Aliphatics with one triple bond are referred to as alkynes and have the formula C_nH_{2n-2} (Moore, 1984).

2.1.2 Oxygenated alicyclic hydrocarbons

When hydrocarbons chains are joined to make a ring, they are known as alicyclic. The term oxygenate indicates that they contain oxygen. These differ from the previously described aliphatic hydrocarbons as they may be branched, but not in the form of rings. A compound only needs to have one ring to be considered alicyclic, whether aliphatic chains are attached to it or not. They also may have double or triple bonds. However, if a compound contains a 6-membered ring with alternating double and single bonds, then it belongs to the aromatic family (see below). Alicyclic compounds often have the prefix, “cyclo” and have the formula (same as the aliphatic alkenes) C_nH_{2n}.

2.1.3 Aromatic hydrocarbons monocyclics

Monocyclic aromatic hydrocarbons are made of a basic benzene ring with six carbon atoms, six hydrogen atoms, and three double bonds. Although the carbon atom is bonded to three other atoms rather than four, the ring is not considered unsaturated and its stability results from the resonating electron structure (Moore, 1984). Consequently, the stability of the molecule increases with the number of possible arrangements of the electrons.

Aromatic compounds owe their name to the fact that they possess a characteristic odor. The simplest aromatic compound is benzene, and there is a wide range of benzene derivates of great commercial and environmental importance, such as Toluene, Ethylbenzene and Xylenes.

2.1.4 Aromatic hydrocarbons polycyclics

Polycyclics aromatic hydrocarbons (PAH) - otherwise known as polynuclear aromatic hydrocarbons - are fused compounds built on a benzene ring. The resulting structure is a molecule where all carbon and hydrogen atoms lie on one plane. The PAH differ from one another in the number and position of the aromatic rings.

Logically, the physical and the chemical properties of PAH will vary according to molecular weight. An example here is that water solubility and vapour pressure decrease almost logarithmically with increasing molecular weight. Consequently, PAH have the tendency to be absorbed by sediments and deposited in bottom sediments, accumulating to high concentrations. Volatilization can play an important role in the transport of PAH. Laboratory studies, (Southworth, 1979) have shown that the volatilization rates of most PAH increases with increasing vapour pressure.

2.1.5 Chlorinated hydrocarbons

Chlorinated hydrocarbons are also called organochlorines, and are the hydrocarbons containing chlorine.

2.2 Physical properties

2.2.1 Water solubility

The water solubility, also known as aqueous solubility, is the maximum amount of a substance that can dissolve in water at equilibrium at a given temperature and pressure. This parameter is used to determine the fate of compounds in the environment, as compounds having high water solubilities tend to behave in the same way as the water intensity in which they flows.

2.2.2 Vapour pressure

One of the most important physical characteristic describing the behaviour of a compound is its vapour pressure, as it is a measure for its tendency to evaporate. More precisely, it is the pressure that a vapour exerts when it is in equilibrium with its pure liquid or solid form. As a result, the higher the vapour pressure of a constituent, the more readily it evaporates into the vapour phase. As a general rule, compounds having vapour pressures higher than 0.5 mm Hg are considered to be easily detectable, as they then occur in the source area (Alvarez, 1997).

2.2.3 Density

The density of a compound is defined as its unit of mass per its unit of volume. The average density is defined as its total mass divided by its total volume. The unit of density is kilogram per cubic metre and the formula is:

$$\rho = \frac{m}{V}$$

where:
ρ = object's density (kg/m^3)
m = object's total mass (kg)
V = object's total volume (m^3)

The most important characteristic of a compound's density is that compounds having higher densities tend to sink rather than float in water.

2.2.4 Soil Adsorption Constant

The estimation of the Soil Adsorption Constant in the following chapter is based on the OECD guideline (2001).
An important parameter that enables the description of the sorption behaviour of a compound is the Soil Adsorption Constant. It is defined as the ratio between the concentration of the substance in the soil and the concentration of the substance in the aqueous phase at adsorption

equilibrium. The adsorption coefficient normalized to the organic content of the soil Koc is a helpful indicator of the binding capacity of a chemical on organic matter of soil and allows comparisons to be made between different chemicals.
This parameter is obtained by calculating Kd (Distribution Coefficient) and Kf (Freundlich Adsorption Coefficient).
Kd is defined as being the ratio of equilibrium concentrations C of a dissolved test substance in a two phase system consisting of a sorbent (soil) and an aqueous phase. When both concentrations are expressed on a weight/weight base, the distribution coefficient is then dimensionless. If not, it will be given in ml.g-1 (in the case that the concentration in the aqueous phase is given on a weight/volume base). Also, Kd is dependent on the sorbent properties.

$$Kd = \frac{Csoil}{Caq} \tag{1}$$

where:
Csoil = concentration of test substance in soil at equilibrium (µg. g^{-1})
Caq = concentration of test substance in aqueous phase at equilibrium (µg. g^{-1} or µg.ml^{-1}).

The second coefficient that is needed for the calculation of the Soil Adsorption Constant is the Freundlich Adsorption Coefficient (Kf). It is defined as the concentration of the test substance in soil (x/m) when the equilibrium concentration Caq in the aqueous phase is equal to one; units are µg.g-^{1} sorbent. For the Freundlich Adsorption Coefficient as well, the concentrations can vary depending on the sorbent properties.

$$\log\frac{x}{m} = \log Kf + \frac{1}{n} \times \log Caq \tag{2}$$

where:
x/m = amount of test substance x (µg) adsorbed on amount of sorbent m (g) at equilibrium
1/n = slope of Freundlich isotherm
Caq = concentration of test substance in aqueous phase at equilibrium (µg. ml^{-1}).

Also, at Caq = 1, $\log Kf = \log\frac{x}{m}$

At last, the Soil Adsorption Constant is obtained by normalizing the Distribution Coefficient (Kd) and/or the Freundlich Adsorption Coefficient (Kf) to the carbon content (foc) of a sorbent (equation 1 and 2),

$$Koc = \frac{Kd}{foc} \text{ (dimensionless or ml. } g^{-1}\text{) or } \frac{Kf}{foc} \text{ (µg. } g^{-1}\text{)} \tag{3}$$

The Soil Adsorption Constant is an indicator for the adsorption between a substance and the sorbent and allows comparisons to be made between different compounds. The Soil Adsorption Coefficients of the different volatile and semi volatile organic compounds analysed in this work, are given in the dimensionless way and are estimated mostly for aquifer material.

2.2.5 Henry's Law Constant

Henry's Law Constant is a measure of a compound's tendency to partition between water and vapour. This constant indicates the likelihood of detecting a constituent in storm water or groundwater for example. Various defining equations for the Henry's Law Constant have been presented in the literature. These defining equations have resulted in Henry's Law Constants with a variety of dimensional units and also a non-dimensional form. Therefore, great care is to be taken when using Henry's Law Constant from the literature, as one form can be the reciprocal of the other (Rathbun, 1998).

Henry's Law applies to dilute solutions and describes the distribution of a solute between water and air phases at equilibrium. If these phases are in equilibrium, then the fugacities, f, must be equal:

$$fa = fw \tag{1}$$

For the air phase:

$$fa = yFPt \tag{2}$$

where:
y = mole fraction of the solute in the air
F = fugacity coefficient
Pt = total pressure in Pascal.

The fugacity coefficient F distinguishes the degree of non-ideality in the air phase. For low concentrations characteristic of environmental situations and pressures, ideal mixtures can be assumed, and F is then equal to 1 (Rathbun, 1998). As the product of the mole fraction y and the total pressure Pt is the partial pressure p of the solute (Dalton's law), it follows that

$$fa = yPt = p \tag{3}$$

For the water phase:

$$fw = \gamma mffr \tag{4}$$

where:
γ = activity coefficient of the solute in water
mf = mole fraction of the solute in water
fr = reference fugacity.

The degree of non-ideality between the solute and water is characterised by the activity coefficient. This coefficient is defined on the convention that when the mole fraction, mf, equals 1, the activity coefficient is 1 as well (Rathbun, 1998). It follows from equation 4 that the reference fugacity is the fugacity of the pure solute in the liquid state at the system temperature. Consequently, this reference fugacity is the vapour pressure of the solute (for typical environmental pressures). This is the reason why the combined equations1, 3 and 4 give:

$$p = \gamma mfp^{\circ} \tag{5}$$

where
p^o = vapour pressure of the solute at the system temperature in Pascal

The most frequent way of writing the Henry's Law Constant is:

$$p = HC \tag{6}$$

where H, the Henry's Law Constant, is the proportionality constant between the concentration of the solute in the water, C, and the partial pressure, p, of the solute in the air above the water. Combining the equations 5 and 6 gives

$$H = \frac{\gamma m f p^\circ}{C} \tag{7}$$

This last equation (equation 7) demonstrates that the Henry's Law Constant has units of pressure divided by concentration, Pa m^3/g mol, or atm m^3/mol for example. The unity of the Henry's Law Constants used in this work is atm m^3/mol.

2.3 Profiles of the physical properties for the different chemical families

Over 50 volatile and semi volatile organic compounds were sampled and analysed during the sampling campaign in January and February 2000, and additionally in January 2001 for some of the semi volatile organic compounds. Their physical properties are illustrated in the following profiles.

2.3.1 Profiles of the most important physical parameters for the VOCs

In the following chapter, the VOCs and the SVOCs that are sampled are described together, according to their chemical family and the most important physical properties. This enables a better understanding of the compounds behaviour in water. The different chemical families are represented by the following colours:

- **blue** for the aliphatic hydrocarbons,
- **red** for the aromatic hydrocarbons monocyclics,
- dark red for the aromatic hydrocarbons polycyclics,
- **green** for the chlorinated hydrocarbons,
- yellow for the oxygenated alicyclic hydrocarbons and
- **turquoise** for the oxygenated aliphatic hydrocarbons.

The different values of the physical properties can be looked up in annex I.

2.3.1.1 Water solubility

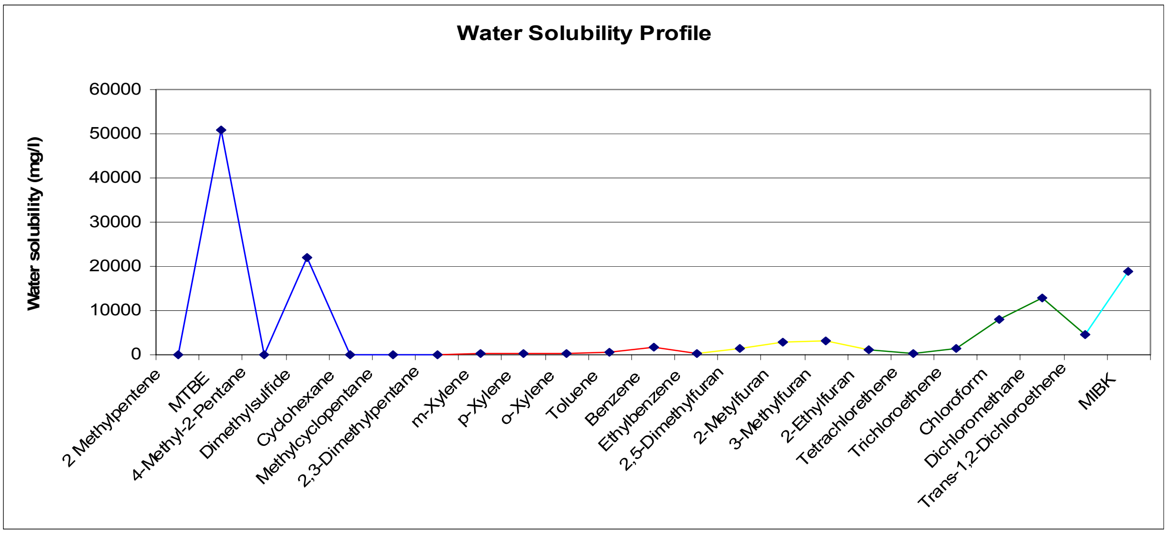


Figure 1: Water solubility profile for the VOCs

Figure 1 shows the water solubilities of the analysed compounds. The water solubility is an important parameter in the sense that it indicates up to which extend a compound dissolves in water. Compounds with very high water solubilities tend to behave in the same way as the water intensity itself. The larger the amount of water, the more compounds can be solved, and vice versa. In general, sorption is inversely related to water solubility (Mackay, 1992).

As it is shown by the profile of figure 1, the different chemical families distinguish themselves from one another. The family having the smallest water solubilities is the aromatic hydrocarbons monocyclics. Their values range from 161 to 526 mg/L, with the exception of Benzene that has an unusual high water solubility (1 790 mg/L). The oxygenated alicyclics hydrocarbons have values ranging from 1070 to 3 030 mg/L, followed by the chlorinated hydrocarbons that have values ranging from 206 to 13 000 mg/L.

The family with the highest water solubilties is the aliphatic hydrocarbons, although some compounds have very low values: the significant gap that exists between the extremes of the same family indicates that in this case, the compounds should be taken individually, rather than as a whole. MTBE has the highest water solubility with a value of 51 000 mg/L and 2,3 Dimethylpentane has the lowest value, with only 5.25 mg/L. MIBK that is an oxygenated aliphatic hydrocarbon, also has a high water solubility.

2.3.1.2 Soil Adsorption Constant

Comparing the water solubility profile to the Soil Adsorption Constant profile, one would expect an opposed developing of the values. The soil adsorption profile is represented in the next figure (Figure 2), for those compounds for which the values are available in the literature. As expected, the compounds with the highest water solubility values are those that have the lowest Soil Adsorption Constant values. This tendency is clearly shown with the chlorinated hydrocarbons for which the values for both parameters are found. The run of both curves is absolutely opposed. The same observation can be made for Benzene: being the aromatic hydrocarbon with the highest water solubility, it is consequently the one with the lowest soil adsorption constant.

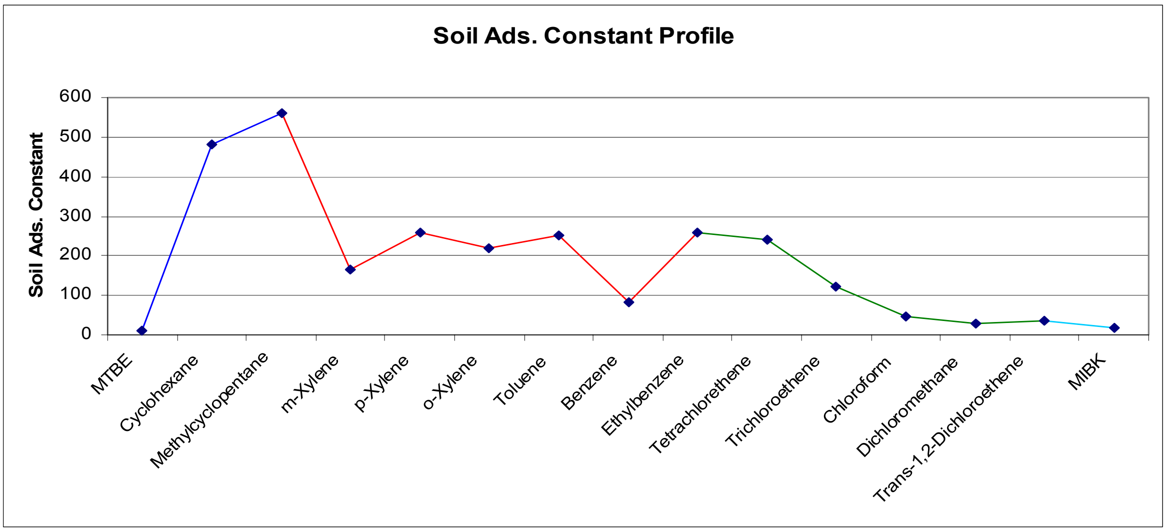


Figure 2: Soil Adsorption Constant profile for the VOCs

2.3.1.3 Vapour pressure

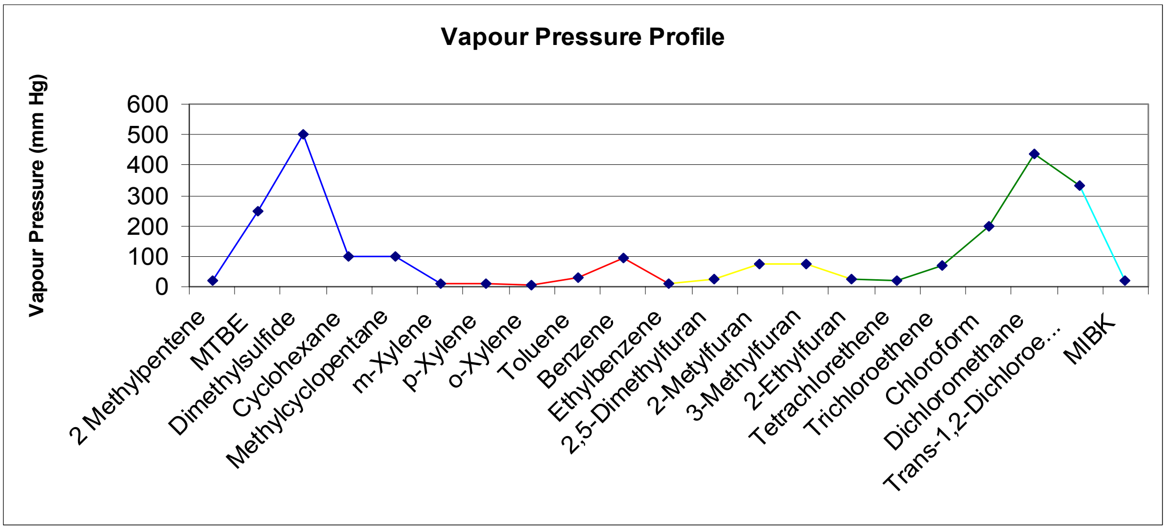


Figure 3: Vapour pressure profile for the VOCs

The vapour pressure of a compound indicates its tendency to evaporate. The higher the vapour pressure of a compound, the greater tendency it has to evaporate. The vapour pressure curve (Figure 3) is similar to the shape of the curve on figure 1, representing the water solubilities. This result makes sense as well, as both parameters are also linked together: the higher the water solubility of a compound, the higher its dispersion in water, and the higher its tendency to evaporate. Compounds like the Xylenes for example, are only slightly soluble in water (about 160 mg/L), and have consequently very low vapour pressures (about 8 mm Hg). Comparing the different parameters, the result is often a logical trend, although a direct conclusion is not appropriate as all the parameters influence one another.

An example here can be MTBE and Dimethylsulfide: MTBE has a higher water solubility than Dimethylsulfide, hence one would expect MTBE to have a higher vapour pressure as well, which is not the case - the vapour pressure values for MTBE and Dimethylsulfide are 250 mm and 502 mm Hg respectively. This indicates that another parameter that is maybe more pronounced for MTBE and less for Dimethylsulfide plays a role here.

From this study, it can be noted that the families with the highest vapour pressure values are the aliphatic and the chlorinated hydrocarbons.

2.3.1.4 Density

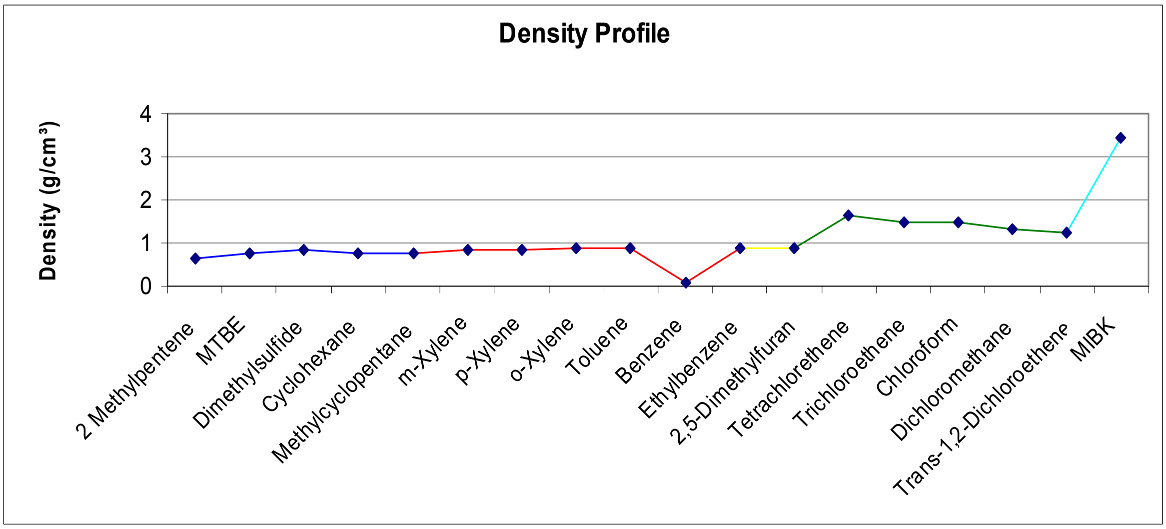


Figure 4: Density profile for the VOCs

The density of a compound indicates its tendency to sink. It is interesting to have the density values in order to compare them with that of water. Compounds with greater densities than water, such as the chlorinated hydrocarbons, have the tendency to sink and most likely reach the groundwater. The profile on figure 4 has a shape that can be compared to that of the profile of the figure 2, representing the Soil Adsorption Constant. It seems that the higher the soil adsorption of a compound, the higher the density. The chlorinated hydrocarbons are the only compounds having greater densities than water, except for the oxygenated aliphatic hydrocarbon MIBK, that has a density close to 3.5 g/cm³, although this compound has a high water solubility compared to other compounds, and its Soil Adsorption Constant is low.

2.3.1.5 Henry's Law Constant

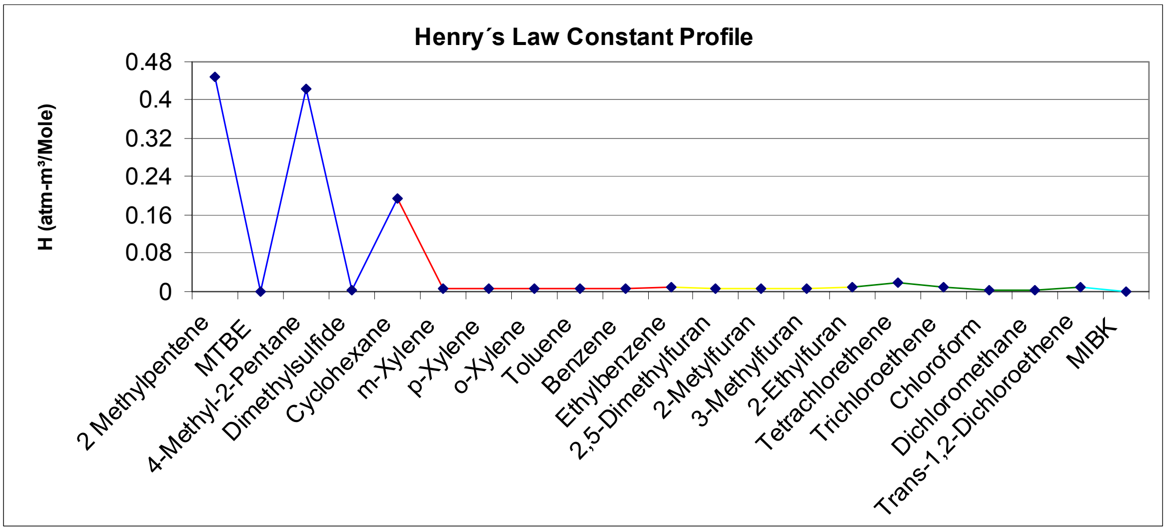


Figure 5: Henry's Law Constant profile for the VOCs

The Henry's Law Constant is a measure of a compound's tendency to partition between water and vapour. The smaller the Henry's Constant, the higher the tendency to partition. There is no significant variation in the curves run. Most values are lower than 0.05 atm.m³/Mole for all the chemical families, which indicates that these compounds are highly volatile. Nevertheless, three exceptions are shown in figure 5. These compounds are all aliphatic compounds: 2-Methylpentene, 4-Methyl-2-Pentene and Cyclohexane, and have following values: 0.45, 0.423 and 0.195 atm.m³/Mole respectively. This last observation might be explained, at least for Cyclohexane, by the fact that this compound has one of the highest Soil Adsorption Constant, with a value of 482.

2.3.2 Profiles of the most important physical parameters for the SVOCs

Because of the lack of data for most of the semi volatile organic compounds, there are only three profiles describing the physical properties.

Here as well, the different families are represented by the different colours mentioned in the above chapter.

2.3.2.1 Water solubility

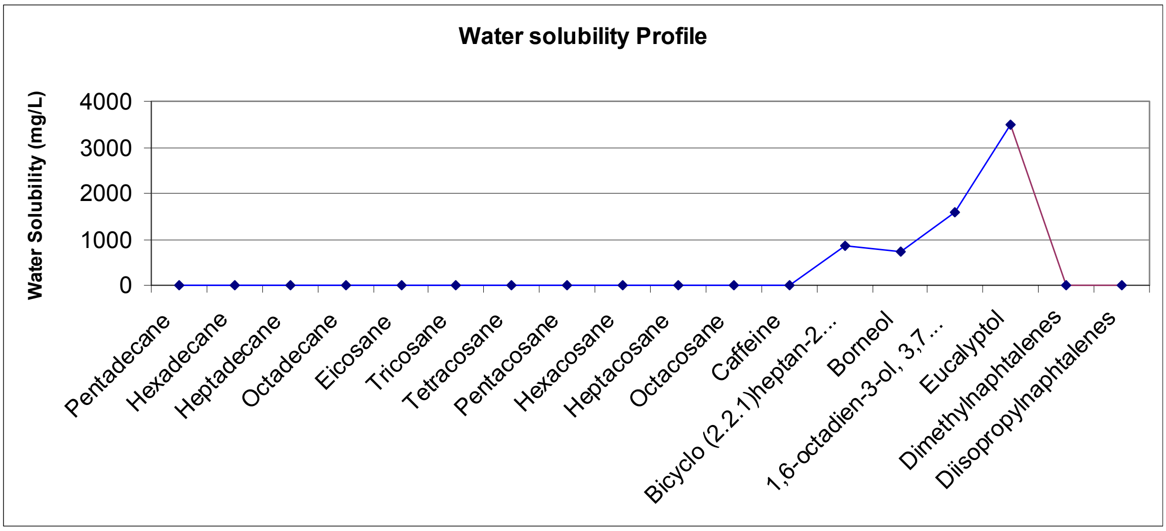


Figure 6: Water solubility profile for the SVOCs

The semi volatile organic compounds shown in the above figure (Figure 6) are all aliphatics except two: Dimethylnaphtalenes and Diisopropylnaphtalenes that are aromatic hydrocarbons polycyclics.

Only four compounds seem to be soluble in water. These are Bicyclo (2.2.1) heptan-2-ol-1,3-trimethyl, Borneol, 1,6-octadien-3-ol,3,7-dimethyl and Eucalyptol. Except these four substances, it seems that the majority of the compounds have a very small solubility in water, so much so, that they are often considered as being insoluble.

2.3.2.2 Density

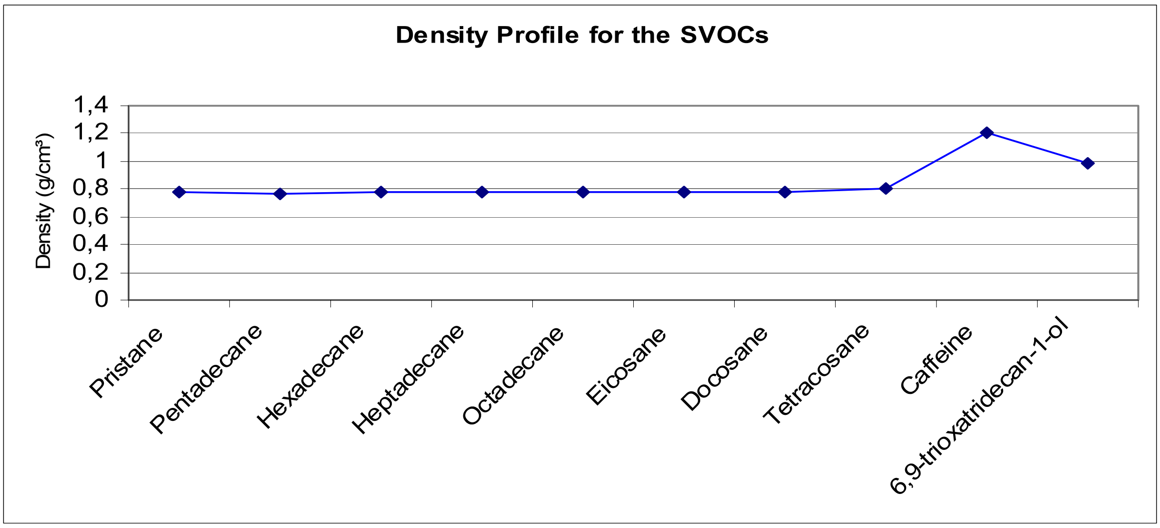


Figure 7: Density profile for the SVOCs

Unfortunately, only a very few values of density have been found for the SVOCs. They are all shown in the profile of figure 7, and all belong to the same chemical family: aliphatic hydrocarbons. They all have smaller densities than water, except Caffeine that has a density of 1.2 g/cm³.

2.3.2.3 Henry's Law Constant

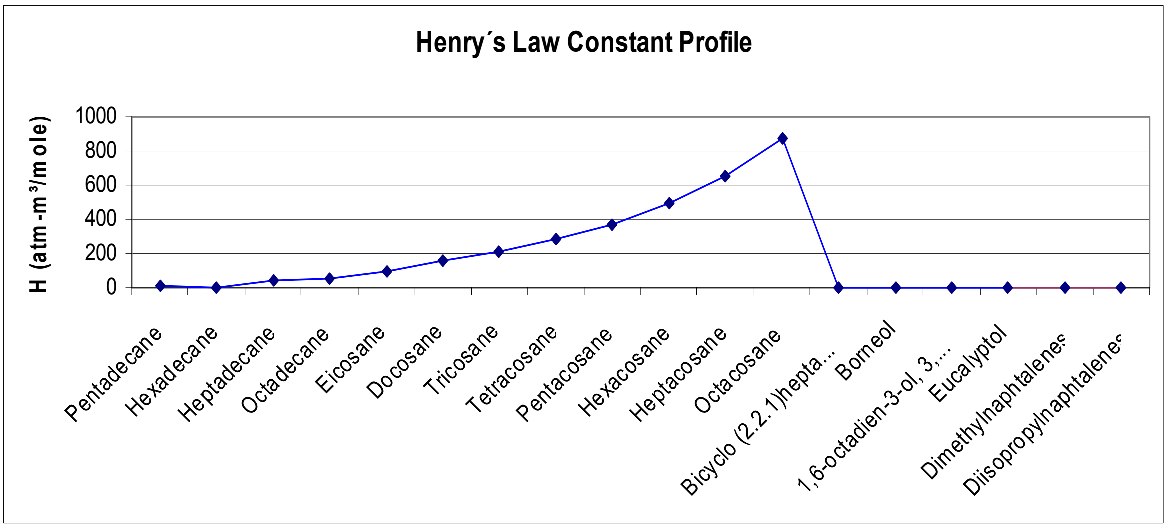


Figure 8: Henry's Law Constant for the SVOCs

Figure 8 shows the Henry's Law Constant profile for the same compounds listed in 2.3.2.1. The curve shows in a very clear way, how the Henry's Law Constant increases with increasing molecular weight from Pentadecane to Octacosane (*n*-alkanes from *n*-C15 to *n*-C28).

3. General characteristics of the study area

3.1 Description of the runoff stations

3.1.1 The city of Ramallah

The city of Ramallah is situated in the West Bank, about 15 kilometres north-west of Jerusalem, at an elevation between 820 and 880 m a.s.l. Close to the water divide, the terrain can be described as being rather flat, but it then steepens up rapidly in the deep valleys of the westwards flowing wadis (Leibundgut 2004). The typical landscape is mountainous whereas it is only moderately hilly in the city itself.

There are approximately 57 000 residents in Ramallah, and the city centre is densely populated. As it is the case in most old cities, the urban structures in Ramallah (e.g.: streets) spread out from the city centre. In Ramallah, the directions of the main urban structures are north, northwest, west and south (Salus, 2001). The further away from the city centre, the lower the density becomes, from both a population and urban structure perspective.

Unlike most western countries that usually have a well functioning drainage system, only 40% of the city of Ramallah is connected to the storm water drainage system, which consists of a 1 km main pipe.

Buildings in Ramallah are typical of a Middle Eastern city. There are two sorts of buildings: 1) family-based houses that have a traditional construction, and 2) more modern and recently constructed houses. There is a direct correlation between the type of building and the drainage network – the newer houses (and corresponding roads) have access to the drainage system, whereas the older, traditional houses usually have drinking water cisterns in their gardens and a part of the water is drained to the garden and infiltrates into it. This means that only a small amount is discharged onto the streets to end up in the city sewers. This represents a great threat in terms of water pollution and water supply for the city of Ramallah.

Organic compounds are sampled in five different runoff stations. Three of the stations are located in the city itself, one is situated on the top of a building, and one is located in the surroundings of the city. The rainfall station that is used for the different analyses is the Library station, as it is not only the most representative station for the study area, but is also one of the most accurate ones. Figure 9 is a map of Ramallah showing where the different stations are located and the drainage system of the city. Additionally, the catchments' area of three stations is also represented. These three stations are: Luthery, Womens Association and Kiswani, and are all belonging to the same drainage system.

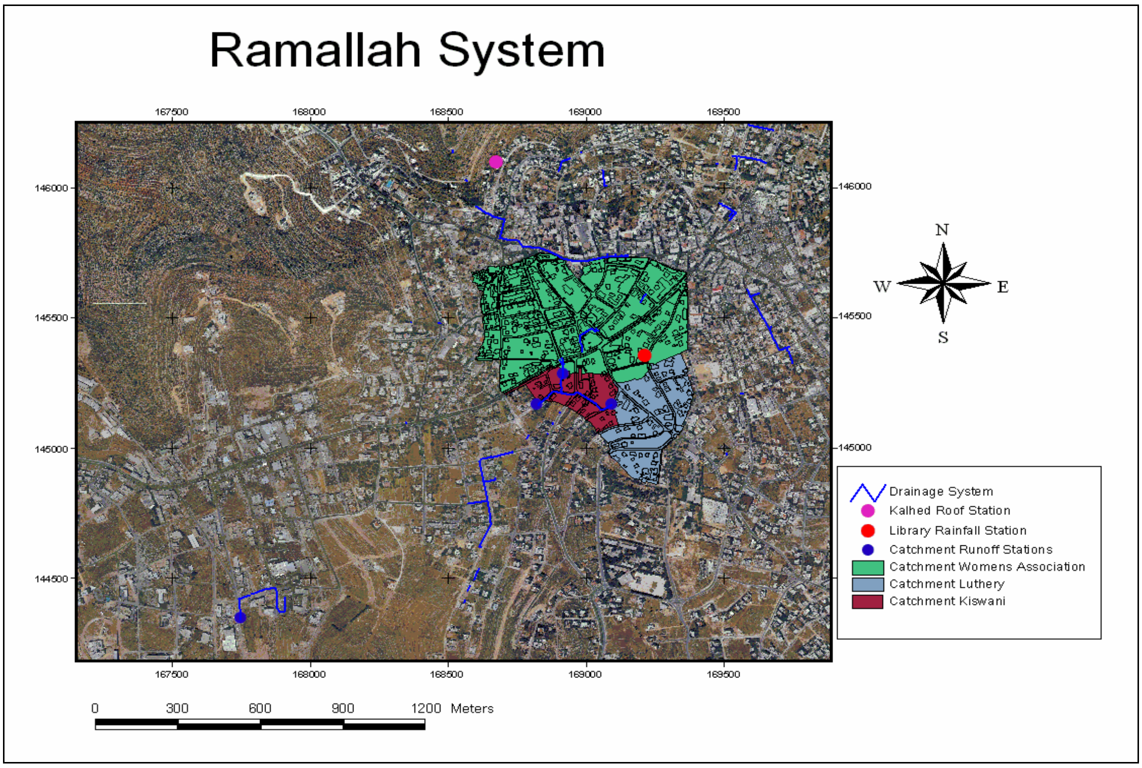


Figure 9: Stations location map and drainage system

3.1.2 Luthery station

The Luthery stations' catchment is, with a catchment area of 99 210 m², the smallest of all runoff stations. It is situated in the south-west part of the city, beneath the Womens Association station. Concerning its land use (Figure 10), the Luthery station has about 27% of urban areas, considering urban areas as being impervious, such as roads, parking lots and buildings.

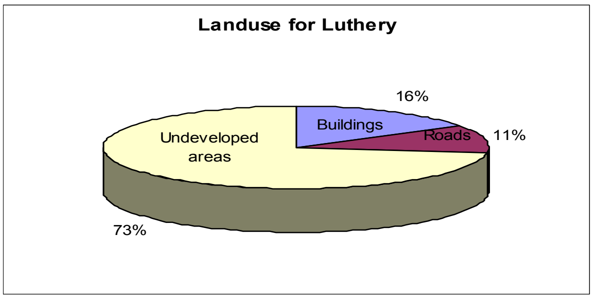


Figure 10: The land use for the Luthery catchment

As it is shows on the figure 11, the Luthery station is situated at the beginning of the stormwater drainage system.

Figure 11: Luthery station

3.1.3 Womens Association station

The Womens association station has a catchment area of 314 640 m², which makes it considerably bigger than the Luthery station. It is also situated on the south-west part of the city, and is located above Luthery station. Considering the land use in the catchment (Figure 12), the percentage of impervious area (roads and buildings) is higher than in the Luthery catchment, as 36% are reached here.

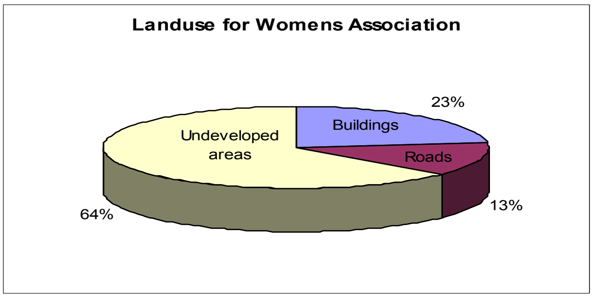


Figure 12: The land use for the Womens Association catchment

Unlike the Luthery station that is situated at the entry of the stormwater drainage system, the Womens Association station (Figure 13) is situated a few meters downstream from the drainage entry.

Figure 13: Womens Association station

3.1.4 Kiswani station

The Kiswani station is the third station belonging to the stormwater drainage system. With a catchment area of 462 570 m², the Kiswani catchment is the biggest of all three of them. Actually, the Kiswani catchment is made up of the Luthery and the Womens Association station, as their runoff flows together into the Kiswani station (Figure 9).

This is the reason why the Luthery and the Womens Association stations can be considered as Kiswanis sub-catchments.

The area that remains once the catchment areas of Luthery and Womens Association are taken away is 48 720 m². To avoid any misunderstanding, the total Kiswani catchment is called Big Kiswani, and the remaining area (without Luthery and Womens Association) is called Small Kiswani. The landuse of the remaining area, Small Kiswani is summarised in the Figure 14.

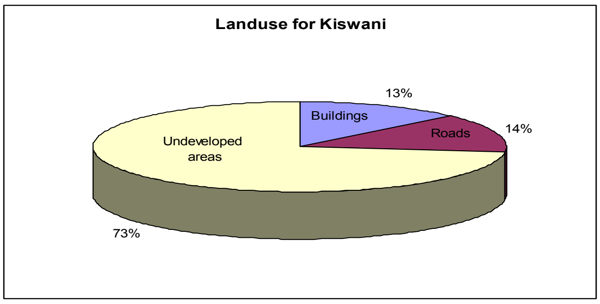


Figure 14: The land use for the Kiswani catchment (48 720 m²)

The percentage of urban area in the Kiswani catchment is the same as the one for the Luthery station, 27%, although Kiswani has a higher proportion of roads (Figure 14).

The following figure (Figure 15) is a picture of the Kiswani station. This station is located at the end of the drainage system.

Figure 15: Kiswani station

As previously mentioned, the runoff of the Kiswani station includes the runoffs of Luthery and Womens Association station. Once arrived in Kiswani, it then flows out into an open area of 10 000 m² (Figure 16). The runoff is then "picked up" in another station called Louloua that is not part of this study.

Figure 16: Open area

The three stations described above are inside the city stormwater drainage system, and for this reason, are later on analysed together, as one system.

3.1.5 Industrial station

The Industrial station is the runoff station that does not belong to the same system as the three stations described above, because it is not situated in the city centre, and does not belong to the main stormwater drainage system.

The Industrial station is the biggest of all stations, and has a catchment area of 686 766 m². Regarding its land use (Figure 17), the Industrial station is the one that has the less impervious areas. The fact that the percentage here is only 17% (less than half of the Womens Association station), seems rather reasonable as this particular station is located outside the city.

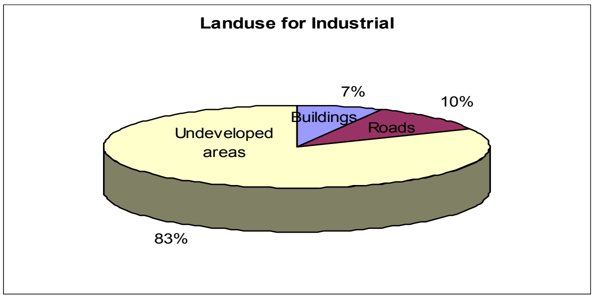


Figure 17: Land use for the Industrial station

The Industrial station (Figure 18) is, just as the Luthery station, located at the entry of the stormwater drainage system and close to a road, which should be underlined. This is also shown in the figure 9, where the different drainage systems are illustrated for Ramallah and its surroundings.

Figure 18: Industrial station

3.1.6 Khaled station

The Khaled station is, in the same way as the Industrial station, not part of the central system, as this station is located on the top of a roof, outside the city centre. For this reason, it is also analysed separately. Samples are taken in the roof gutters, during rain events, and collected in containers.

3.2 Methods

The analysis for the organic volatile and semi-volatile compounds was made in the Interdepartmental Equipment Laboratory (IDEL) of the Faculty of Agricultural, Food, and Environmental Quality Sciences of the Hebrew University of Jerusalem.

3.2.1 Volatile organic compounds extraction and analysis

To begin with, the collected water samples were filtered twice: first, through a glass fiber filter (GF/C, Whatman, 1.2 µm, 47 mm) and then through a membrane filter of 0.45 µm (Millipore, hvlp). After the second filtration, methanol (0.5%) was added to the sample. The sample was then transferred through an extraction disk C-18 (supelco envi tm- 18dsk with a 47 mm diameter) using a special vaccum manifold. Just before the transfer of the sample through the extraction disk, the disk was first cleaned with 10 ml of dichloromethane and then with 10 ml of methanol and 10 ml of distilled water. This process was done twice. After the cleaning of the disk, a 250 ml sample was then transferred through it. The disk was dried under a vacuum, and then, in order to collect the organic compounds that were absorbed to the disk, 15 ml of dichloromethane were transferred to it. The solvent was collected in a glass test tube, and was then heated to 50°C under a weak flow of nitrogen while the solvent was evaporating. This volume was reduced to 1 ml through evaporation, and was then kept in closed vial, sealed with Teflon-lined septum caps, and was conserved at a temperature of 18°C until the analysis phase (Salus, 2001).

During the analysis, the volatile organic compounds were determined by GC-MS (Varian Saturn, 2000) using a capillary column, 30m×0.25mm ID×0.25µm film thickness. The carrier gas was helium at 1.0 $\mathrm{mLmin^{-1}}$. The injector temperature was set to 60°C and 1µL was injected. The column temperature was programmed in such a way that the initial temperature was 50°C, and had an initial delay of 0.1 minutes. After the initial delay, the temperature was raised by 10°C every minute, until it reached a temperature of 160°C. Once the 160°C were reached, the temperature was then raised to 200°C with an increase of 2 degrees per minute. Finally, the temperature was raised to 260°C with an increase of 10°C per minute. The split ratio was 1:50 (Salus, 2001).

3.2.2 Semi volatile organic compounds extraction and analysis

In the case of the Semi Volatile compounds, the samples were injected to a standard purge and trap system model l-3000. Nitrogen flew through the liquid solution during ten minutes (so called purge stage), in order to carry the compounds that were trapped in the tenax column (so called trap stage) away. The release of the compounds happened by heating to 200°C and they were then concentrated in a section of the capillary column, that was cooled down with liquid nitrogen before the injection. The column was then heated to 200°C. This heating provoked an injection of the compounds into the capillary of the gas chromatograph (Salus, 2001).

For the analysis, the semi-volatile compounds were determined by GC/MS using a capillary column, 60m×0.25mm ID×1.4µm film thickness (Restek).

3.3 Description of the hydrology situation.

3.3.1 General situation

Before starting to analyse the behaviour of the different compounds that are measured in the five runoff stations, it is very important to describe the hydrological situation. Good knowledge of hydrological elements such as runoff response to rainfall is necessary to understand these compounds' behaviour. In order to do this, three stations (Luthery, Womens Association and Kiswani) inside the drainage system are used, for which runoff data is collected.

The two other stations (Industrial and Khaled) did not provide any runoff data, and therefore are not used.

As already mentioned in chapter 3.1.1, the rainfall station used here is the Library station, as it is representative for the whole study area.

Figure 19 shows the general situation in the Womens Association station from the 18-31 January 2000. This period includes four sampling days (20, 26, 27 and 31 January).

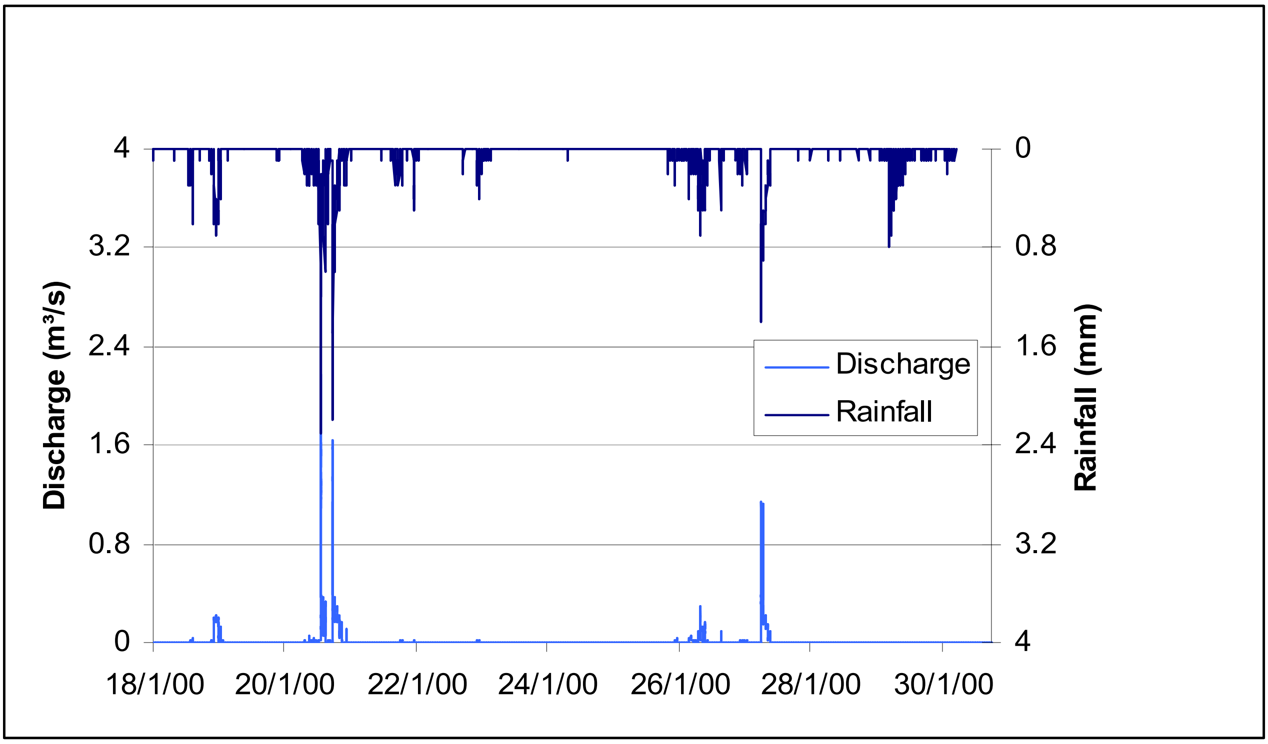


Figure 19: Measured runoff and rainfall in the Womens Association station

The hydrological analysis focuses on the sampling days that have all the information needed (runoff and concentration data). These days are January 20, 26 and 27 in the year 2000. January 31 can unfortunately not be used, as the Womens Association station did not provide any runoff data on that day. The runoff events on January 20 are analysed on their own, whereas the events on January 26 and 27 are analysed together, as they are adjacent in time.

The two following figures (20 and 21) show the sub-division of these events: The event that happened on January 20 is divided into three sub events and the combined event on January 26 and 27 are divided into eight sub events.

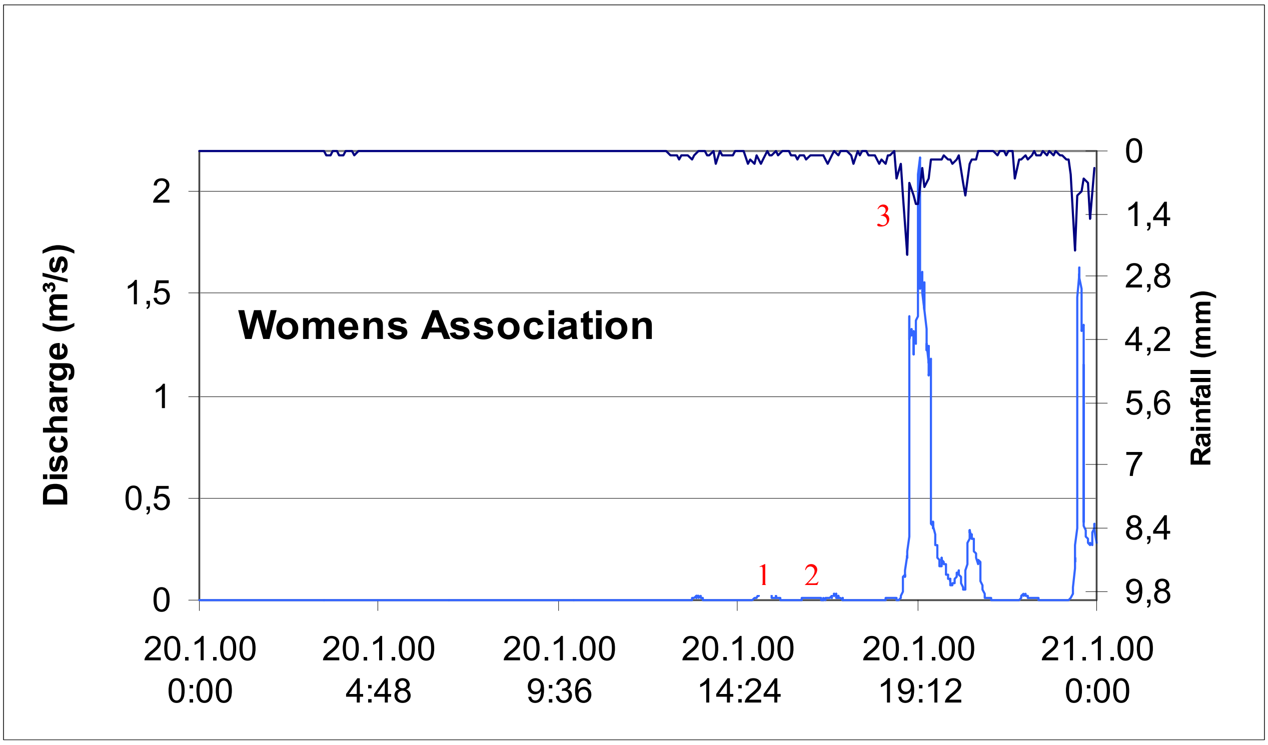


Figure 20: Sub events on January 20

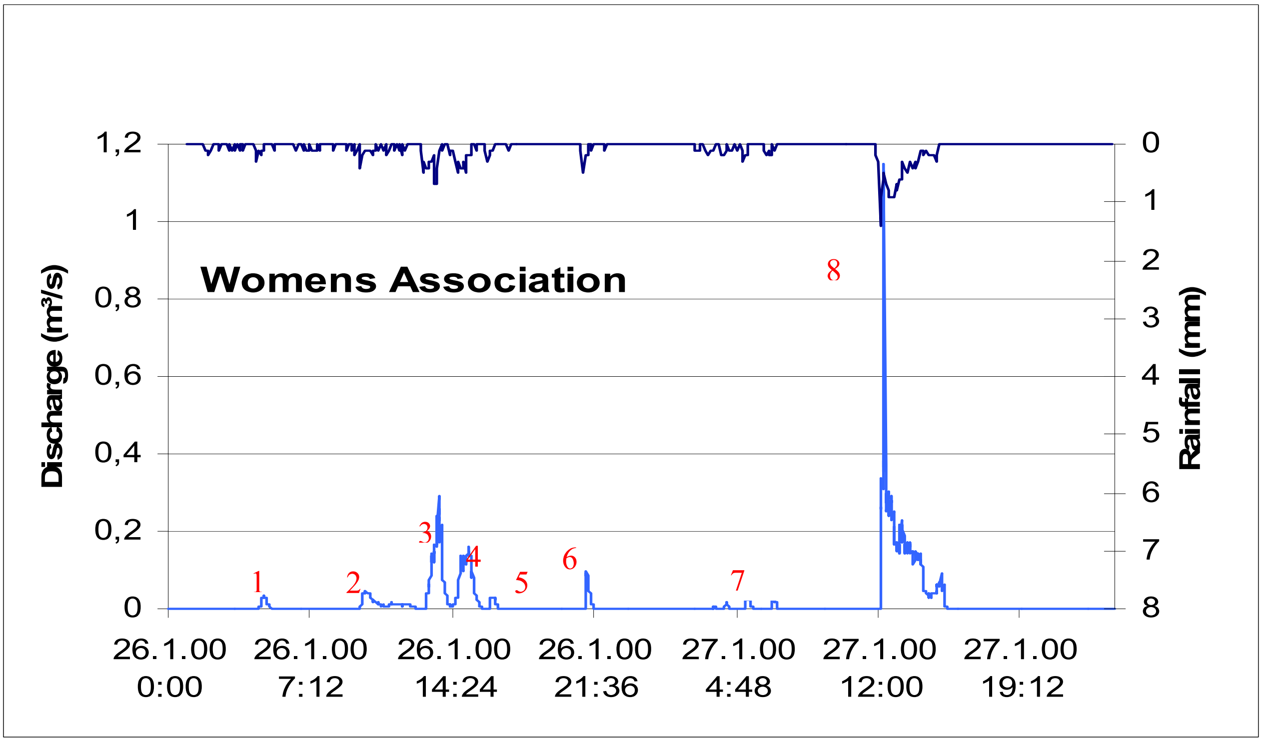


Figure 21: Sub events on January 26 and 27

The parameters that are calculated here are a) runoff and b) rainfall volume, which together enables the calculation of c) the runoff coefficient RC, and d) the contributing area for RC=1. Additionally, the areas of the roads and buildings are specified, in order to compare these results with the calculated contributing areas. The results of these calculations are summarised for each station in the tables 1, 2 and 3.

3.3.2 Results

Luthery station:

Table 1: Calculated parameters for the Luthery station

Day	Event	Rainfall (mm)	Runoff Volume (m³)	Runoff Coefficient RC	Contribution area (km²) for RC=1
20.01.00	1*	1.7	23.53	0.14	0.013
	2	2	37.91	0.19	0.018
	3	15.7	1171.12	0.77	0.077
26-27.01.00	1	0.9	21.35	0.24	0.023
	2	3.1	106.30	0.35	0.034
	3	4.5	163.40	0.37	0.036
	4*	4.1	133.00	0.33	0.032
	5	0.9	30.28	0.34	0.033
	6	1.6	38.68	0.24	0.024
	7	3.7	42.02	0.11	0.011
	8*	17.7	682.86	0.39	0.038

*: *event of sampling*

Luthery station	**Road area (km²)**	**Building area (km²)**	**Road+Building area (km²)**
	0.0107	0.0159	0.0266

Womens Association:

Table 2: Calculated parameters for the Womens Association station

Day	**Event**	**Rainfall (mm)**	**Runoff Volume (m^3)**	**Runoff Coefficient RC**	**Contribution area (km^2) for RC=1**
20.01.00	1*	1.7	63.73	0.12	0.037
	2	2	48.12	0.08	0.024
	3	15.7	4024.00	0.81	0.256
26-27.01.00	1	0.9	33.63	0.12	0.037
	2	3.1	161.66	0.17	0.052
	3	4.5	469.90	0.33	0.104
	4*	4.1	380.77	0.30	0.092
	5	0.9	31.18	0.11	0.034
	6	1.6	73.51	0.15	0.045
	7	3.7	58.60	0.05	0.015
	8*	17.7	1856.89	0.33	0.104

**: event of sampling*

Womens Association	**Road area (km^2)**	**Building area (km^2)**	**Road+Building area (km^2)**
	0.0414	0.0731	0.1145

Kiswani:

Table 3: Calculated parameters for the Kiswani station

Day	Event	Rainfall (mm)	Runoff Volume (m³)	Runoff Coefficient RC	Contribution area (km²) for RC=1
20.01.00	1*	1.7	776.43	0.98 8.32	0.456
	2	2	804.96	0.87 7.37	0.402
	3	15.7	5785.35	0.79 7.71	0.368
26-27.01.00	1	0.9	104.83	0.25 1.14	0.116
	2	3.1	414.59	0.29 0.97	0.133
	3	4.5	1442.05	0.69 3.69	0.320
	4*	4.1	1238.26	0.65 3.63	0.302
	5	0.9	174.59	0.38 2.32	0.174
	6	1.6	258.71	0.35 1.87	0.161
	7	3.7	468.22	0.27 2.04	0.126
	8*	17.7	8157.32	1.00 6.51	0.460

**: event of sampling*

Kiswani	**Road area (km²)**	**Building area (km²)**	**Road+Building area (km²)**
	0.0588	0.0953	0.1541

3.3.3 Discussion

Tables 1, 2, and 3 show that the three stations for which the hydrological situation is described have different results and patterns. The reasons for these differences are due to the catchments themselves (e.g.: land-use, catchment size).

The Luthery station has runoff coefficients ranging from 0.11 to 0.39 and contributing areas ranging from 0.011 to 0.036 km². The result for the third event on January 20 appear to be outside this range (RC=0.77) and is the upper limit of the results. For this reason, this event should be analysed with caution. The runoff coefficients and the contributing areas do not vary significantly from one event to the other.

This is not the case for the Womens Association catchment, where the runoff coefficient and the contributing areas are more variable. The runoff coefficients here range from 0.05 to 0.33 and the contributing areas from 0.015 to 0.104 km². Again, the third event on January 20 is outside the range, and therefore should be interpreted carefully.

The reason why the parameters behave differently in these two stations might be due to the land-use of the two catchments: The Luthery station is known to be mostly residential, with houses surrounded by gardens. The many gardens that are found in this catchment play a role in the runoff formation, and influence the runoff coefficients in this catchment in the sense that the runoff will be stored by the garden. This characteristic can explain why no significant variation is found in the runoff coefficients here.

On the other hand, the lack of gardens in the Womens Association catchment can explain why the runoff coefficients and the contributing areas are more variable, as the storage capacity is lower in this catchment that is less residential.

Concerning the contributing areas for both catchments, it seems that the small runoff events are only generated by the roads (event 1 and 2 on January 20 for example), whereas an additional factor plays a role for the bigger events (event 8 on January 27 for example): buildings. The contribution areas are analysed in detail in the next chapter (chapter 3.3.4).

The results for the Kiswani station are very surprising, as they do not correlate well with the two other stations. Therefore, the interpretation of this station is done separately.

The runoff coefficients here range from 0.25 to 1, and the contributing areas range from 0.116 to 0.460 km². Surprisingly, the contributing areas are mostly greater than the roads and building areas together. Hence, these values seem to be too high.

The runoff coefficient (in red) values are calculated for Small Kiswani. Coefficients over 1 are calculated for each event, except for event 2 on January 26. These results are incoherent as it is not possible to have more runoff than rainfall. Additionally, it is unlikely that the Small Kiswanis area (0.48 km²) can generate such an important runoff.

There are two potential explanations for this high runoff. The first is that a great amount of surrounding runoff entered the catchment. This is unlikely, as it would mean that the contributing catchment area is much bigger than the delimitated one. The second possible reason is that a calibration problem occurred with the runoff data itself. For this reason, the calculated parameters for the Kiswani catchment are taken with caution, and are used in a comparative way.

3.3.4 Contribution areas

The following figure (Figure 22) is a map of Ramallah, where the major runoff contributing areas as well as the major sources of pollution are located for the Luthery and the Womens Association catchments. Because of the uncertainty concerning the runoff data of the Kiswani station, this station is not used for this investigation.

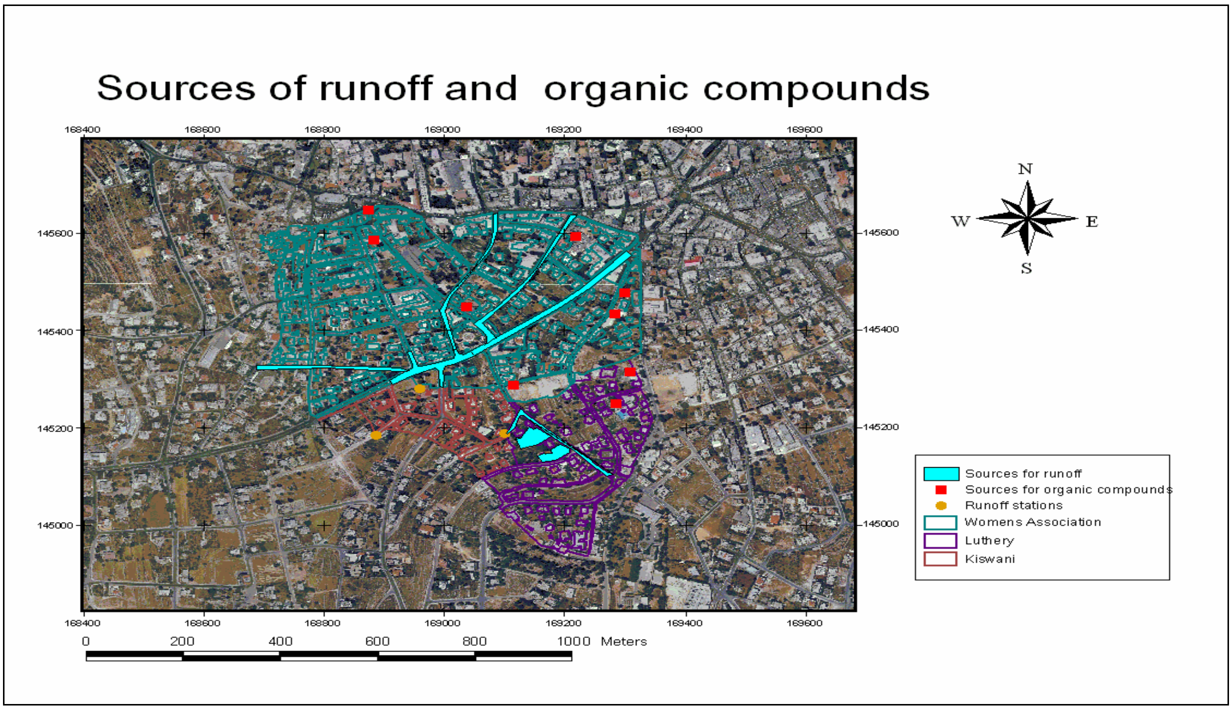


Figure 22: Sources of runoff and organic compounds

As Lopes and Bender (1998) concluded in previous papers that urban land surface (e.g.: parking lots) are the primary non-point source of VOCs in urban stormwater, nine possible sources of organic compounds are additionally located on the map. There are eight parking lots and one garbage conglomeration. Fluids leaking from vehicles that are stored in the parking lot on the paved surface can potentially contaminate the stormwater of this area. These contaminants may contain oil, grease, Benzene, Ethylbenzene, Xylene, Toluene and MTBE, for example.

Gas stations - considered as a point source - can also contaminate the stormwater primarily due to spills and leaks while fuelling, but also from cleaning operations and maintenance activities. As the figure shows, no point source such as a gas station has been found in either of the catchments.

For the Womens Association catchment, the principal source of runoff is the west main-road which starts at the city centre. A few side roads are also considered as important runoff sources, due to their steep slope.

For the Luthery catchment, there is only one road (catchments size) that is considered as runoff-generating. Two supplementary runoff-generating areas are also shown for this catchment: two important paved areas in the direct surrounding of the station.

The runoff-generating areas have been quantified for the Luthery station and for the Womens Association station. The quantified area for the Luthery catchment is 0.006 km² and the one

quantified for the Womens Association catchment is 0.016 km^2. It is now interesting to investigate the correlation of these areas with the results of the tables 1 and 2.
In chapter 3.3.3, the results of the calculated parameters show that the roads are probably the main runoff generating source for the small runoff events, whereas the big runoff events are additionally generated by the buildings.

In order to verify this observation, the runoff events are divided into small and big events. Events having runoff volumes greater than 133 m^3 are considered as big for the Luthery catchment, and those greater than 380 m^3 are considered as big for the Womens Association station. These are, in both cases: Event 3 on January 20, event 3 and 4 on January 26 and 27. The rest of the events are considered as small. Three parameters are used: a) the contributing area for RC=1, b) the quantified contributing area of each station, which together enables the calculation of c) the fraction of contributing area for RC=1 relative to the quantified contribution area. The results are summarised in the two following tables for the Luthery and for the Womens Association station (Table 4 and 5).

3.3.4.1 Results

Table 4: Contribution area for Luthery

		Event	**Runoff Coefficient RC**	**Contribution area (km^2) for RC=1**	**Fraction of Contribution area for RC=1 relative to Quantified contribution area (km^2)**
Small Events	**20.01.00**	1*	0.14	0.013	2.16
		2	0.19	0.018	3.00
	26-27.01.00	1	0.24	0.023	3.83
		2	0.35	0.034	5.66
		5	0.34	0.033	5.50
		6	0.24	0.024	4.00
		7	0.11	0.011	1.83
Big Events	**20.01.00**	3	0.77	0.077	12.83
	26-27.01.00	3	0.37	0.036	6.00
		4*	0.33	0.032	5.33
		8*	0.39	0.038	6.33

Table 5: Contribution area for Womens Association

		Event	**Runoff Coefficient RC**	**Contribution area (km²) for RC=1**	**Fraction of Contribution area for RC=1 relative to Quantified contribution area (km²)**
Small Events	**20.01.00**	1*	0.12	0.037	2.31
		2	0.08	0.024	1.50
	26-27.01.00	1	0.12	0.037	2.31
		2	0.17	0.052	3.25
		5	0.11	0.034	2.12
		6	0.15	0.045	2.81
		7	0.05	0.015	0.93
Big Events	**20.01.00**	3	0.81	0.256	16.00
	26-27.01.00	3	0.33	0.104	6.50
		4*	0.30	0.092	5.75
		8*	0.33	0.104	6.50

3.3.4.2 Discussion

The fraction of the contribution area for RC=1 relative to the quantified contribution area are calculated in order to evaluate the influence of the quantified areas on runoff generation. Small fractions show that the runoff is probably generated by the quantified areas only. However, bigger fractions show that the event is probably generated by a larger number of streets. The fractions for the big events are marked in red in the tables.

For the Luthery station, the fractions range from 2.16 to 5.66 for the small events, and from 5.33 to 12.83 for the big events.
In the Womens Association station, the fractions for the small events range from 0.93 to 3.25 and from 5.75 to 16 for the big events.

Nevertheless, there are two exceptions in the Luthery station (events 2 and 5 on January 26 and 27) that are out of range, as their fractions fit into the range of the big events. These two cases are also marked in red. They have runoff coefficients close to those of the big events, and as they represent the upper limit of the small events, they have bigger fractions. This probably comes from the fact that the parameters behave in a fairly regular and constant way in the Luthery catchment because of the higher storage capacity of the catchment (gardens). For this reason, it is not appropriate to create an artificial limitation of small/big events for this catchment.
In the Womens Association station, where the calculated parameters distinguish themselves much more from one another, the limit between small/big events is much clearer. This is why the results in the Womens Association are more easily interpreted.
These results confirm that the runoff in both stations is probably generated by the roads at least for the small events and more precisely by the quantified ones.

3.4 Load calculation for the different chemical families

In order to discover a potential link between the hydrological situations described in chapter 3.3 and the parameters describing the behaviour of the different chemical families described in chapter 2.3, the loads are calculated for each chemical family in the three stations for which runoff data is available. These stations are those belonging to the drainage system: Luthery, Womens Association and Kiswani.

Because of the possible error that occurs in the runoff data of the Kiswani station, a correction is carried out for the Kiswani station before undertaking the load calculation.
In order to do this, a correction factor A is calculated, by dividing the transferred runoff volume for Big Kiswani and the measured runoff volume for Big Kiswani. The transferred runoff volume is obtained by multiplying the average runoff coefficient between Luthery and Womens Association together with the rainfall during the specific event, and the area of Big Kiswani. The results are summarised in the table below (Table 6).

Table 6: Correction factor for Kiswani station

Day	Event	RC (average between Luthery and WA)	Rainfall (mm)	Runoff volume for Big Kiswani (transferred) in m³	Runoff volume for Big Kiswani (measured) in m³	A= correction factor
20.01.00	**1**	0.11	6.2	315.47	2325.02	0.13
26.01.00	**4**	0.315	4.1	597.40	1238.26	0.48
27.01.00	**8**	0.36	17.7	2947.00	8157.32	0.36

In order to attenuate the runoff values for Kiswani, they are multiplied with the correction factor before the different loads are calculated.
The results for the loads calculations are shown in the following table (Table 7).

3.4.1 Results

Table 7: Load calculation fort he different chemical families

Chemical Family	Days	Load for Luthery (µg)	Load for Womens Association (µg)	Load for Luthery+Womens Association (µg)	Load for Kiswani (µg)	Load fraction arriving in Kiswani
Aliphatic Hydrocarbons	**20/01/00**	6.00E-02	3.17E-04	6.03E-02	2.83E-03	0.04
	26/01/00	7.41E-04	0	7.41E-04	2.08E-02	28.11
	27/01/00	1.67E-04	1.13E-04	2.80E-04	2.89E-03	10.31
Aromatic Hydrocarbons Monocyclics	**20/01/00**	1.23E-01	1.36E-03	1.24E-01	9.89E-03	0.07
	26/01/00	7.98E-04	1.36E-03	2.15E-03	1.21E-01	56.23
	27/01/00	2.75E-03	1.02E-03	3.78E-03	4.62E-02	12.23
Chlorinated Hydrocarbons	**20/01/00**	3.83E-03	8.94E-04	4.72E-03	2.07E-02	4.38
	26/01/00	3.42E-04	3.77E-05	3.80E-04	8.19E-03	21.55
	27/01/00	0	9.82E-04	9.82E-04	3.82E-02	38.94
Oxygenated Alicyclic Hydrocarbons	**20/01/00**	7.41E-03	2.23E-04	7.63E-03	2.99E-03	0.39
	26/01/00	6.84E-04	4.09E-05	7.25E-04	2.60E-02	35.92
	27/01/00	0	0	0	0	0

3.4.2 Discussion

The load fraction arriving in Kiswani on the three sampling days has the same behaviour for the aliphatics, the aromatics monocyclics and the oxygenated alicyclics hydrocarbons (assuming that the oxygenated alicyclics hydrocarbons have physical properties that are closer to those of the aliphatics and the aromatics than those of the chlorinated hydrocarbons).
The general aspect is that the fraction of load arriving in Kiswani on January 20 is the smallest, followed by the greatest fraction on January 26, and then an intermediate fraction on January 27. As shown in table 7, this observation can be made for all families except for the chlorinated hydrocarbons.
In order to explain the variations of the fractions of load arriving in Kiswani on the different sampling days, it is important to keep the sizes of the respective events of sampling in mind (Tables 1, 2 and 3). The event sizes increases from January 20 until January 27: the smallest

runoff event is measured on January 20, followed by a bigger event on January 26, and finally, the biggest event that is measured on January 27.
In all three cases, only a minimal fraction of load arrives in Kiswani on January 20, compared to the fractions of the January 26 and January 27. It seems that almost all the compounds got lost on their way to Kiswani. This is most probably because they volatilized before arriving.
All three families have their biggest fraction of load arriving in Kiswani on January 26, followed by a smaller fraction on the following day. For the aliphatics, the arriving load on January 27 is about 37% of the load arriving on the previous day, whereas only 20% is calculated for the arriving load on January 27 for the aromatic monocyclics. Here also, the smaller loads of January 27 can be explained by the fact that a part of the compounds probably volatilized. The fact that 37% of the previous day is calculated for the aliphatics and only 20% for the aromatics has probably to do with the different sorbtivities of the compounds. The aromatic hydrocarbons are known to have a higher tendency to be sorbed than the aliphatics hydrocarbons. This physical property can explain why a smaller percentage of aromatics arrive to Kiswani on January 27 compared to the aliphatics.

The only family that does not behave in the same way is the chlorinated hydrocarbon family, even though here too, the smallest fraction is calculated on January 20. The difference is found on January 26 and January 27, as the fractions increase. It seems that the fractions of load arriving in Kiswani for this family increase throughout the sampling period. This behaviour can be explained by the fact that the chlorinated hydrocarbons are the only compounds that have a greater density than water, which means that they tend to accumulate rather than volatilize.

Additionally the loads calculation is done for MTBE (aliphatic hydrocarbon). MTBE is a gasoline oxygenate, that is added to gasoline to increase the gasoline's oxygen level and decrease vehicular carbon monoxide emissions and ozone in the atmosphere. The results are summarised in the following table (Table 8).

Table 8: Load calculation for MTBE

Streets as source	Days	Load for Luthery (mg)	Load for Womens Association (mg)	Load for Luthery+Womens Association (mg)	Load for Kiswani (mg)	Fraction of load arriving in Kiswani
MTBE	**20/01/00**	1.39E-02	6.61E-05	1.40E-02	4.51E-04	0.03
	26/01/00	4.56E-04	0	4.56E-04	5.95E-03	13.05
	27/01/00	1.67E-04	0	1.67E-04	2.62E-03	15.73

The results here are quite surprising, in the sense that the behaviour of MTBE differs from the behaviour of the aliphatic family to whom it belongs. The smallest fraction does arrive on January 20, however it then seems that MTBE accumulates (just like the chlorinated hydrocarbons) throughout the sampling events. This example shows that MTBE does not behave in the expected way for the aliphatic Hydrocarbons.
First, one can observe that the loads in the Luthery station are greatly higher than those in the Womens Association station. This cannot be explained by a point source such as a gas station, as none is found in the catchment (see Figure 22). A non-identified point source, such as a leaking car parked near to the station can also be a reason. Yet, a point source does not seem to be an appropriate explanation here, as no major load difference is noticeable in the Luthery catchment. A point source would have probably occurred on one day only and would have

provoked a larger load increase, which is not the case here. Conversely, the quasi-absence of MTBE load in the Womens Association station compared to the two other stations is difficult to explain.

The accumulation of the MTBE loads during the seven days period is difficult to explain with a potential non-identified point source in Luthery station, as this augmentation occurs throughout a period of seven days and not just on one day. This suggests that lateral inputs from the surrounding streets play a role in the accumulation.

The possibility that the streets and the urban land surface might not be the only sources of MTBE is unlikely in this case. Although Squillace (1996) and Pankow (1997) hypothesized that urban air is a potential non-point source of MTBE, this option can not be used here, as MTBE is not detected on the roof station (atmosphere occurrence) on none of the days of sampling.

4. Analysis for the VOCs and the SVOCs

4.1 Specified analysis for the most frequent VOCs

A specified analysis is done, for the VOCs that are detected the most frequently in the runoff. Based on a total of 24 measurements, those compounds considered as being frequently detected are those identified over ten times. Those compounds are the following (listed with decreasing frequency of occurrence): Benzene, p-Xylene+m-Xylene, o-Xylene, Ethylbenzene, Toluene, Dichloromethane, Dimethylsulfide, MTBE, Tetrachloroethene, and finally Chloroform.
As it has already been explained in chapter 3, the three stations belonging to the drainage system are linked together in the sense that the runoffs of Luthery and Womens Association stations flow together into the Kiswani station. The concentration measured in the Industrial station and in the Khaled roof station does not belong to the same system and ought to be analysed separately.

As the runoff data is incomplete throughout the sampling period, the rainfall data is used to estimate an approximate runoff for January 31. The runoff event on that day is comparable to the one on January 26 (see Figure 19).
Also, an error in the runoff data occurs in the Luthery as well as in the Kiswani station. This error is indicated by a red arrow in the first diagrams of both stations. These inexistent runoffs are to be ignored.

The compounds' concentrations on the different sampling days, and their physical properties can be looked up in the annexis I and II

4.1.1 BTEX Compounds

4.1.1.1 Description of the BTEX compounds

BTEX is an acronym that stands for Benzene, Toluene, Ethylbenzene and Xylenes. These compounds are found in petroleum derivates such as gasoline. The BTEX compounds are all in all the most frequently detected compounds, and all belong to the same chemical family: aromatic hydrocarbons monocyclics.

Benzene
Benzene is a colourless gas that has a slightly sweet odour. It is usually possible for most people to smell benzene in the air, when it reaches levels of roughly 1500 parts of benzene per billion parts of air. Benzene is formed from both natural and human processes. As being a part of gasoline, benzene is used in motor fuels. It is also used as an important industrial solvent and in the production of drugs, plastics, synthetic rubbers and dyes.
Natural sources of benzene include volcanoes and forest fires.
Benzene is the most dangerous aromatic hydrocarbon (McCann, 1994). The cumulative effect of Benzene exposure to small amounts causes chronic poisoning. The two principal effect of Benzene are the destruction of the bone marrow (that leads to a loss of red and white blood cells) and sometimes leukaemia.

Toluene

The principal use for Toluene is in the production of Benzene. Toluene can also be used as an octane booster or enhancer in gasoline, as a solvent, and in solvent extraction processes. A few examples for its use as a solvent can be in aerosol spray paints, wall paints, adhesives, natural gums and resins for example (EPA, 1994).

Although Toluene does not have the same chronic effects on the bone marrow as Benzene, it can cause liver and kidney damage. At high concentration, the effects of Toluene on an exposed person can be more dangerous than the effects of Benzene (McCann, 1994).

Ethylbenzene

Ethylbenzene is a colourless, flammable liquid that smells like gasoline. It is found in natural products such as coal tar and petroleum and is also found in manufactured products such as ink, insecticides and paints. Ethylbenzene is also used in the production of another chemical, styrene. Other uses of Ethylbenzene can be as a solvent, in fuels, or again, to make other chemicals.

The health effects of Ethylbenzene exposure are various. A few examples are throat irritation and chest constriction, irritation of the eyes, and neurological effects such as dizziness (EPA, 1994).

Xylenes

Mixtures of o- p- and m-Xylenes are extensively used in the chemical industry as solvents for products including paints, inks, dyes, pharmaceuticals and detergents.

In the petroleum industry, Xylenes are used as antiknock agents in gasoline, and as an intermediate in synthetic reactions.

High levels of Xylene exposure for short periods are associated with irritation of the skin, eyes, nose and throat (ATSDR, 1997).

4.1.1.2 BTEX's behaviour in the stations

Luthery Station

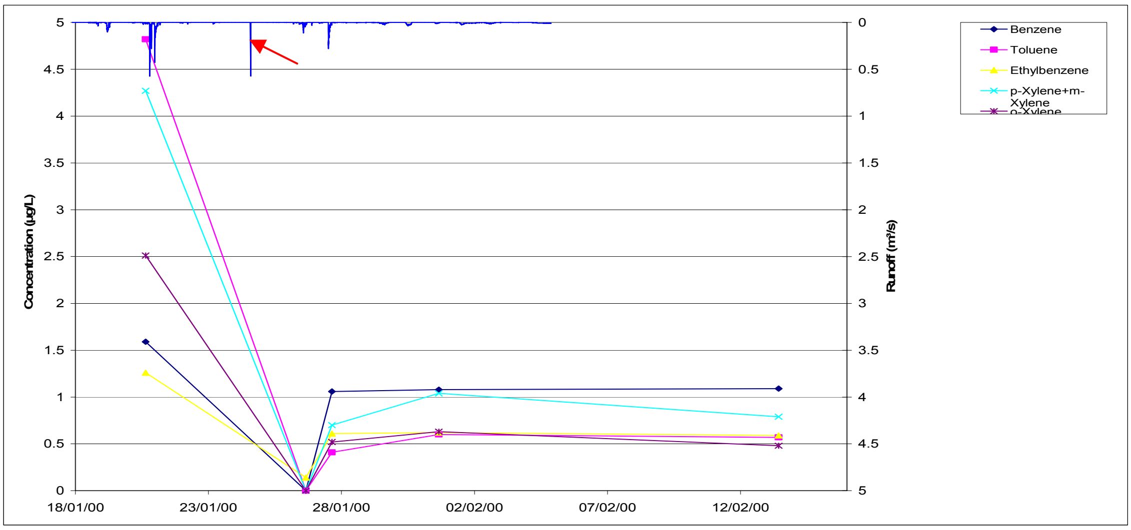


Figure 23: BTEX's behaviour in the Luthery station

As it is shown on the figure 23, all the BTEX compounds behave in a similar way in the Luthery station. The highest concentrations are measured on January 20. This can be explained by the fact that the biggest runoff event of the sampling period took place on that day. The runoff event is big enough on that day and is able to wash out most compounds. The compounds that have the highest water solubilities, like Toluene and p/m-Xylene (see values in annex I) have the highest concentrations. Astonishingly, this is not the case for Benzene that has the second lowest concentration, although Benzene is the most water soluble compound of the BTEX group. Besides that, Benzene also has the lowest Soil Adsorption Constant, and tends to evaporate more easily than the rest. Maybe the high volatilization of Benzene can explain the low concentration.

It seems as though the small runoff event on January 26 is not important enough to wash out the BTEX compounds, as only Ethylbenzene is measured on that day. Having the highest Soil Adsorption Constant, it is possible that some of the Ethylbenzene has not been totally washed out on January 20, and the second runoff event is then able to wash it out.

The runoff event on January 27 is more important than the one on the previous day, and all compounds are measured. During this third runoff event, Benzene and Toluene do not have the same behaviours as on January 20, as the Benzene concentration here is higher than the Toluene concentration. The higher concentration of Benzene on January 27 is difficult to explain as these compounds usually appear together. A possible explanation can be a point source giving in Benzene on that day (use of Benzene as a solvent).

It seems that from January 27 on, the concentrations stay more or less constant for all compounds. The runoff events on January 31 and on February 13 are too small to influence the concentrations. This long tailing of the curve illustrates also the fairly high Soil Adsorption Constant that characterises the aromatic hydrocarbons compared to the aliphatics for example.

The Luthery station is the station where the highest concentrations are measured. This can be explained by the fact that the runoff measured here is minor compared to the other stations. For this reason, the compounds measured in this station, have much higher concentrations than in the other stations. Also, the highest concentrations are measured on January 20 for all the BTEX compounds. Because of the small catchment size, the compounds are fairly rapidly washed out of the catchment. This can explain the high concentrations measured on January 20.

Womens Association

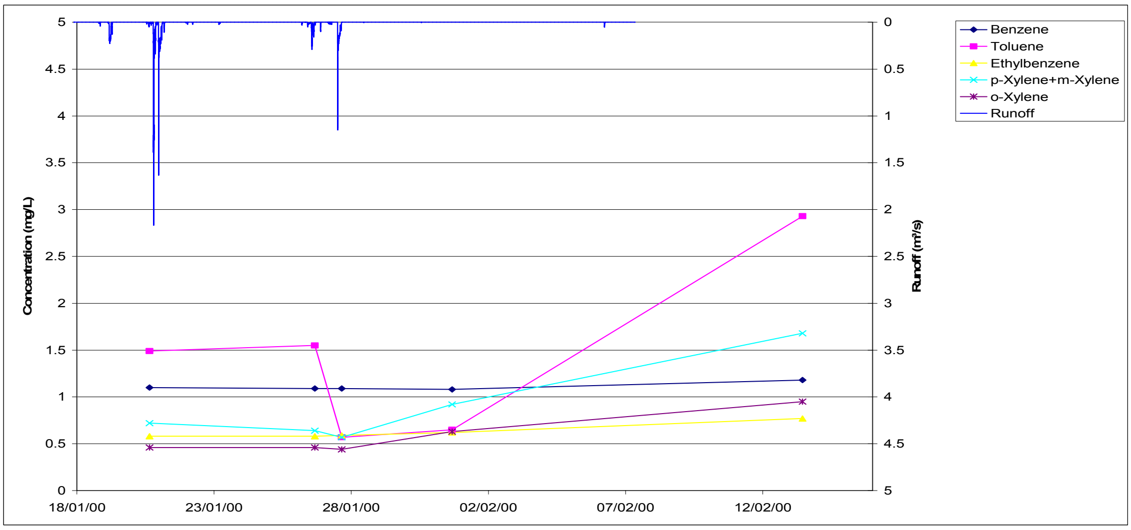


Figure 24: BTEX's behaviour in the Womens Association station

The behaviour of the BTEX compounds in the Womens Association station is quite different from the behaviour of these compounds in the Luthery station. These differences are to be explained with the difference in catchment size and in runoff event size, as the physical properties of the compounds stay the same.

Here as well a trend can be recognised between the compounds. They all behave in more or less the same way, and no major variations are observed, except for Toluene.

Benzene is the compound that does not seem to be influenced by the runoff, as its concentrations stay close to constant over the whole sampling period. The Xylenes and Ethylbenzene also behave in a similar way, and a slight increase of concentration is observed on February 13. Because the runoff events decrease throughout the sampling period, the slight increase of concentrations at the end of the sampling period can be explained by the "dilution effect". The smaller runoff provokes a concentration increase. Additionally, because of the catchment size, the compounds have a longer soil-contact time, and have the time and the possibility to undergo adsorption, as they do not get washed out immediately.

Because of the high water solubility of Toluene compared to the other compounds, this is the compound that shows the biggest variability in its behaviour. The reason for the concentration decrease on January 27 can be explained by the fact that most of the Toluene has already been washed out on the previous days. Therefore, Toluene is the only compound that undergoes the dilution effect so strongly.

Kiswani station

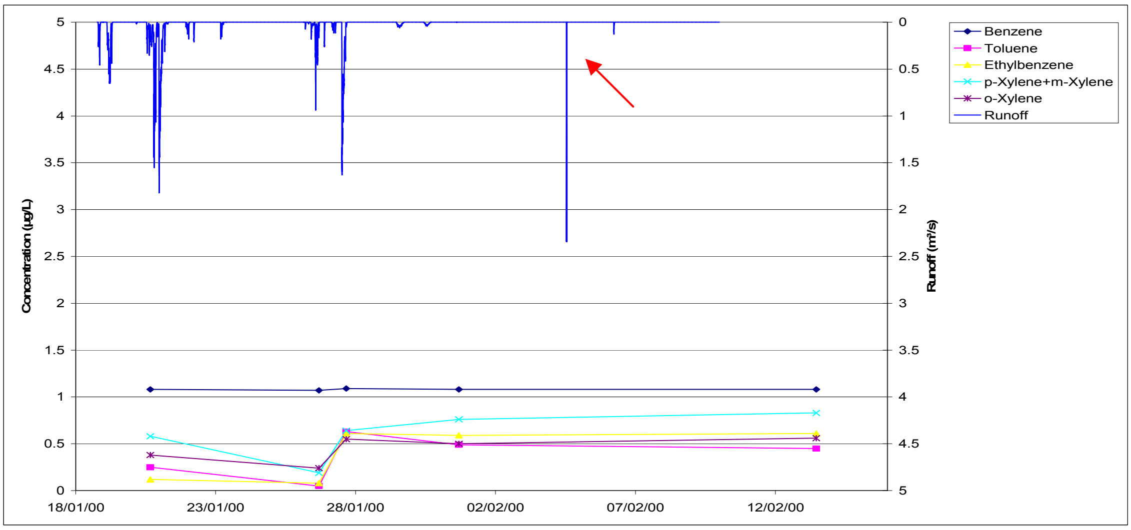


Figure 25: BTEX's behaviour in the Kiswani station

Because Luthery, Womens Association and Kiswani station are part of the same drainage system, and knowing that Luthery's and Womens Association's runoffs flow together in Kiswani, the behaviour of the compounds in this station is expected to be a "fusion" of both other stations, as they have a direct impact on Kiswani station. For this reason, the compound's behaviour in Kiswani can also be explained by their behaviour in the two stations described previously. The only problem here underlies on the delay in the time of sampling, as the samples are not taken at exactly the same time in the different stations. The BTEX's behaviour in the Kiswani station is quite similar to the one in the Luthery station. The difference is that the initial concentrations are a great deal lower than in the Luthery station. This can be explained by the much higher runoff in Kiswani.

Unlike the Luthery station, concentrations are measured on January 26 for all compounds. These concentrations can be explained by the concentrations measured in Womens Association on the same day. The compounds with the lowest concentrations on January 26 are those that have the highest vapour pressures (Toluene and Ethylbenzene) as it is probable that most of it evaporated on the way to Kiswani. Here as well, an increase is observed on January 27, followed by a more or less constant behaviour of the compounds during the rest of the sampling period.

In this station as well, Benzene keeps a constant behaviour, which is somewhat difficult to explain.

Industrial station

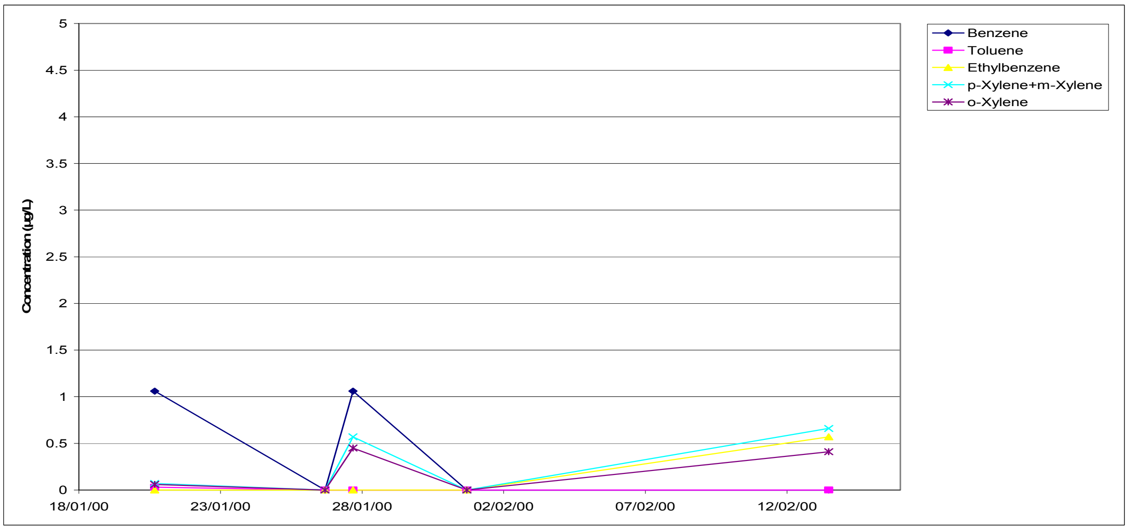


Figure 26: BTEX's behaviour in the Industrial station

The first observation that can be made on the BTEX's behaviour in the Industrial station is that the concentrations are much lower than in the three stations that are described above. As no runoff data is available for this station, it is hard to know how the runoff influences the concentrations in this station. The fact that the Industrial station is not exactly situated in the city centre can be an explanation for this. The car traffic is probably less dense in this catchment compared to the other stations, which can explain the lower BTEX concentrations here.

Toluene is only measured on January 20, and at a very low concentration. It is possible, that because of its high vapour pressure compared to the other compounds, and because of its very low concentration, Toluene evaporates throughout the sampling period, which can explain why Toluene is only measured on that day.

Ethylbenzene has an opposite behaviour, in the sense that it is only measured on the last sampling day, February 13. Ethylbenzene having the highest Soil Adsorption Constant, it is possible that only the third runoff event is able to solve the Ethybenzene.

Khaled station

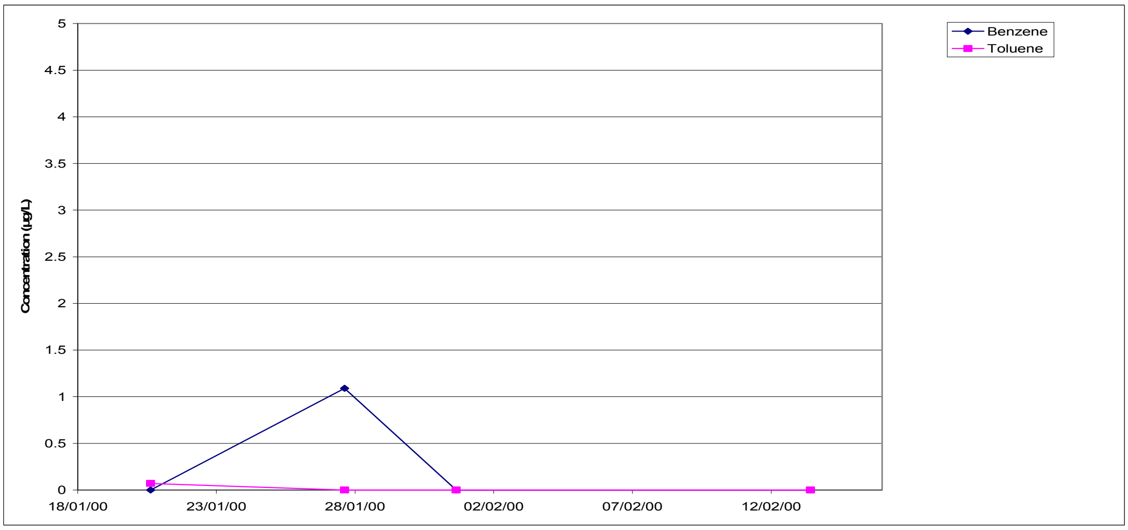


Figure 27: BTEX's behaviour in the Khaled station (roof station)

Only two compounds are measured in the roof station: Benzene and Toluene; Toluene on January 20 and Benzene on January 27. These two compounds are those among the BTEX compound, that have the highest vapour pressures, and that tend to evaporate easily, which can explain their presence in the atmosphere. Nevertheless, it is difficult to explain why they did not occur on the same day, as these two compounds are usually used together.

4.1.2 Dichloromethane

4.1.2.1 Description of Dichloromethane

Dichloromethane is a compound that is used in many applications, although the most important use is as the principal active ingredient in organic-based paint strippers. It is used in industrial paint removers where it is found in very high concentrations (60-80%). The second most important use of Dichloromethane is in chemical processing.

It has been predicted that the use of Dichloromethane should continue to decline, because of the environmental concerns. For this reason, users of Dichloromethane are put under great pressure, in order to limit usage, control emissions and to reduce worker exposure (Mannsville, 1993).

Chlorinated hydrocarbons are, just as the aromatic hydrocarbons very hazardous. High concentrations of Dichloromethane can cause narcosis, lung irritation, pulmonary edema, and is a probable human carcinogen. In the body, Dichloromethane decomposes and forms carbon monoxide and large inhalation amounts have already resulted to fatal hearth attacks (McCann, 1994).

4.1.2.2 Dichloromethane's behaviour in the stations

Luthery station

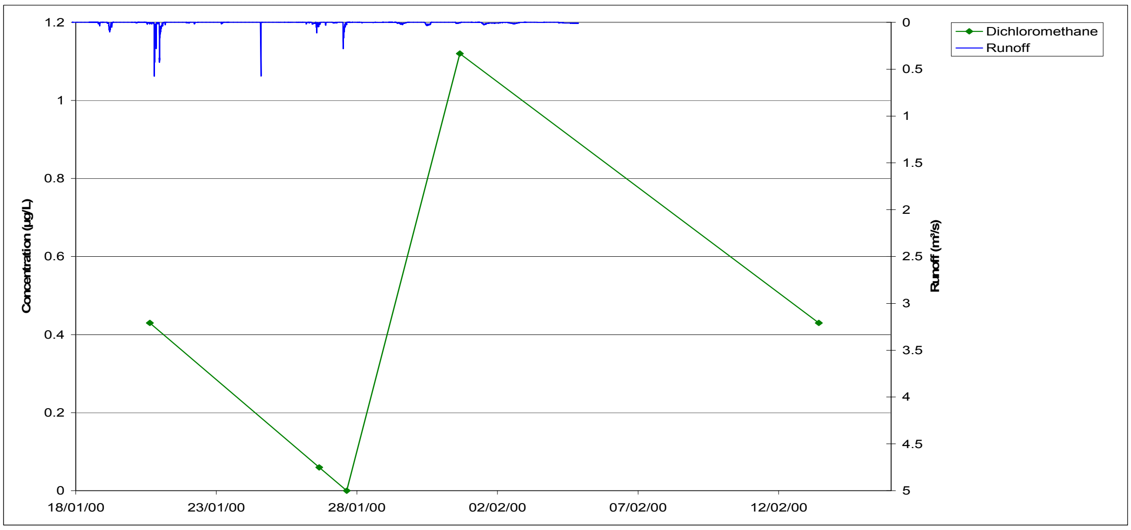


Figure 28: Dichloromethane's behaviour in the Luthery station

The Dichloromethane concentration on January 20 is slightly higher than 0.4µg/L. The rapid decrease of concentration on January 26 and 27 can be explained by the fact that the compound already has been washed out by the big runoff event that took place on January 20. Considering the small catchment's size, this effect is underlined. Again, the concentration peak on January 31 probably results from the dilution effect.

The missing runoff data on February 13 makes an interpretation of the measured concentration difficult on that day. One among many other explanations can be that a similar runoff event to the one on January 20 took place on that day because of the same measured concentration on both days.

Womens Association station

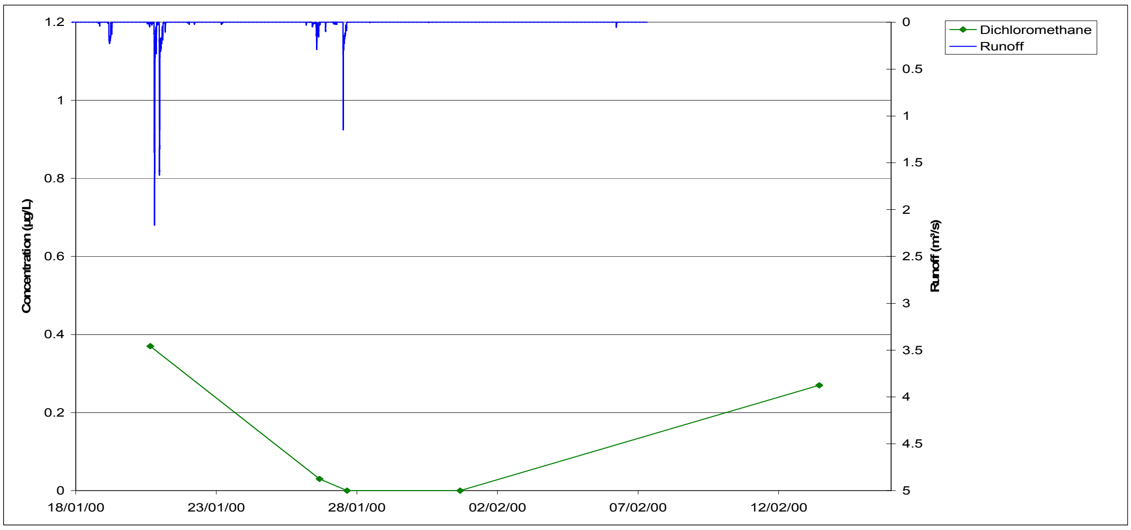


Figure 29: Dichloromethane's behaviour in the Womens Association station

The highest concentration of Dichloromethane in the Womens Association station is measured on January 20. A rapid decrease of the concentration is then observed on January 26. It is probable that the big runoff event on January 20 washed out the majority of Dichloromethane on that day. In order to explain the 0 µg/L concentration on January 27 one can refer to the specific occurrence characteristics of this compound (use of the compound). It does not seem that there is any input of this compound between these two runoff events. The last measurement does not have any corresponding runoff data, but as here as well the concentration measured on this day is close to the one measured on January 20, it can be expected that both runoff events are similar.

Kiswani station

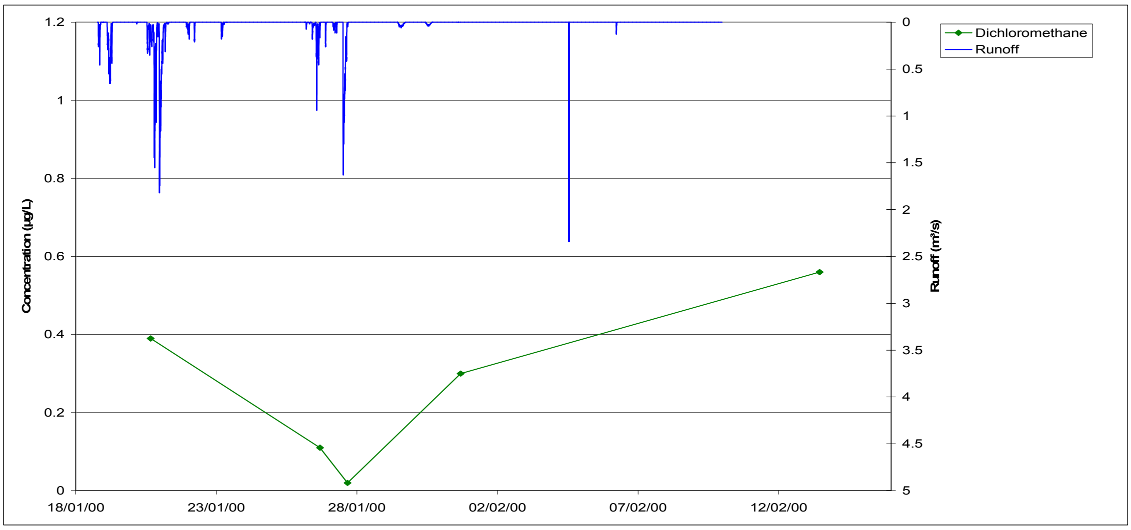


Figure 30: Dichloromethane's behaviour in the Kiswani station

As already mentioned, the concentration run in Kiswani is directly linked to the concentration run in the two other stations. Additionally, the influence carried by Womens Association is dominant because of its catchments size. For this reason, the run of the concentrations can be explained in the same way as for the Womens Association station. Thus, the concentration run in Kiswani is more similar to the one of Womens Association, except on January 31. Because no concentration is detected in Womens Association on that day, Kiwanis run of concentration is directly linked to the concentration measured in Luthery on that day.

Also, the concentration difference that exists between Luthery and Kiswani (1.1µg/L in Luthery and 0.3µg/L in Kiswani) illustrates the volatility of this compound. Of course, the delay in sampling time should be kept in mind. The final increase of the concentration can be related to the dilution effect.

Industrial station

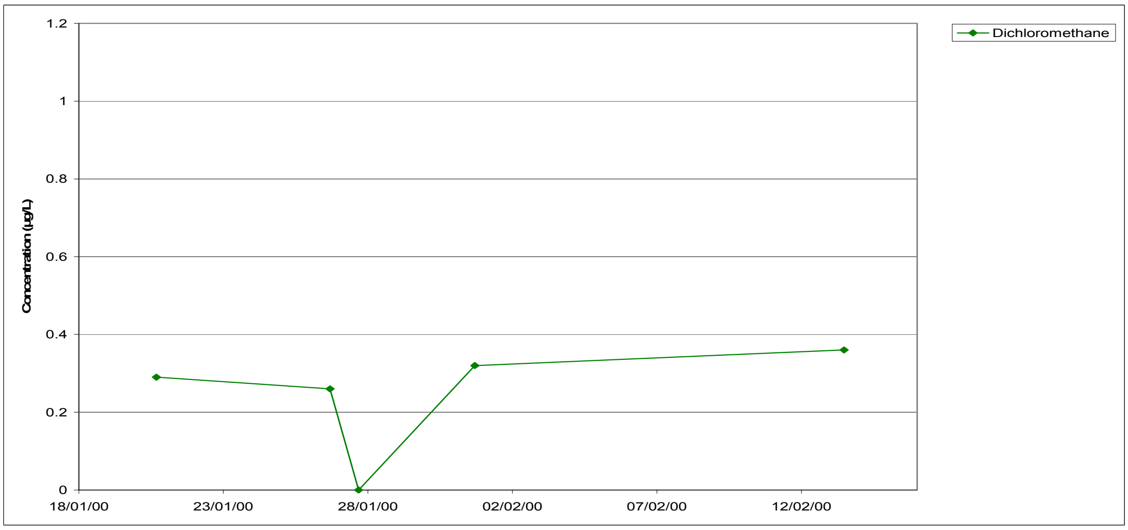


Figure 31: Dichloromethane's behaviour in the Industrial station

Not only the concentration run of Dichloromethane in the industrial station, but also the concentration values are comparable to those in Womens Association. However, a higher concentration is measured in Industrial on January 26 compared to the one measured in Womens Association. This difference in concentration can be explained by a probably less important runoff event on January 20 in Industrial. This means that a minor amount is washed out on January 20, and therefore more Dichloromethane is available to be washed out on January 26. Additionally, the smaller percentage of roads and buildings in the catchment suggests a smaller runoff respond to the rainfall.

Khaled station

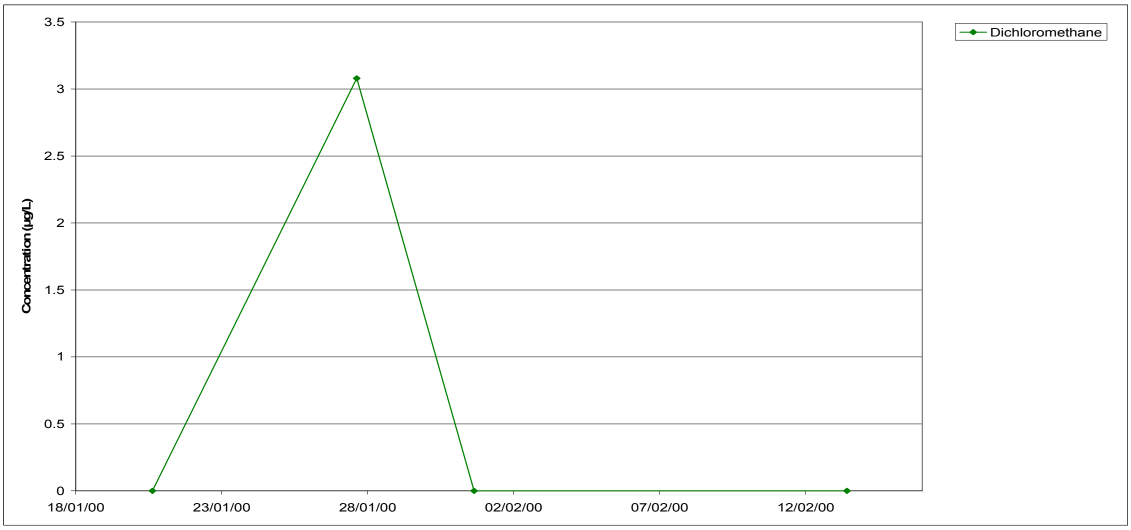


Figure 32: Dichloromethane's behaviour in the Khaled station

Dichloromethane is astonishingly found in the roof station on January 27. Because of the high density of this compound, it is on the one hand not expected to be found in the atmosphere, and on the other hand, certainly not in such a high concentration. Of course, the possibility of an error during measurement should also be taken into consideration.

4.1.3 Dimethylsulfide

4.1.3.1 Description of Dimethylsulfide

Dimethylsulfide is a volatile organic compound belonging to the aliphatic hydrocarbon family. No information has been found concerning its use and its potential health effects on the humans.

4.1.3.2 Dimethylsulfide's behaviour in the stations

Luthery station

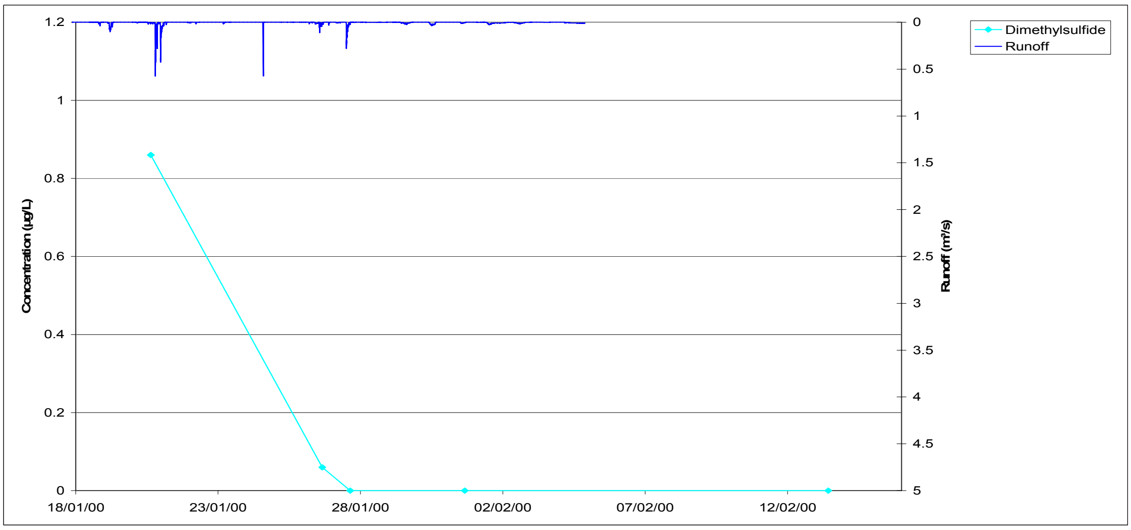


Figure 33: Dimethylsulfide's behaviour in the Luthery station

Probably because of its very high water solubility and its high vapour pressure, Dimethylsulfide is only measured on January 20 in the Luthery station. Because of the small catchments' size, most of the Dimethylsulfide is probably directly washed out on that day. For this reason, this compound is only measured on the first day of sampling.

Womens Association

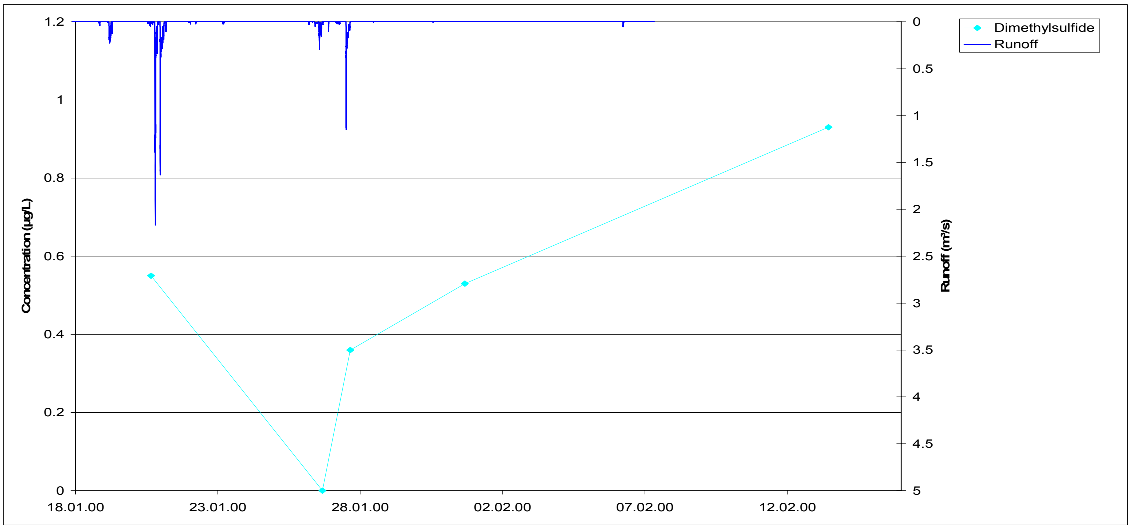


Figure 34: Dimethylsulfide's behaviour in the Womens Association station

The concentration run of Dimethylsulfide in the Womens Association station is different than in the Luthery station. Because of its very high water solubility, Dimethylsulfide tends to correlate with the runoff intensity. Here as well, the concentration increase towards the end of the sampling period can be explained by the dilution effect that acts on the compounds because of the probably smaller runoff events at the end of the sampling period.

Kiswani station

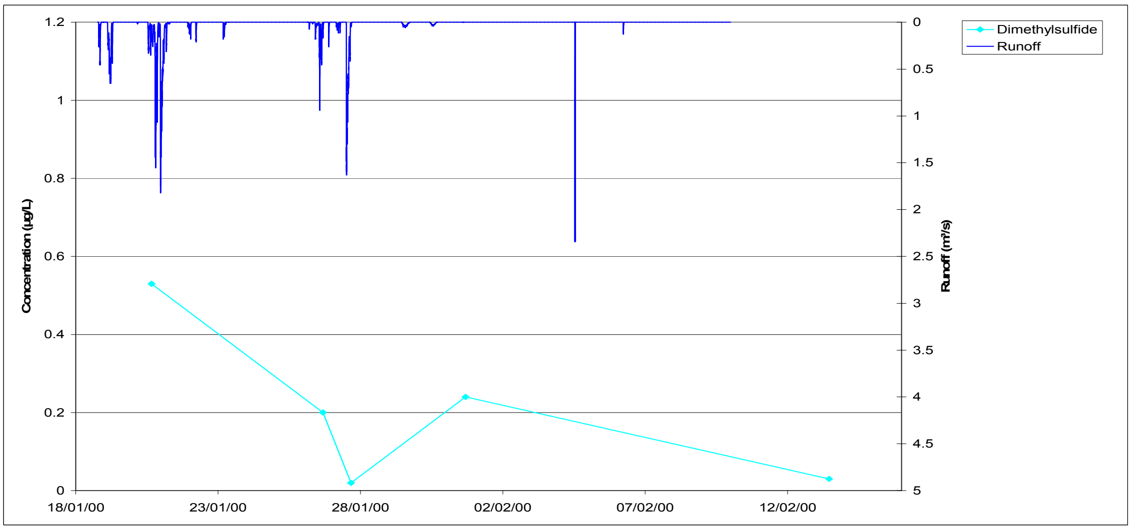


Figure 35: Dimethylsulfide's behaviour in the Kiswani station

The Dimethylsulfide concentration in Kiswani results directly from the concentrations in Luthery and Womens Association. For this reason, the highest concentration is measured on January 20 (as Luthery and Womens Association both have high concentrations on that day). The concentration peak on January 31 is difficult to explain, whereas the last concentration decrease can be explained by the very high vapour pressure of the compound: volatilization of the compound on its way to Kiswani. Again, the delay in sampling time is also to be taken into consideration.

Industrial station

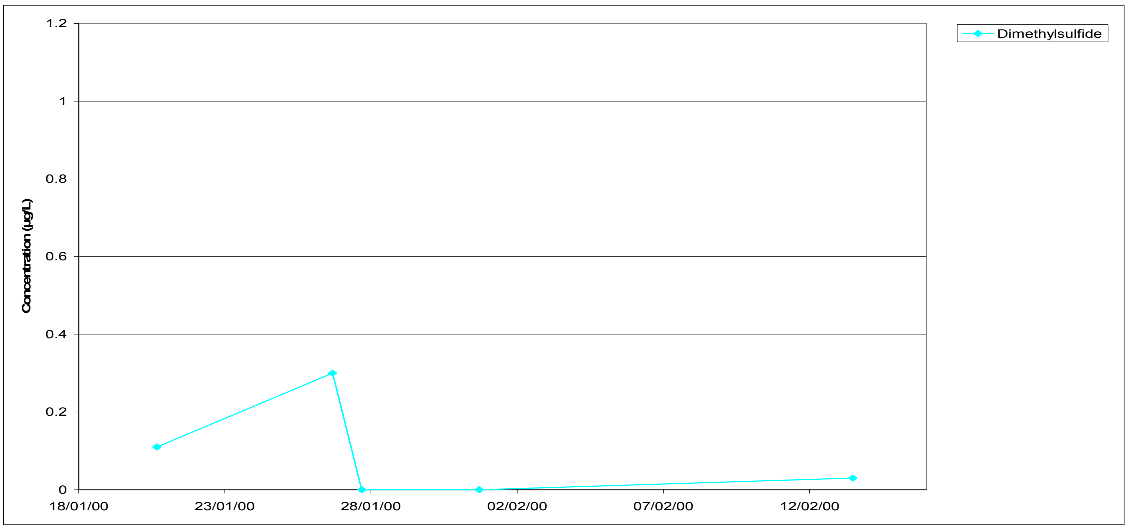


Figure 36: Dimethylsulfide's behaviour in the Industrial station

Although no runoff data is available for this station, an approximation of it is possible using the runoff data of the other stations. Nevertheless, an exact adaptation is not possible, as the industrial catchment runoff mostly depends on the precipitation, as this catchment is less densely built up than the other catchments.

The behaviour in the Industrial station is surprising regarding the peak of the concentration on January 26. Referring to the above mentioned points, the peak is expected on January 20 (as it is the case in the other stations).

This peak can eventually be explained by an additional input such as a point source or by an error during the measurement.

Khaled station

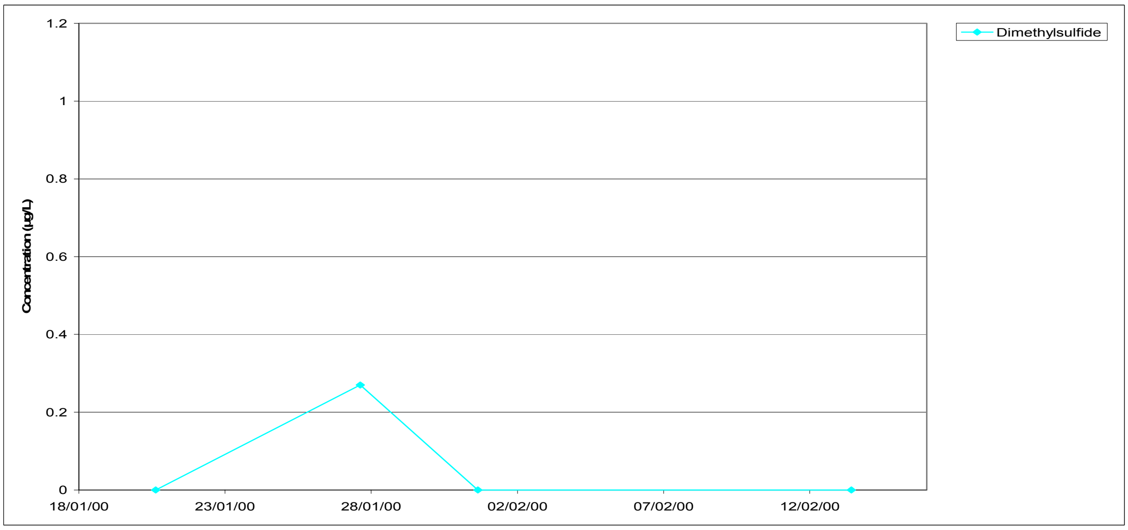


Figure 37: Dimethylsulfide's behaviour in Khaled station (the roof station)

Dimethylsulfide is only measured on the roof station on January 27. The fact that Dichloromethane is also only measured on that day in Khaled (just like Benzene and Dichloromethane), can awaken the suspicion that special atmospheric conditions occurred on that day. Nevertheless, a possible error in measurement is also to be considered.

4.1.4 MTBE

4.1.4.1 Description of MTBE

The largest use for MTBE is as a gasoline additive. An insignificant part of it is also used as a chemical intermediate to produce high purity Isobutylene.
The environmental release of MTBE can take place at industrial sites implicated in the manufacture of MTBE, in the blending of MTBE with gasoline, from spills or leaks, or fugitive emissions at automotive service stations (EPA, 1994).
The health effects of MTBE on humans are nausea and dizziness for example.

4.1.4.2 MTBE's behaviour in the stations

Luthery station

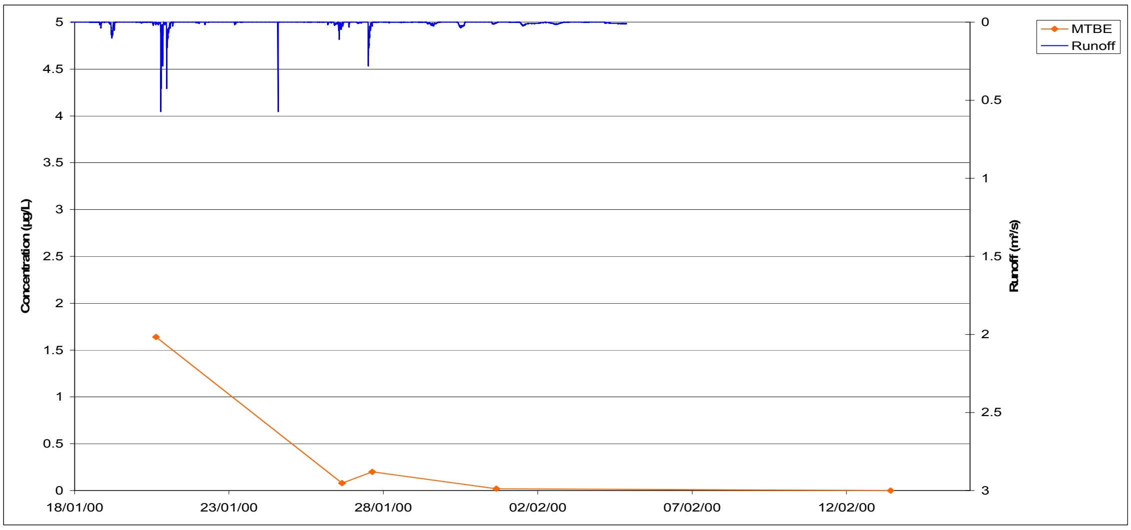


Figure 38: MTBE's behaviour in the Luthery station

MTBE has just like Dimethylsulfide a very high solubility in water. Therefore, a similar behaviour of these two compounds is observed. MTBE's highest concentration is also measured on January 20. However, small concentrations are measured on January 26 and 27. This can be explained by the slightly less evaporative behaviour of MTBE (vapour pressure). Here again, because of the small catchment size, the MTBE is washed out rapidly.

Womens Association station

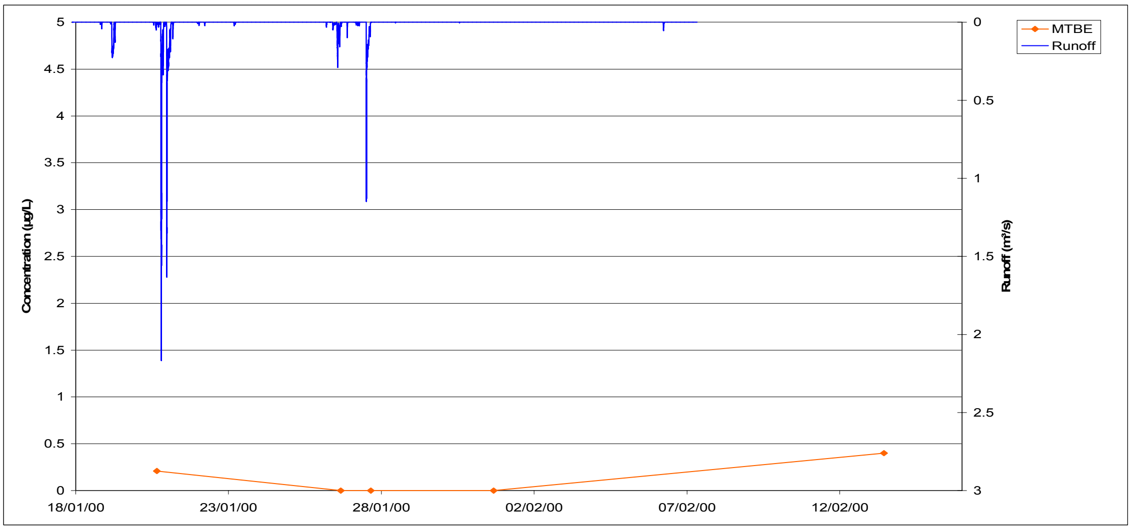


Figure 39: MTBE's behaviour in the Womens Association station

MTBE is only detected during the first and the last sampling day in the Womens Association station. The first detected concentration can be explained by the big runoff event on January 20. Based on its high water solubility together with its high volatility and its low Soil Adsorption Constant, the compound tends to be washed out rapidly from the catchment. No MTBE is left to be washed out on January 26, nor on January 27. The measured concentration on February 13 is slightly higher than the one measured on January 20. A similar runoff event on February 13 can eventually explain the concentration measured on that day, assuming there is no significant runoff on the previous days.

Kiswani station

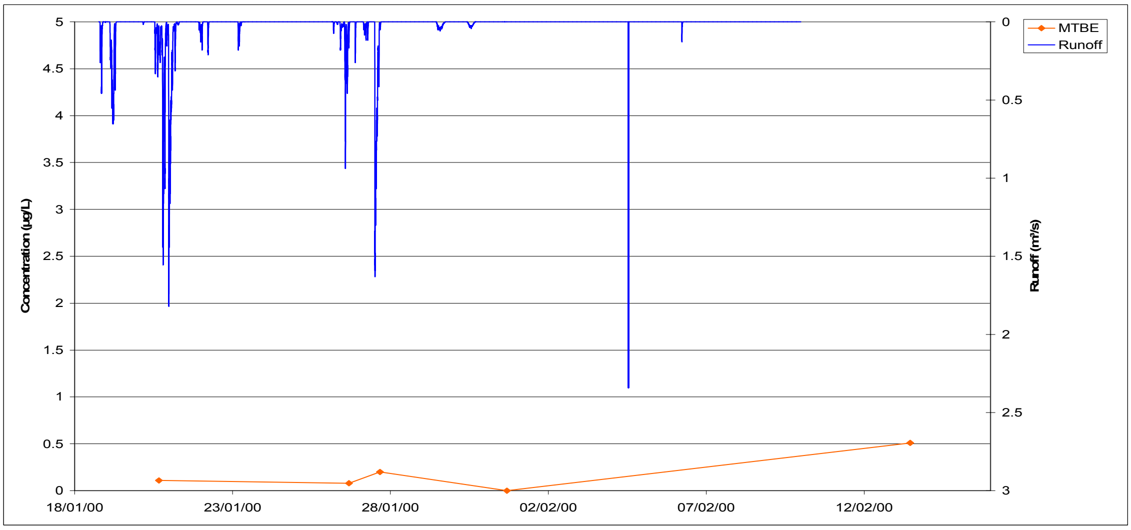


Figure 40: MTBE's behaviour in the Kiswani station

Here as well, the variation of the MTBE concentration in Kiswani station can be explained with the variations observed in the Luthery and the Womens Association stations. As no concentrations are measured on January 26, 27 and 31 in the Womens Association station, the measured concentrations in Kiswani on those days are directly linked to those measured in

Luthery. In the same way, the concentration measured on February 13 is directly linked to the concentration measured in Womens Association on that day, as none is detected in Luthery on that day.

Industrial station

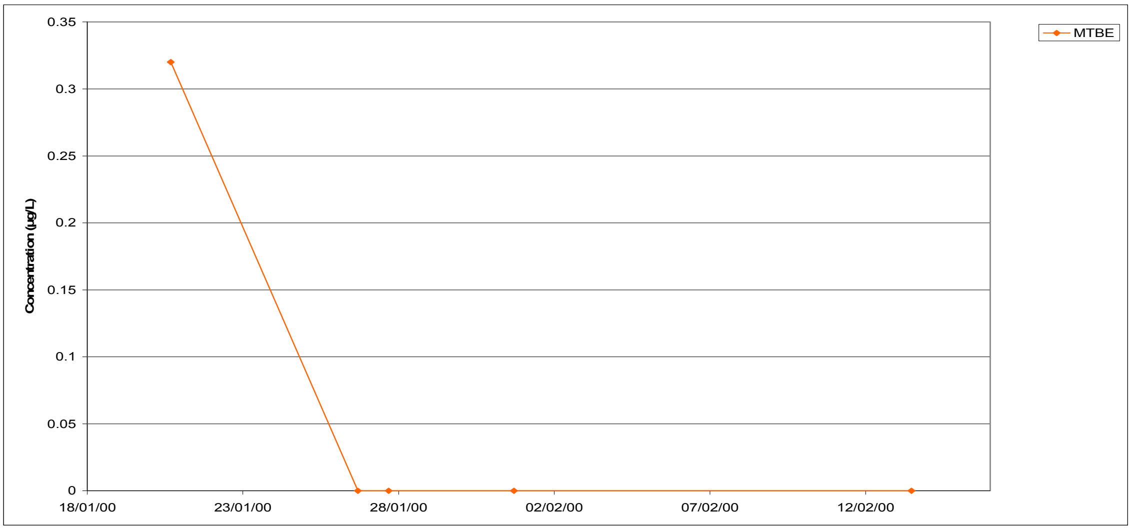


Figure 41: MTBE's behaviour in the Industrial station

As MTBE is a gasoline additive and as it is only detected on January 20, the possibility of a point source causing this concentration exists.

The fact that MTBE is not measured on the roof station, might be explained by the fact that MTBE is extremely volatile, which means that the particles are very dispersed in the atmosphere. Nevertheless, this does not necessarily mean that no MTBE is present in the atmosphere. The possibility that MTBE is present, but in such a dispersed way, that it can not be measured also exists.

4.1.5 Tetrachloroethene

4.1.5.1 Description of tetrachloroethene

Tetrachloroethene is a manufactured chemical that is primarily used in the dry-cleaning of fabrics, including clothes. It can also be used for degreasing metal parts and in manufacturing other chemicals. Tetrachloroethene is a non-flammable, colourless liquid at room temperature.

4.1.5.2 Tetrachloroethene's behaviour in the stations

Luthery station

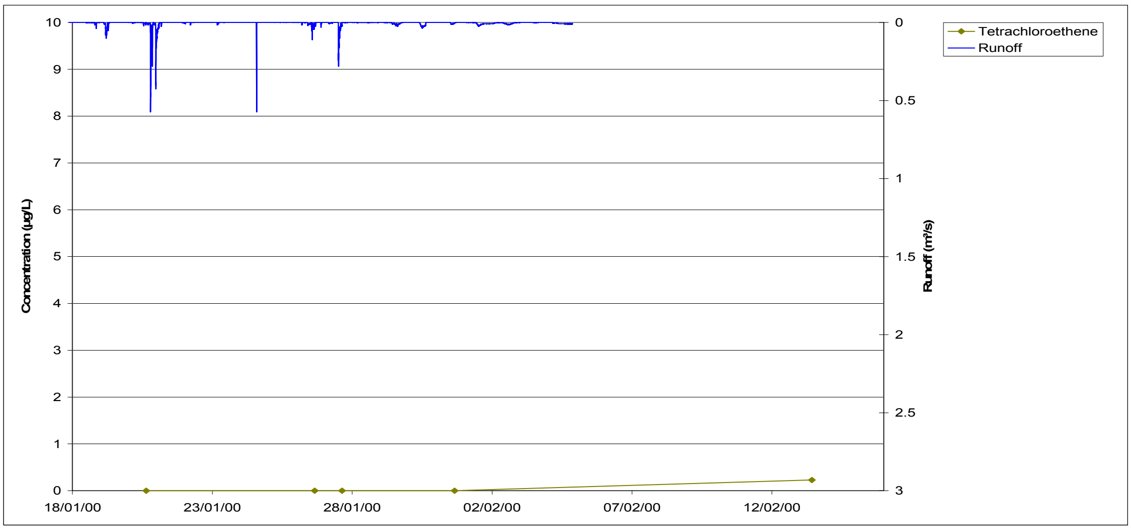


Figure 42: Tetrachloroethene's behaviour in the Luthery station

Tetrachloroethene is only measured on February 13. It seems as though the previous runoff events are not able to dissolve the compound. It is only after the fourth runoff event that Tetrachlorethene is dissolved. The reason for this behaviour can be linked to the fact that Tetrachloroethene is highly sorptive and has a higher density than water, which indicates that this compound has the tendency to sink down rather than volatilize. This aspect can be a reason why Tetrachloroethene is only measured on the last sampling day.

Womens Association station

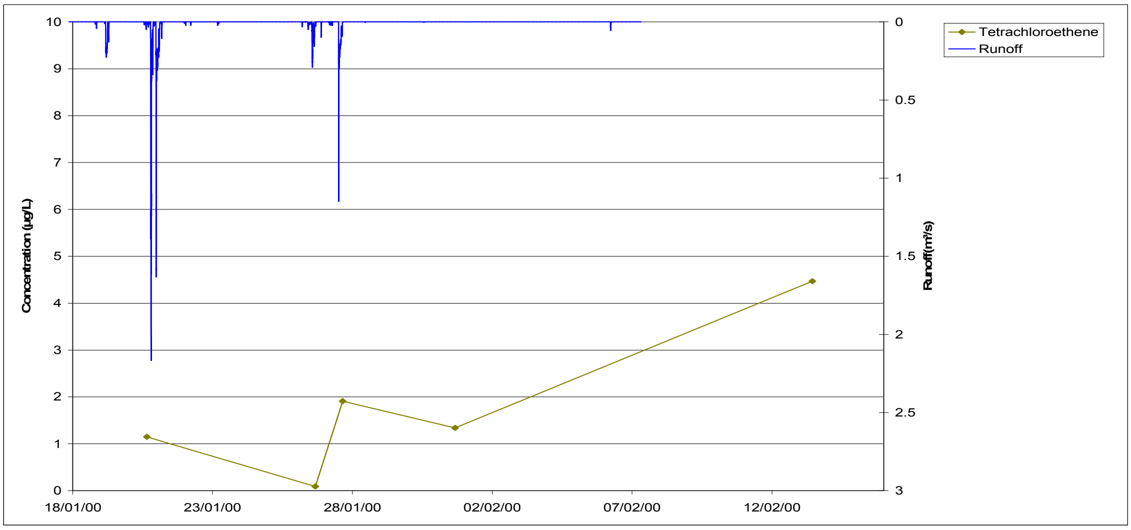


Figure 43: Tetrachloroethene's behaviour in the Womens Association station

The behaviour of Tetrachloroethene in the Womens Association station differs to the one in Luthery station. The runoff events here are much more important than in the Luthery station, which means that the compound can be dissolved. The increase of the concentration towards the end of the sampling period is here as well probably linked to the dilution effect that is also observed for other compounds.

Kiswani station

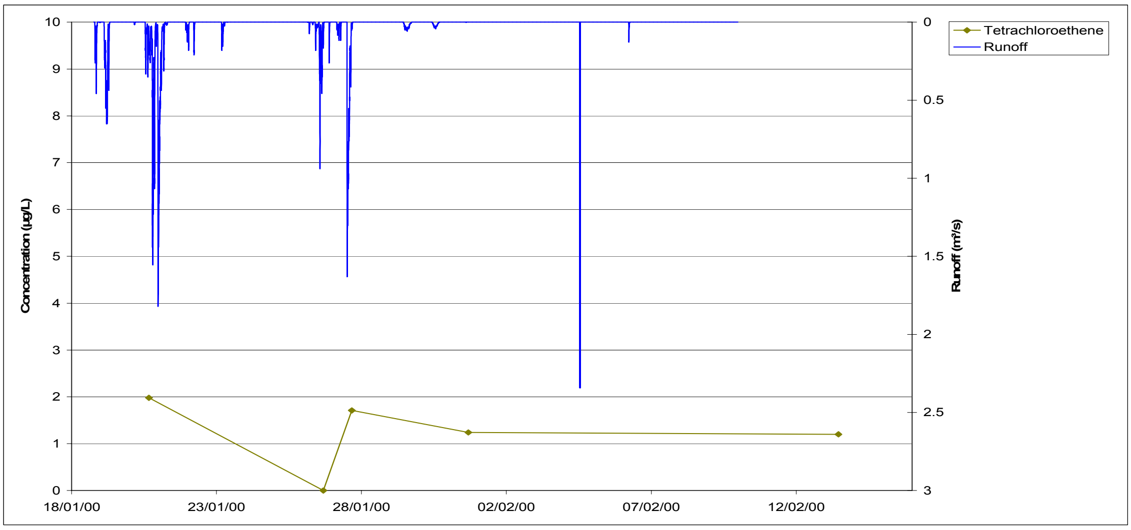


Figure 44: Tetrachloroethene's behaviour in the Kiswani station

As the Tetrachloroethene concentrations in Kiswani are only influenced by those of the Womens Association during the four first measurements (as Tetrachloroethene is only detected on February 13 in Luthery), it is not surprising to have the same variations of concentration in both stations. The long tailing that is seen from January 27 on, has probably to do with the high sorptivity of this compound.

Industrial station

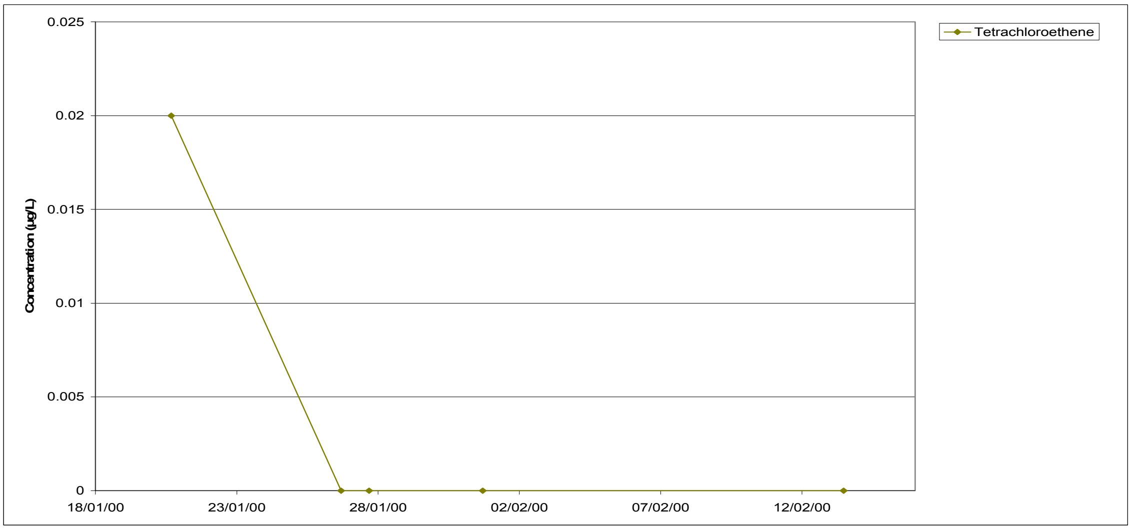


Figure 45: Tetrachloroethene's behaviour in the Industrial station

Tetrachloroethene is only measured on January 20 in the Industrial station. The big runoff event on that day is the only one that is able to dissolve the compound, and therefore it is not detected on the other days.

As Tetrachloroethene has a higher density than water, it is not quite likely to find it in the roof station. For this reason, Tetrachloroethene is not detected on the roof station.

4.1.6 Chloroform

4.1.6.1 Description of Chloroform

Chloroform is a colourless liquid with a pleasant non-irritating odour and a slightly sweet taste. It only burns when it reaches very high temperatures. In the past, chloroform was used as inhaled anesthetic during surgery but not any more. Today, chloroform is used to make other chemicals and can also be formed in small amounts by adding chlorine to water.
Breathing about 900 parts of chloroform per million parts air for a short time can cause dizziness, fatigue and headache. Breathing air, eating food or drinking water with high levels of chloroform for a long period of time may damage liver and kidneys. Chloroform can also cause skin irritation (ATSDR, 1997).

4.1.6.2 Chloroform's behaviour in the stations

Luthery station

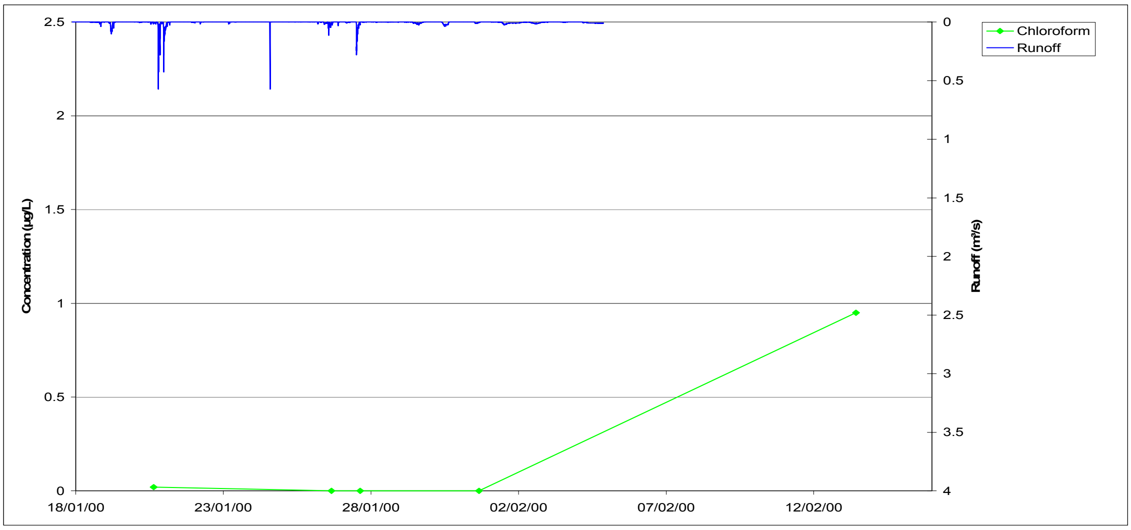


Figure 46: Chloroform's behaviour in the Luthery station

The description of Chloroform's behaviour in the runoff is based on its high volatility rather than its high density, as the runoff water is permanently in motion. Therefore, the characteristics of its high density can be disregarded in this case.
Just as for Tetrachloroethene, Chloroform is only measured on February 13 in the Luthery station. The absence of Chloroform at the beginning of the sampling period can be explained by the high volatility and the fairly low Adsorption Constant of the compound. The detected Chloroform on February 13 could have been washed out from the atmosphere (high water solubility of Chloroform) or from a point source.

Womens Association station

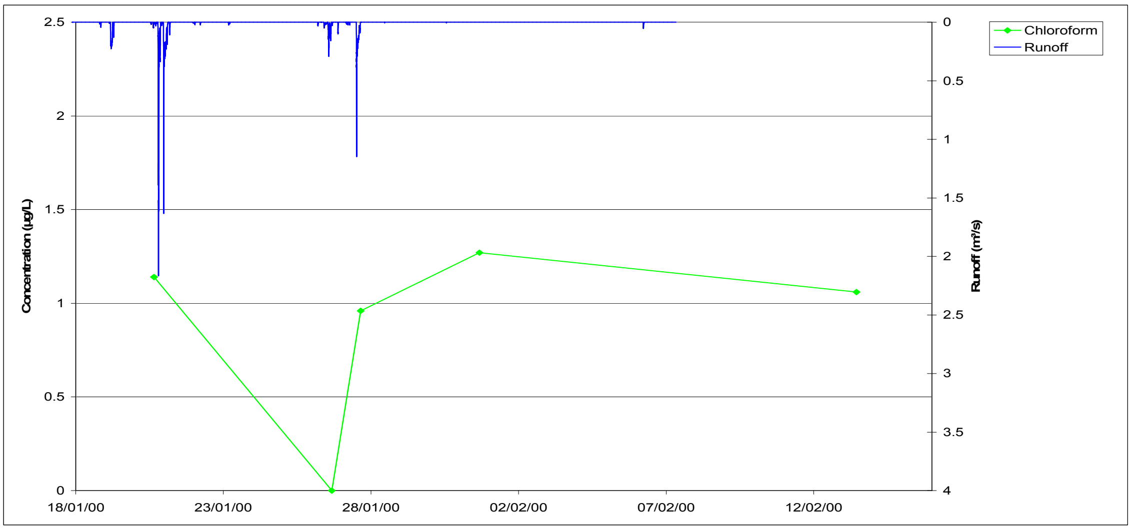


Figure 47: Chloroform's behaviour in the Womens Association station

Because of its very high water solubility, the concentration run of Chloroform directly depends on the runoff intensity. A slight decrease of the concentration is noticeable at the end of the sampling period, which probably is linked with the high volatility of this compound.

Kiswani station

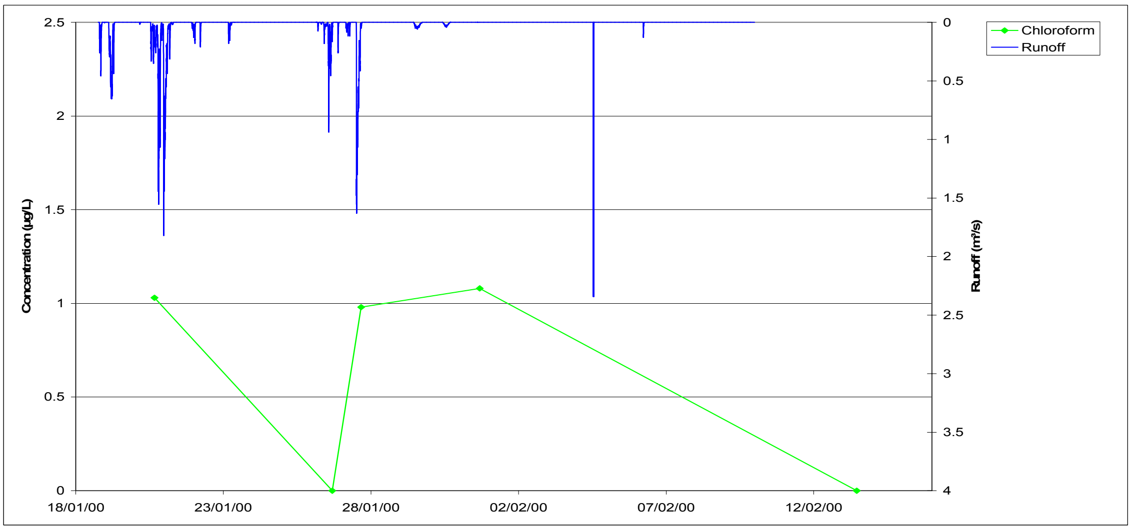


Figure 48: Chloroform's behaviour in the Kiswani station

The four first measurements of Chloroform in the Kiswani station are only influenced by the behaviour in the Womens Association station (as no Chloroform is measured during the first four sampling days in the Luthery station), which explains that both curves are identical not only in form, but also in concentrations, although slightly lower concentrations are measured in Kiswani, probably due to the fact that Chloroform tends to volatilize. However, here again, the delay in sampling time is to be taken into consideration.

The final decrease of the concentration can be explained by the fact that, by the time that the Chloroform present in Luthery and Womens Association station arrives in the Kiswani station, most of it has already volatilised.

Industrial station

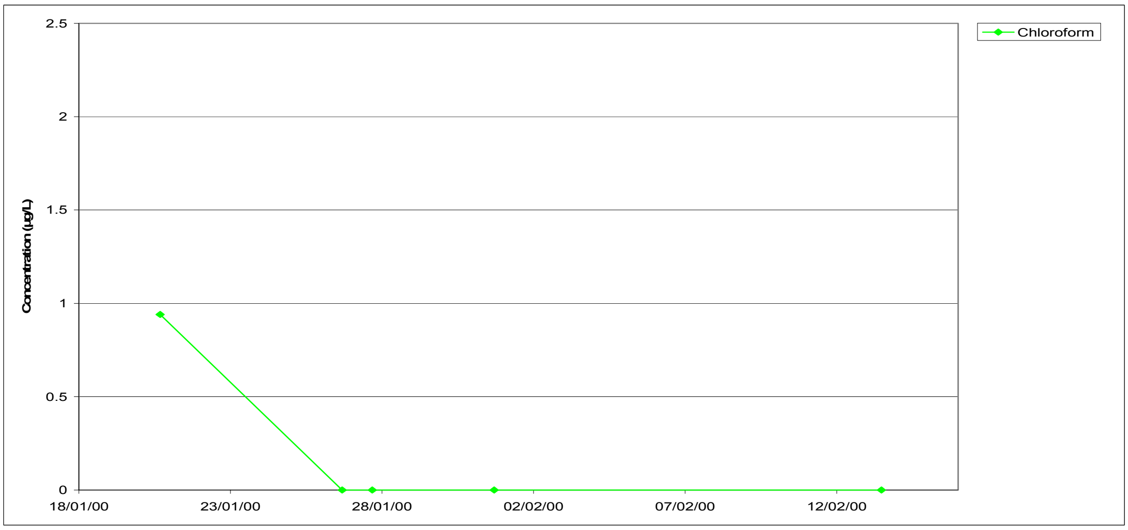


Figure 49: Chloroform's behaviour in the Industrial station

Just as Tetrachloroethene, Chloroform is only detected on January 20 in the Industrial station. Here as well, different possibilities can explain this single detection (see explanations chapter 4.1.5.2, Industrial station).

Chloroform is, just like Tetrachloroethene, not detected on the roof, for the same reasons.

4.2 VOCs in the Ein Mazbah spring

14 Volatile organic compounds have been sampled in ten different springs located in and around Ramallah during two consecutive years: 1999 and 2000.
Because the major part of the analysis focuses on the centre of Ramallah, only one spring is analysed here, as the other springs are located too far out, and probably are not influenced by the city. The most interesting spring for this purpose is the Ein Mazbah spring, as it is located close to the centre of the city.

Although 14 compounds are measured in the springs, data is provided only for six of them in the Ein Mazbah spring. The compounds for which data is collected are: Methylene-Chloride, 2-Butanone, Benzene, MTBE, Tetrachloro-Methane, and Toluene.
Unfortunately, data is only available for two compounds over the two years; therefore a possible trend is difficult to distinguish. These two compounds are Benzene and Methylene-Chloride. The two following figures show the concentrations of these compounds during both years.

4.2.1 Results

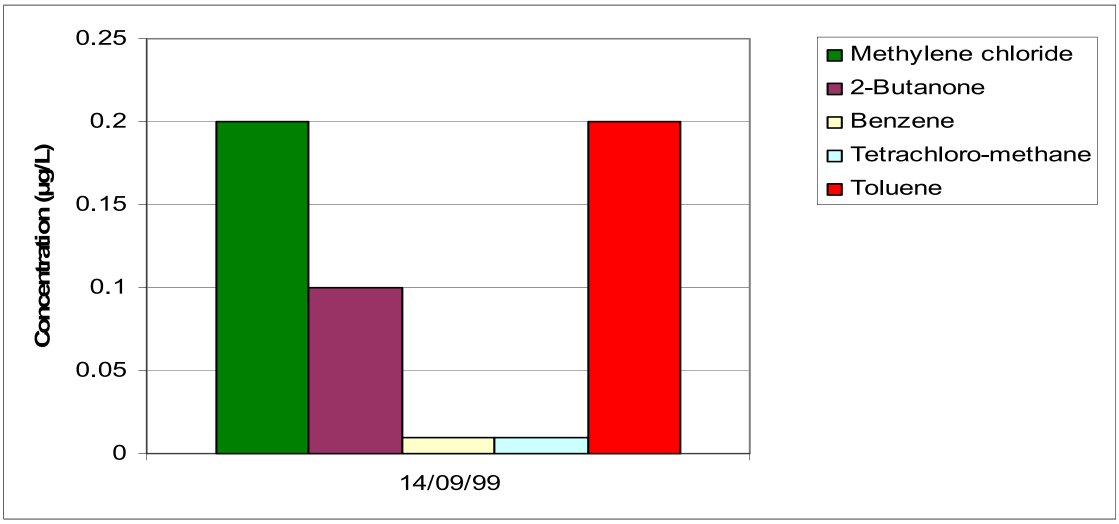


Figure 50: VOC concentration in Ein Mazbah in 1999

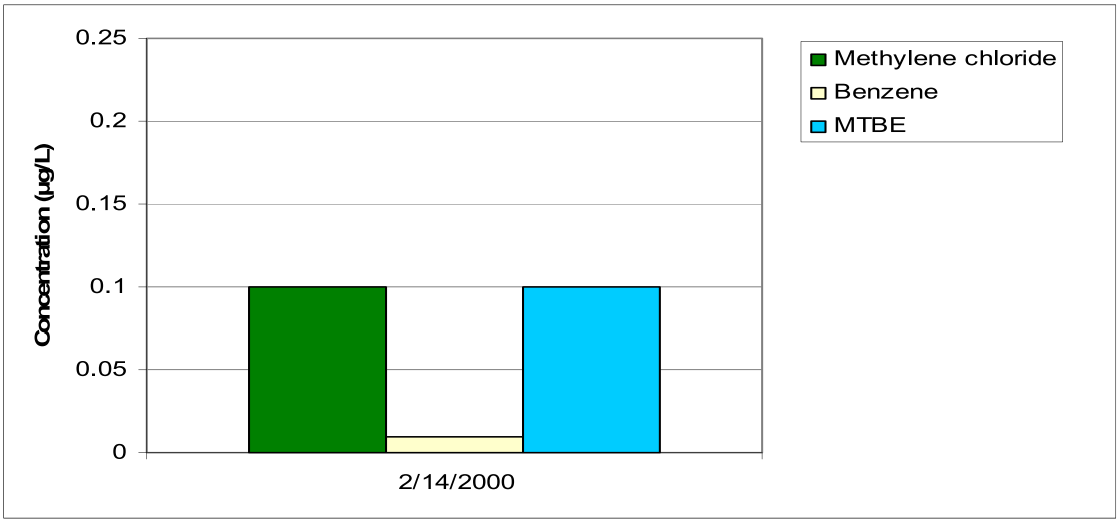


Figure 51: VOC concentrations in Ein Mazbah in 2000

4.2.2 Discussion

In 1999, the compounds having the highest concentrations (0.2µg/L) are Methylene-Chloride, which is a chlorinated hydrocarbon, and Toluene, which is a gasoline related compound. The two compounds with the lowest values also belong to the same chemistry families. These are Benzene and Tetrachloro-Methane, and the concentration is <<0.1 µg/L for both of them. Surprisingly, Toluene is found at a considerably higher concentration than Benzene in the spring although Benzene has a higher water solubility than Toluene (see annex I). This can probably be explained by the fact that gasoline contains a greater deal of Toluene than Benzene. Therefore, assuming that both compounds have the same source (gasoline), Toluene has a higher concentration in the spring.

In the year 2000, Methylene-Chloride (0.1 µg/L) and the gasoline additive MTBE (0.1µg/L) are detected in higher concentrations than Benzene (<<0.1 µg/L), probably because chlorinated compounds and MTBE are more resistant to transformation in situ than the gasoline related compound Benzene (Howard, 1991).

From one year to the other, the Methyl-Chloride concentration is reduced by half, whereas the Benzene concentration remains the same. No increase in the concentration is observed for any of the compounds. Nevertheless, no conclusions can be made here: both the short period of time and the small number of compounds are insufficient to extract a trend from these results.

It is now interesting to compare the concentrations of MTBE (gasoline additive) in the Ein Mazbah spring with values measured in urban areas in Germany. In the context of a research project of the DVGW (the German technical and Scientific Association for Gas and Water) 80 samples were drawn and analysed for MTBE in 170 observation wells, all located in urban areas in 1999. The results are summarised in the following table (Table 9).

Table 9: MTBE concentrations in groundwater located in German urban areas

MTBE concentration in µg/L	**Frequency of detection in %**
<0,05	51
0,05 – 0,09	10
0,10 – 0,49	21
0,50 – 4,90	14
> 5,0	4

Source: DVGW, 2000.

In approximately half the samples, the measured MTBE concentration is <0.05 µg/L. The second highest frequency of detection (21%) has MTBE concentrations ranging from 0.10 to 0.49µg/L. With a measured concentration of 0.1µg/L in Ein Mazbah, it seems that the Ramallah concentration of MTBE in groundwater is comparable to the concentrations in Germany.

4.3 Specified analysis for the most frequent SVOCs

Because runoff data is only available for one station in 2001, the specified analysis of the most frequent SVOCs is restricted to the year 2000 for which the runoff data is available for three stations.

4.3.1 Aliphatic hydrocarbons in the stations

4.3.1.1 *n*-alkanes

Luthery station

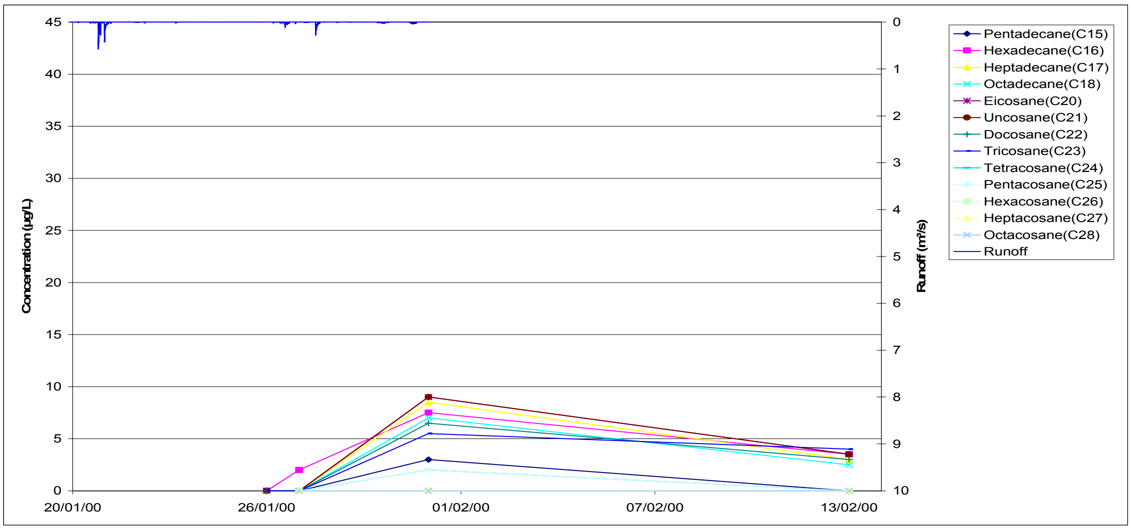


Figure 52: n-alkane's behaviour in the Luthery station

To start with, no *n*-alkanes are detected on January 26. Also, only Hexadecane is detected on January 27. Having the second smallest molecular weight, a rather small Soil Adsorption Constant, and being the most volatile compound of this group as, its Henry's Law Constant is significantly lower than the other compounds (see annex I), it is astonishing to detect this particular compound. As compounds having higher water solubilities are found in this group, it is expected to detect one of those instead (e.g.: Octadecane and Eicosane).

As already mentioned at the beginning of chapter 4.1., the runoff event on January 31 is estimated to be similar to the event measured on January 26 (this is also valid for the rest of this chapter). The occurrence of nearly all compounds on January 31 is hard to explain as, comparatively, only one compound is detected on January 26 although the runoff conditions are similar. Because of the common use of these compounds in gasoline, an eventual explanation of their occurrence from January 31 on can be due to a point source.

Taking the Womens Associations results into consideration, a non-point source can be indicated here as well (see following paragraph: Womens Association).

The only non-detected compounds of this group are Pentacosane, Hexacosane, Heptacosane and Octacosane. The common property of these four compounds is that they are the most insoluble compounds in water and have very high Henry's Law Constants (see annex I). For these reasons, it is probable that these last four mentioned compounds are only floating on the water surface. If the water surface was part of the taken samples is unknown. If this is not the case, this can be an explanation for the absence of these compounds during the measurement, as they might have been disregarded during sampling.

A decrease of the concentration is observed for all compounds on February 13. This is probably linked to the dilution effect, as the runoff event on that day is comparable to the one on January 20.

Womens Association station

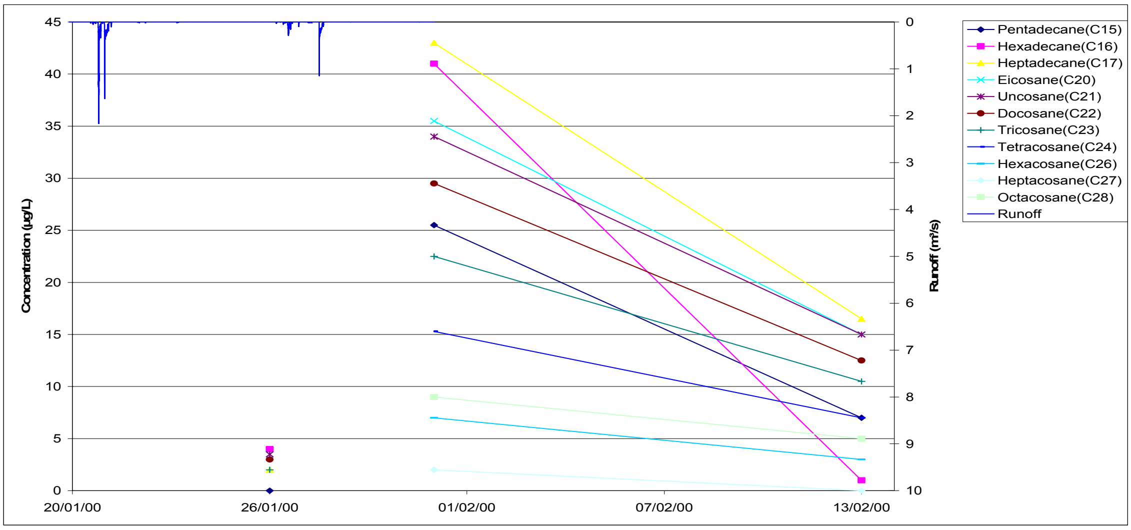


Figure 53: n-alkane's behaviour in the Womens Association station

The majority of the compounds is detected on January 26, and the highest concentration is 4 µg/L for Hexadecane. No data is available for Tetracosane, Pentacosane, Hexacosane, Heptacosane, and Octacosane on this day, and none at all is available on January 27.

The measured concentrations on January 31 are significantly higher than those measured on January 26. For example an increase from 4 µg/L to 41 µg/L is observed for Hexadecane. As very high concentrations are measured not only in Womens Association but also in Luthery on January 31, a non-point source seems to be a plausible explanation for it. An almost parallel decrease of concentration is then observed at the end of the sampling period for all compounds except for Hexadecane, whose high slope is outstanding. The reason for this can be the higher volatility of this compound in comparison to the others.

Kiswani station

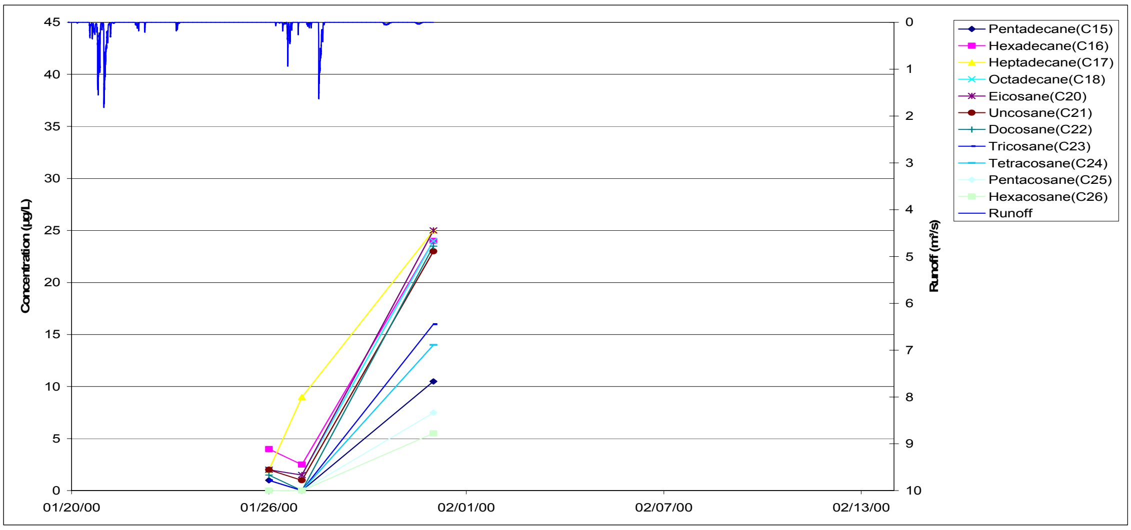


Figure 54: n-alkane's behaviour in the Kiswani station

Unlike the two previous stations, no concentration data is available on February 13. Here as well the strong impact of Womens Association and Luthery station is illustrated, as the run of the concentrations matches, which is expected. Only one compound, Heptadecane does not fit into the series, although this is not the case in the two previous stations. Therefore, the possibility of a measurement error is brought forward for this specific compound.
A point source in this case is not probable, as it does not seem likely that an emission of Heptadecane only occurs, as the considered compounds are mostly used together in gasoline.

Industrial station

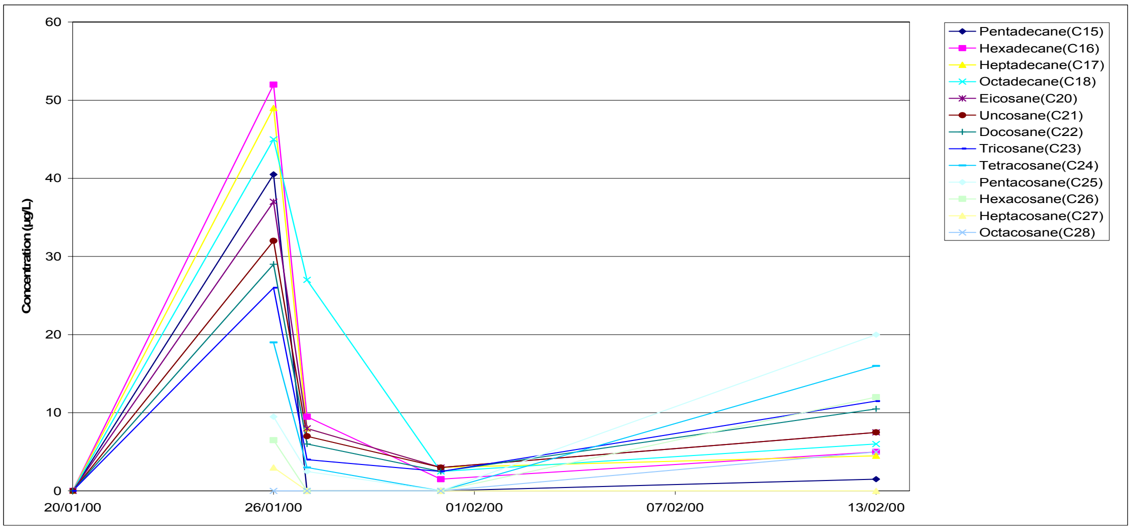


Figure 55: n-alkane's behaviour in the Industrial station

In the Industrial station, almost all compounds are measured for all sampling days. Although no data is available for Tetracosane, Pentacosane, Hexacosane, Heptacosane and Octacosane on January 20, an idea of the missing curve run is possible using the general run, which tends to indicate that their concentrations on January 20 equals 0 µg/L, like the others. The highest concentrations are measured on January 26 in the Industrial station, which does not correlate with the time occurrence of the peak with the previous stations.

This time-delay can find its origin in an input source that is mobile, for example as a plume of these compounds in the atmosphere that is then washed out by precipitation – a so called atmospheric fallout. In this case, it obviously reaches the Industrial station first, situated about 1.2 km away from the system of the three previously described stations, and then continues its way towards the other stations. Also, the decreasing concentrations from Industrial, to Womens Association, to Luthery can be an argument that encourages this course direction.

The concentrations decrease then rapidly on January 27 and slightly less on January 31. As these compounds tend to show a similar behaviour, the outstanding decrease of Octadecane is surprising, in the sense that the concentration decrease on January 27 is not as marked as for the other compounds. The fact that this compound regains its expected run towards the end of the sampling period suggests a possible measurement error. A general increase of concentration is observed for all compounds at the end of the sampling period, probably due to the dilution effect.

Khaled station

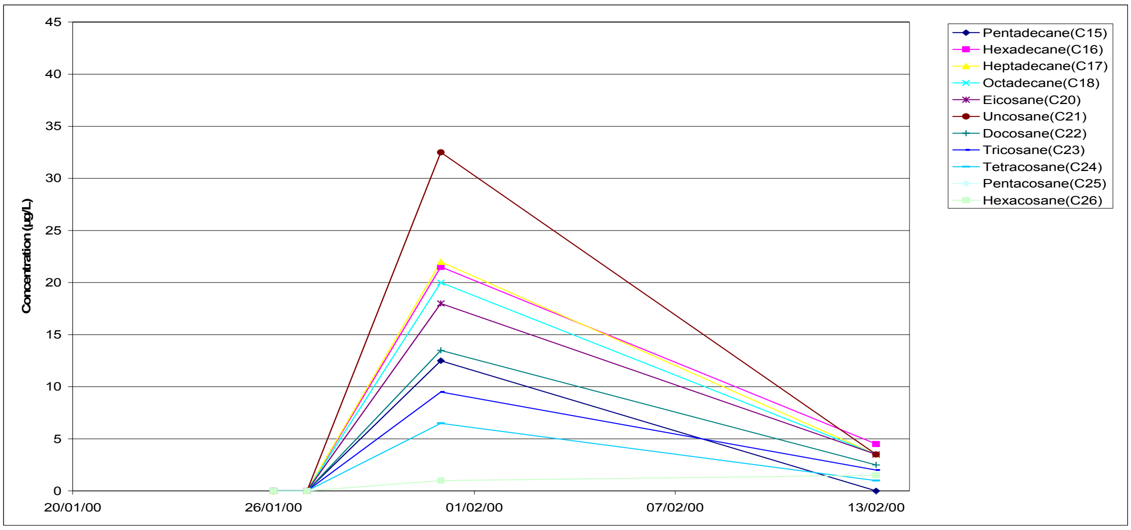


Figure 56: n-alkane's behaviour in the Khaled station

The Khaled station indicates the compounds' concentrations in the atmosphere. The greatest concentrations are measured on January 31. This result correlates well with the suggestion of a mobile input source (atmospheric fallout), as here, the concentration peak is also found on January 31. Also the location of Khaled that is situated northward to the previously mentioned system reinforces this assumption (see station location map in chapter 3.1.1). The final decrease of the concentrations on February 13 is probably due to the previous major wash out that took place on January 31.

4.3.1.2 Rest of the aliphatics

Luthery station

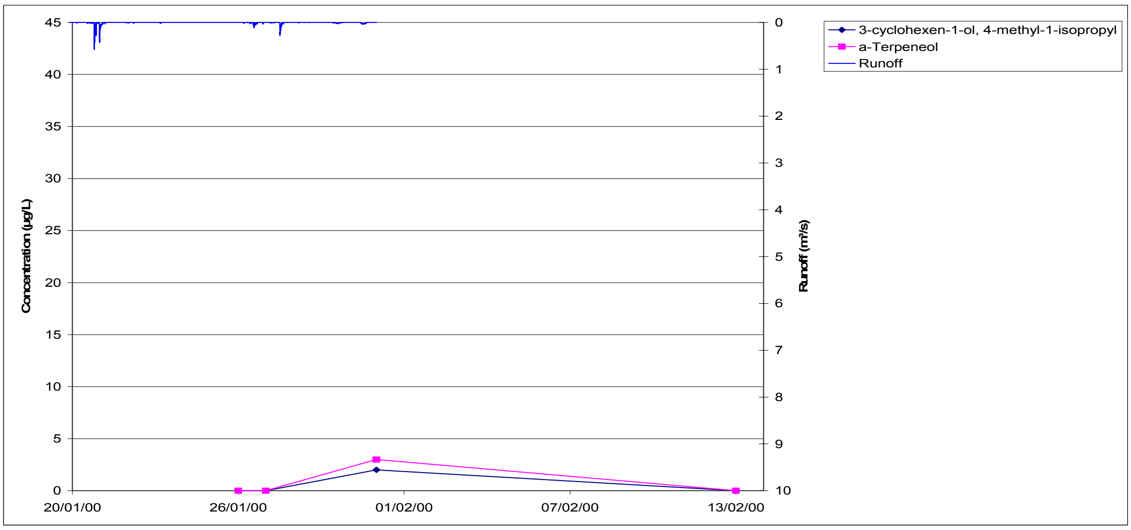


Figure 57: Aliphatics' behaviour in the Luthery station

Belonging to the same chemical family as the previously mentioned compounds (aliphatic hydrocarbons), the behaviour of these two compounds correlates very well with the one described for the *n*-alkanes in the same station. (Results: see *n*-alkanes, Luthery station)

Womens Association station

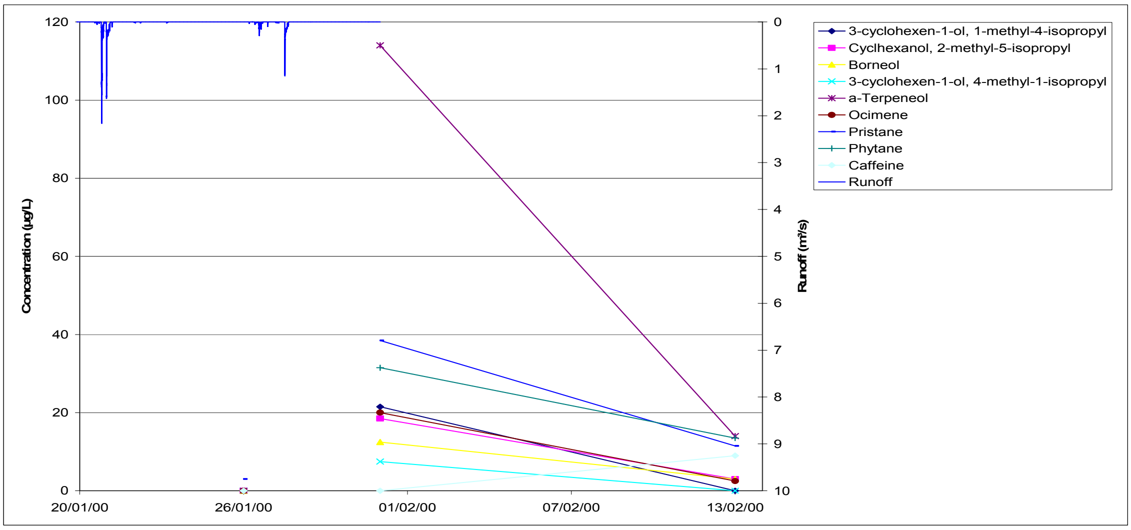


Figure 58: Rest of Aliphatics' behaviour in the Womens Association

Here as well, the good correlation with the *n*-alkanes in the Womens Association station indicates the same behaviour of the compounds.

The outstanding steep slope of a-Terpinol seems comparable to the one observed for Hexadecane in the previous chapter. Unfortunately, no data of the physical properties is available for a-Terpinol. The fact that these two compounds behave in a similar way, can be an indication for similar physical properties. Based on the similar behaviour of these two

compounds, it can be concluded that a–Terpinol has, just like Hexadecane, a high water solubility and a low Henry's Law Constant.
For the general results see chapter 4.3.1.1, Womens Association station.

Kiswani station

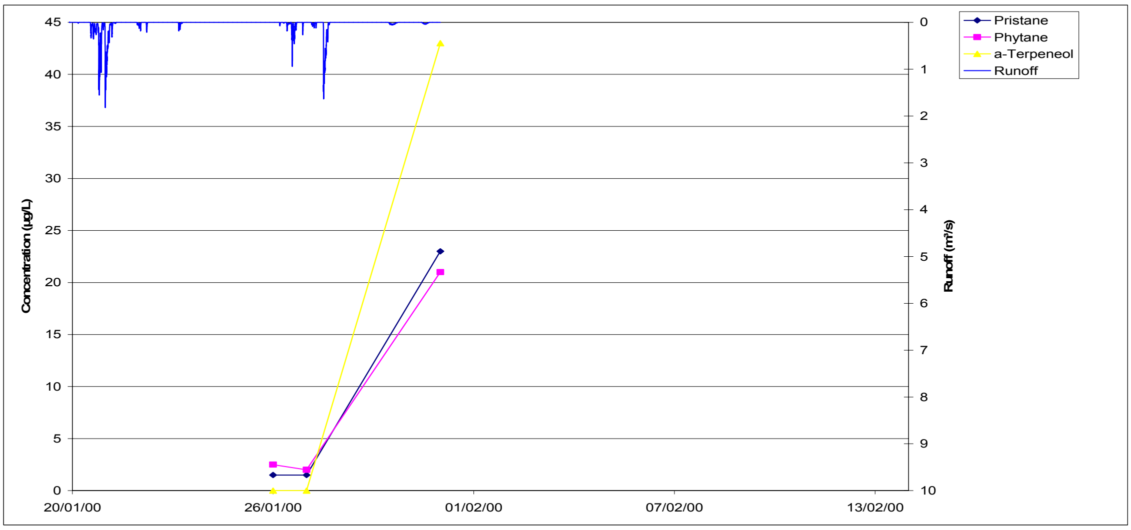


Figure 59: Rest of Aliphatics' behaviour in the Kiswani station

For results and interpretation, please see chapter 4.3.1.1, Kiswani station.

Industrial station

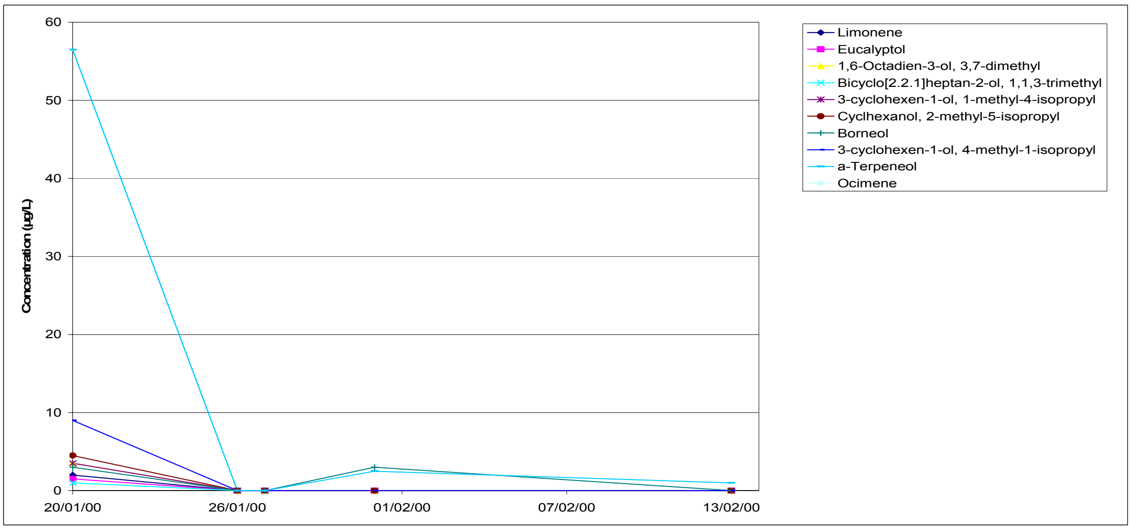


Figure 60: Rest of Aliphatics' in the Industrial station

The highest concentrations for these aliphatic compounds are measured on January 20. As the concentration runs here do not correlate with those described before, it is unlikely that the compounds studied here are contained in the mobile input source. In addition, most of them occur in households, which underlines the possibility of different origins for the two mentioned groups of compounds (*n*-alkanes and the rest of the aliphatics).

The concentration runs here depend on the size of the runoff event. Therefore, the peak of concentration on January 20 is directly linked with the big runoff event of that day. The second peak on January 31 can be explained in the same way.
The behaviour of a-Terpeneol is outstanding here as well. Its high water solubility and its low Henry's Law Constant can probably explain why a-Tepineol behaves in this way (see chapter above for reasons).

4.3.2 Aromatic hydrocarbons in the stations

Kiswani station

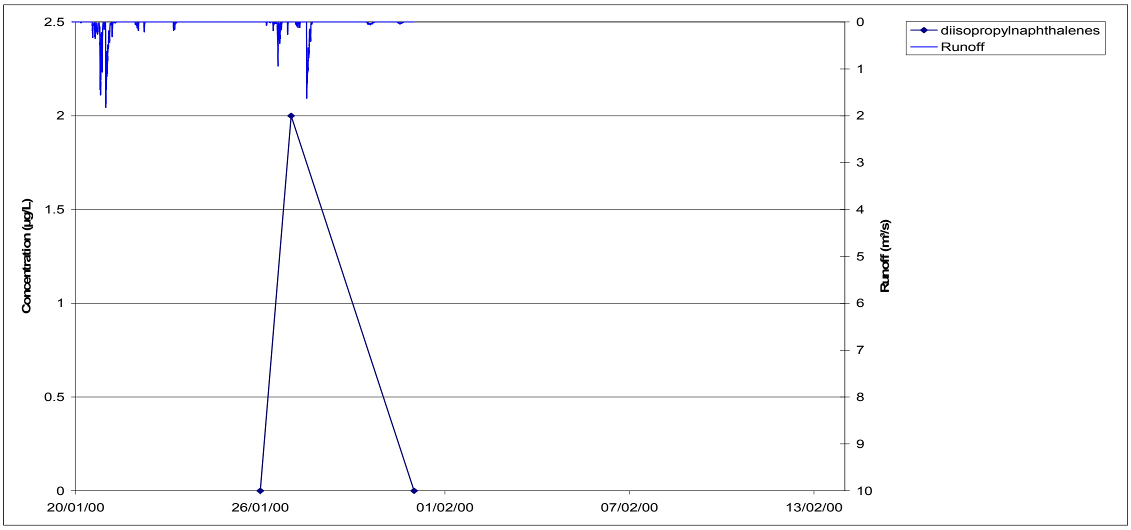


Figure 61: Aromatics' behaviour in the Kiswani station

The only aromatic detected in Kiswani is Diisopropylnaphtalenes, and only on one single day. Although no data has been found about the physical properties of this compound, this single peak can be related to a point source. Nevertheless, the fact that this is the only aromatic compound that is detected in this station and additionally, only on one day tends to an error during measurement.

Industrial station

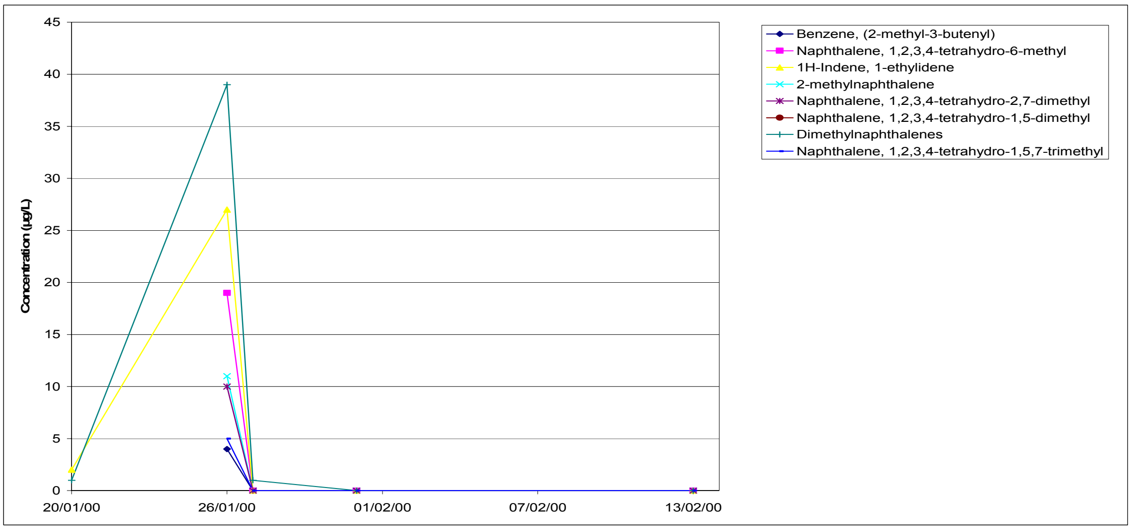


Figure 62: Aromatics' behaviour in the Industrial station

Although the runoff event on January 20 is the most intense, no significant concentration is measured on that day. The concentration peak occurs on January 26 followed by a rapid decrease in the concentration run. Due to the missing information about the physical properties and the sources of these aromatic compounds, an interpretation is difficult in this case.

Nevertheless, the concentration peak occurs on January 26, just as it does for the *n*-alkanes in the Industrial station. Because both peaks occur simultaneously for these two families, it can be concluded that these aromatic compounds also are present and washed out from the mobile input source.

4.4 SVOCs in the Ein Mazbah spring

Semi volatile organic compounds have been measured in the Ein Mazbah spring on September 14, 1999 and on February 14, 2000. As the Ein Mazbah spring is located north-west from the city centre, it is interesting to find out if these concentrations reflect on an anthropological influence from the city.
In order to do this, two stations located in the city are used: Luthery and Womens Association station. SVOCs have been measured on February 13 in the stormwater which is convenient for a comparison as the delay in measurement spring/stormwater is only one day. As no runoff sampling has been completed in 1999 for the SVOCs, this investigation focuses on the year 2000 only.
Also, the Kiswani station cannot be used here, as no measurements have been done is this station in February 2000.

The compounds are grouped into alkanes, alkenes, cycloakanes and cycloalkenes. The measured concentrations have then been added together, for all groups. The total concentration is estimated to 12µg/L in year 1999 and to 36µg/L in year 2000 for the Ein Mazbah spring, whereas the summations of these groups are 26.5µg/L for the Luthery, and 141.5µg/L for the Womens Association station. The average SVOC concentration in the city stormwater is then estimated to 84µg/L.

The following figure (Figure 64) is a picture of the Ein Mazbah spring. The spring is located on the side of a road, and as it is seen, the direct surroundings of the spring is characterised by the presence of garbage conglomerations.

Figure 63: Ein Mazbah spring

Assuming that the samples are taken from the pipe discharge only (and not from the polluted water in the basin) the spring pollution can be related to the pollution in the city, as in this case, the samples do not have any contact with the surroundings.
The high measured concentrations in the spring can be explained by a large amount of compounds entering the aquifer, as the aquifer in question is a karst aquifer. In this case, the compounds can flow through it without being sorbed.

The SVOCs concentration measured in year 2000 is three times higher than the concentration measured in the previous year. This significant increase seems to be alarming, but then again, the same observation as for the volatile organic compounds also measured in the spring can be made here: the short period of time (one year) is not appropriate to extract a trend from these results. Also, the fact that the exact terms of the summation are not available makes an accurate comparison difficult.

5. Comparison between Ramallah and other cities

5.1 Comparison with urban runoff samples in 16 U.S. cities

A study of the occurrence and concentrations of VOCs in urban waters across the United States (Delzer, 1996) was conducted by the United States Geological Survey (USGS) from 1991 through 1995 in 11 states. As the water samples were analysed with the same method using purge and trap gas chromatography-mass spectrometry, this study can be compared with the Ramallah results.

This investigation had two purposes: first, the 16 cities whose stormwater was analysed were required to obtain permits to discharge stormwater from their municipal storm-sewer system into surface water. For this reason, it was important to know if the detections of the VOCs (mostly toxic) were less than the lower limit for drinking water (MCL) defined by the U.S. Environmental Protection Agency (EPA).

Secondly, as the Clean Air Act amendments of 1990 mandates seasonal or year-round use of oxygenated compounds in gasoline (e.g.: MTBE) in some parts of the United States, the data that was collected provided some information about the air quality.

The presence of oxygenates in gasoline enhances combustion and decreases the emissions of carbon monoxide from cars. They are also used to reduce the ozone levels in the air. Depending on the region and its specified air quality, oxygenates can either be added to gasoline in the winter months (when winter concentrations of carbon monoxide exceed the established air-quality standards) or in the summer months (in order to diminish ozone pollution).

Stormwater was sampled in 118 drainage basins, all having different land use, including residential, commercial and industrial areas, as well as highways. Their areas ranged from 0.013 to 27.7 km², and had a median of 0.41 km². Compared to the catchment areas in Ramallah, that range from 0.09 (Luthery) to 0.46 km² (Kiswani), those of the United States are considerably larger. Samples were collected manually and from a variety of stormwater conveyances such as culverts, concrete pipes, lined ditches and channels (Delzer, 1996).

The concentrations of 62 VOCs were measured and the ten most frequently detected ones were summarised in the USGS report. These compounds were: Toluene, Total Xylene, Chloroform, Total Trimethylbenzene, Tetrachloroethene, Naphtalene, MTBE, Dichloromethane, Bromodichloromethane, and Ethylbenzene.

The comparison with the compounds measured in Ramallah is possible as the 10 most frequently detected ones are the same, except for three compounds. The most commonly detected VOCs in Ramallah are: Benzene, p-Xylene+m-Xylene, Ethylbenzene, Toluene, Dichloromethane, Dimethylsulfide, MTBE, Tetrachloroethene, and Chloroform. Total Trimethylbenzene, Naphtalene and Bromodichloromethane are not measured in Ramallah.

5.1.1 Results

Table 9: VOC concentrations in Ramallah and in the United States

	Ramallah			**United States**			
VOC	Median detected conc. (µg/L)	Maximum detected conc. (µg/L)	Frequency of detection (percent)	Median detected conc. (µg/L)	Maximum detected conc. (µg/L)	Frequency of detection (percent)	MCL (mg/L)
Total Xylene	1.1	6.7	70.8	0.4	15.0	17.5	10.00
Ethylbenzene	0.3	1.3	66.6	0.3	2.0	5.0	0.70
Toluene	0.6	4.8	66.6	0.3	6.6	23.3	1.00
Dichloromethane	0.3	3.1	70.8	0.3	13.0	5.9	0.005
MTBE	0.1	1.6	45.8	1.5	8.7	6.9	0.013
Tetrachloroethene	0.6	1.9	45.8	0.6	42.0	8.0	0.005
Chloroform	0.4	1.3	41.6	0.7	7.0	13.4	0.10

5.1.2 Discussion

The results of the concentrations measured in Ramallah and in the United States are similar, although the maximum detected concentrations measured in the United States are considerably higher than in Ramallah. Considering the median detected concentrations only, the concentrations are similar. The total Xylene and Toluene concentrations are higher in Ramallah, whereas MTBE and Chloroform have higher concentrations in the United States. Nevertheless, no major fluctuation of concentration is observed except for MTBE. The fact that oxygenates must be added to gasoline in some areas of the United States can explain their high MTBE concentrations, as MTBE is the most commonly used oxygenate. Currently, oxygenates are added to more than 30% of the gasoline used in the United States (U.S. Environment Protection Agency, 1994).

The situation in Palestine differs from the United States in many ways. The old models of vehicle, the poor road network and the low quality fuel are a few examples for this, and explain why the gasoline related compounds - Total Xylenes, Ethylbenzene and Toluene - have higher concentrations in Ramallah. Additionally, there are no specific emission standards for air pollutants in Palestine (Qumsieh, 2001) which can explain why the MTBE concentrations in Ramallah are lower than in the United States.

The frequencies of detection for gasoline related compounds in Ramallah also confirm the lower use of MTBE, as its 45% detection frequency appears to be out of range, compared to the three remaining ones (ranging from 66.6% to 70.8%). The fact that the percentages of detection for Total Xylene, Ethylbenzene and Toluene are similar can indicate a common source for these compounds: very probably gasoline. The frequencies of detection do not correlate as much for these compounds in the United States. It seems that other sources should be taken into consideration, such as industry for example, as these compounds are not only gasoline additives, but also commonly used as solvents.

Furthermore, the Toluene concentration is higher than the Benzene concentration in both cases, which is probably directly linked to the composition of gasoline. Indeed, gasoline’s fraction of toluene (10.43%) is about twice a high than its fraction of benzene (4.90%).

5.2 Comparison with urban runoff samples from a Parking Lot in Brooklyn Centre.

In this chapter, not only the concentrations of Toluene and Benzene, but also the behaviour of these two compounds in the runoff in Ramallah and in a parking lot in Brooklyn centre are described and compared.

The selected asphalt parking lot is situated adjacent to a county government building in Brooklyn centre. Its contributing drainage area is 10 030m², and does not include any point sources (e.g.: gasoline stations). The precipitation volume is estimated to be 20mm, the runoff volume is estimated to be 163.7m³, and the runoff coefficient of 0.82 is within the range of 0.7 to 0.95 reported for asphalt surfaces (Novotny, 1995). Toluene and Benzene are sampled eight times throughout the runoff event on August 16, 1998.

5.2.1 Behaviour of Toluene and Benzene during the runoff event.

The following figure shows the concentration behaviour of Benzene and Toluene in the case of the parking lot (Figure 64) and is then compared with the behaviour of these two compounds in runoff for the Womens Association station (chapter 4.1.1.2).

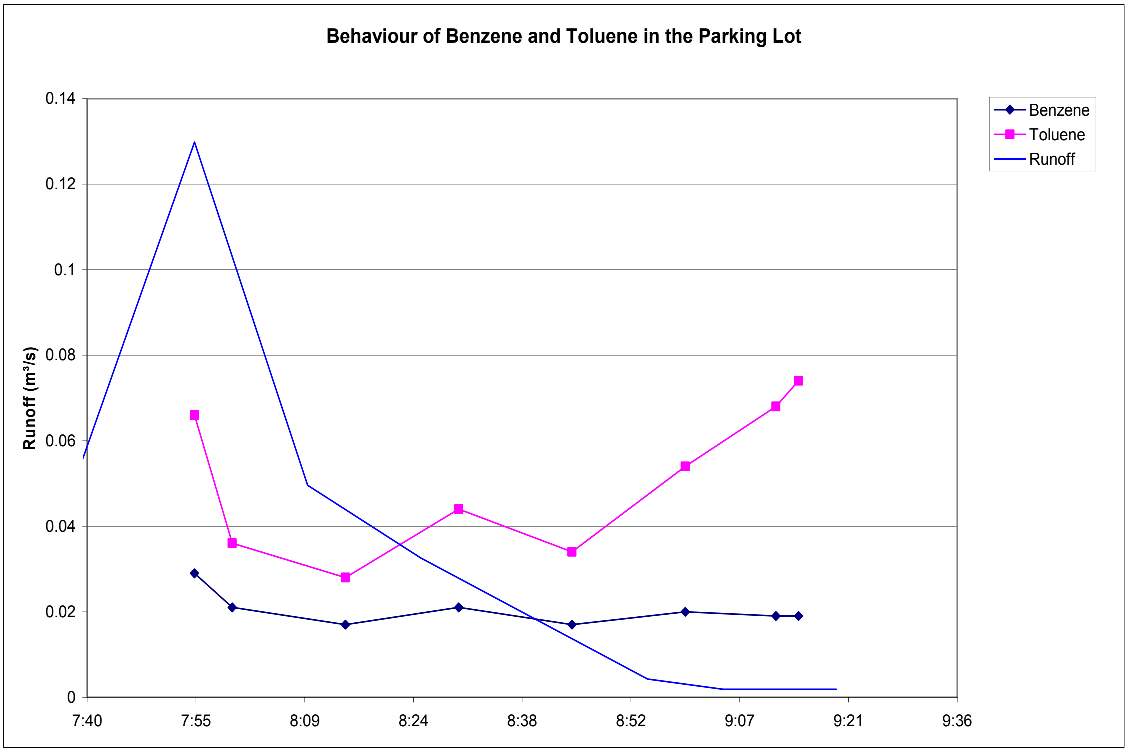


Figure 64: Benzene and Toluene behaviour in runoff for the parking lot

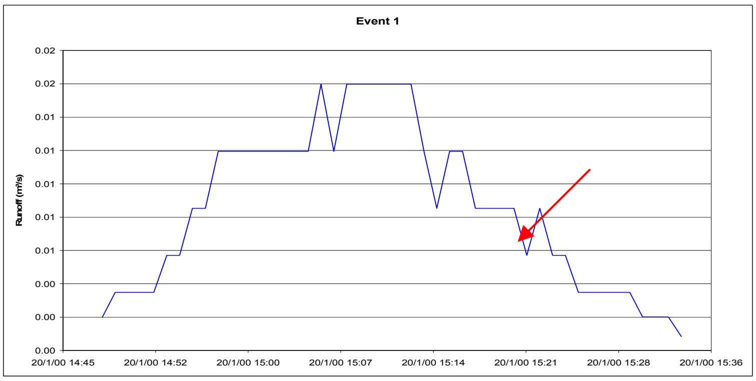
The measured concentrations range from 0.017 to 0.029µg/L for Benzene and from 0.028 to 0.074 µg/L for Toluene. The highest concentration of Benzene is measured during the first flush, whereas the highest Toluene concentration is measured at the very end of the runoff event. This behaviour can be described as a “dilution effect”. Indeed, the decrease of runoff towards the end of the event provokes an increase of concentration, as less water is available. This is not the case for Benzene, which seems to keep a fairly constant concentration

throughout the runoff event, without noticeable variation in its run. The same remarks have already been made for Benzene and Toluene in Ramallah. It seems that these two compounds have the same behaviour in both places: the concentration of Benzene keeps a fairly constant run, whereas Toluene undergoes a dilution effect.
Knowing that the compounds' behaviour is similar in both places, one can compare their concentrations.

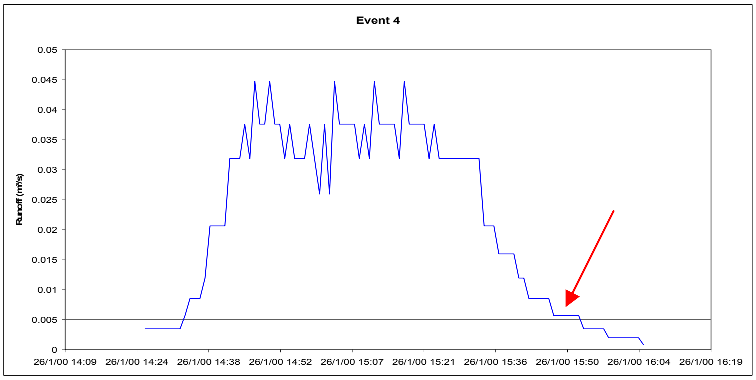
5.2.2 Comparison of the compounds' concentrations

Unlike the measurements that are done for the parking lot, only one sample is taken for each event in Ramallah. For this reason, it is necessary to situate the time of sampling for the Ramallah events before comparing the concentrations, as the concentrations vary depending on whether the sample is taken at the runoff peak or during the recession. The sampling times have been located for the three sampling events described in the chapter 3.3 for the Luthery and the Womens Association station. Kiswani station is not used for this purpose because of the uncertain runoff data. As the same observations occur in both stations, only the results of the Luthery station are shown. The three following figures show the sampling time during the runoff events: a) event 1 on January 20, b) event 4 on January 26 and c) event 8 on January 27.

a)



b)



c)

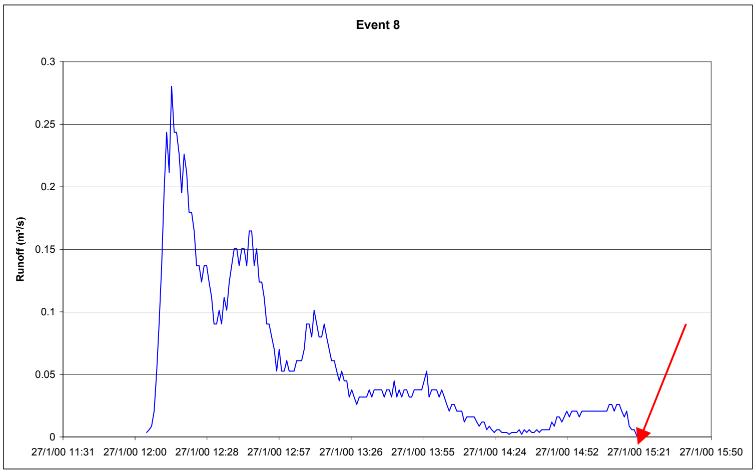


Figure 65: Sampling times during runoff events: 20, 26, 27 January

The moment of sampling is shown by a red arrow. In all three cases, the samples are taken during the recession of the runoff event, whereas no samples are taken during the so-called first-flush. The three sampling times can be described as such: the sampling time for event 1 is at the middle of the recession, the sampling time for event 8 is at the very end of the runoff event, and the sampling time for event 4 is during the second half of the recession. For this reason, the concentrations measured in Ramallah are only compared with the concentrations measured during the second half of the runoff recession curve in Brooklyn (the three last measurements). The results are summarised in the following table (Table 10).

Table 10: Concentrations of benzene and toluene in Ramallah and in the parking lot

	Luthery station		**Womens Association**		**Parking Lot in Brooklyn**		
Events	Conc. Benzene (µg/L)	Conc. Toluene (µg/L)	Conc. Benzene (µg/L)	Conc. Toluene (µg/L)	Last samples	Conc. Benzene (µg/L)	Conc. Toluene (µg/L)
1	1.59	4.82	1.10	1.49	6	0.020	0.05
4	1.07	1.45	1.09	1.55	7	0.02	0.07
8	1.06	0.41	1.09	0.57	8	0.02	0.07
Means	1.24	2.22	1.09	1.20	Means	0.02	0.06

The concentrations measured in Ramallah are considerably higher than the concentrations measured in Brooklyn. The Benzene concentrations are over 50 times higher, and the Toluene concentrations are about 30 times higher in Ramallah. The various reasons for the higher Benzene and Toluene concentrations in Ramallah are considered below.

To begin with, it is important to note that Palestine is developing rapidly. The population is growing and consequently so is energy consumption. The fact that transportation reaches about 60% of the total energy used in Palestine, and that the annual increase of the rates of private cars and other vehicles in the West Bank are estimated at 12% and 6% respectively (ICBS, 1995), is alarming. The main issue here is that a large percentage of Palestinian cars (approximately 30%) have been constructed in the 1970s, around 60% of them have been constructed from 1980 -1990, and only 10% of them from 1990 - 1996 (ARIJ survey, 1996). Because the fuel burning efficiency is lower in older models, the emission of pollutants is higher. Also, a large number of Palestinian cars (old models) do not have any catalytic converters, which reduce the emissions from an internal combustion engine. This is not the case in the United States, where all cars are nowadays supplied with catalytic converters.

Additionally, unlike the United States that have organised and structured transport systems, the only mode of transport in the West Bank is road transportation. There is only a very limited public transport system (e.g.: buses, underground). Also, the road network is underdeveloped and below the level that is required for economic development (Qumsieh, 2001). The old models combined with the poor condition of the road network (increase in congestion and emissions from vehicles) and the high concentrations of cars on the roads are all factors that increase the pollution.

Another point to be highlighted here is that there are no rules and regulations in gasoline stations in the West Bank. Unfortunately, the activity inside gas stations often gives only little consideration to the environment. A few examples for this can be that the underground storage tanks are not controlled for leaks, or that the surface tanks often have small leaks that are not repaired (Qumsieh, 2001). Also, it seems that the underground storage tanks are made of steel with no lining, which increases the risk of leakages and groundwater contamination.

These points can explain the higher pollution of gasoline-related compounds in Ramallah compared to the United States where the road structure is strongly developed and organised, the cars more recent, and the gasoline stations regulated by laws.

A final point is that there is no point source in the parking lot. Although no gasoline station has been found in the Luthery station or in the Womens Association station, the possibility of a leaking car (also considered as a point source) close to the station that can increase the concentrations in Ramallah should also be taken into consideration.

5.3 Comparison with urban runoff samples from "Le Marais" catchment in Paris.

The aim of an important research program in 1994 entitled "Production and transport of wet weather pollution in urban catchments" was to improve knowledge on the characteristics, the origins and the transport of pollution during a rain event. This research program was launched by the CEREVE (Centre d´Enseignement et de Recherche sur l´Eau, la Ville et l´Environnement: a Water Research Centre) and performed on an experimental catchment, located in the central district "Le Marais" in Paris. A study determining aliphatic hydrocarbons in urban runoff samples (Moilleron, 2002) was also done in the same catchment. The sampling period took place in 1996 and 1997 and different types of runoff were analysed: roof, courtyard and streets runoff. As the compounds' concentrations were only available for the streets runoff, this comparison only focuses on the latter type of runoff.

The "Marais" catchment (Figure 66), situated in the centre of Paris, has an area of 0.42 km^2 and is densely populated. The land use of the catchment can be divided into 54.4% roof areas, 22.4% of streets and courtyards and 23.2% of public squares and gardens. All in all, approximately 90% of the catchment is impervious.

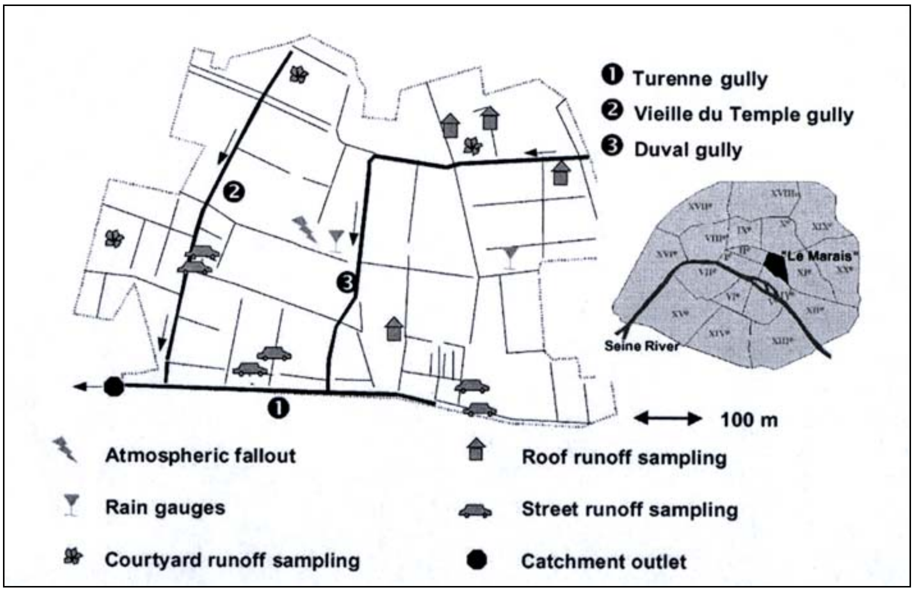


Figure 66: Location map for"Le Marais"

The street runoff from six different streets is collected in three gullies: Duval, Vielle Du Temple and Turenne gully (see Figure 66).

The aliphatic hydrocarbons that are identified in the runoff water samples are more than 30 *n*-alkanes from *n*-C$_{10}$ to *n*-C$_{40}$. Those that are analysed in Ramallah go from *n*-C$_{15}$ to *n*-C$_{28}$. Additionally, two isoprenoids Pristane and Phytane are also identified in both cases. The results of the compounds concentrations are summarised in the following table (Table 11).

5.3.1 Results

Table 11: Aliphatic hydrocarbons in Ramallah and in Paris

Compound	Number of Carbon	Mean conc. (µg/L) in Ramallah	Max. conc. (µg/L) in Ramallah	Mean conc. (µg/L) in Paris	Max. conc. (µg/L) in Paris
Pentadecane	15	8.2	40.5	10.1	39.3
Hexadecane	16	5.7	52.0	8.1	36.8
Heptadecane	17	12.6	49.0	5.5	32.1
Pristane	17	9.9	38.5	3.6	32.7
Octadecane	18	11.2	45.0	5.8	34.2
Phytane	18	9.6	36.5	3.4	27.4
Eicosane	20	11.2	37.0	3.4	26.1
Uncosane	21	10.9	34.0	2.8	22.3
Docosane	22	10.6	29.5	3.4	24.4
Tricosane	23	10.7	26.0	2.2	13.5
Tetracosane	24	9.0	19.0	3.8	19.6
Pentacosane	25	6.4	20.0	3.4	22.0
Hexacosane	26	3.5	12.0	4.5	22.0
Heptacosane	27	2.0	3.0	3.6	21.2
Octacosane	28	7.0	9.0	4.5	30.7
Total		128.5	450.0	68.1	404.3

5.3.2 Discussion

The maximum concentrations of aliphatics range from 3 to 52µg/L in Ramallah, and from 13.5 to 39.3 µg/L in Paris. This difference in range contrasts with the similar total maximum concentrations of 450µg/L for Ramallah and 404.3µg/L for Paris.

The mean concentrations range from 2.0 to 12.6µg/L for Ramallah and from 2.2 to 10.1µg/L for Paris. Here, the range is similar. The major difference is found in the total concentrations. The total aliphatic concentration is estimated to be 128.5µg/L in Ramallah and 68.1µg/L in Paris, i.e. aliphatic pollution in Ramallah is almost twice as much as in Paris.

At this stage, it is important to have some information about the sources and the maturity of these high concentrations. For this purpose, the carbon preference index, and the two isoprenoids Pristane and Phytane are used.

5.3.2.1 The carbon preference index (CPI):

Criteria such as the carbon preference index, enables the aliphatic hydrocarbons to be grouped together in order to find out if their origin is natural or anthropogenic. The CPI corresponds to the ratio of compounds with an uneven number of carbons (natural origin) and those with an even number of carbons (anthropogenic origin). Therefore, a predominance of the uneven hydrocarbons results to an important CPI (>1), whereas a CPI that is close to 1 determines the anthropogenic, petroleum-related origin of the compound (Gonzales, 2001; Wang, 1999).

$$CPI = \left[\frac{\sum(Cuneven)}{\sum(Ceven)} \right]$$

The CPI calculated for Ramallah is 0.87 and the one calculated for Paris (using the 30 compounds that are identified) is 0.93. This means that traffic pollution is the origin for the pollution in both cities.

5.3.2.2 The Isoprenoids Pristane and Phytane

The isoprenoids are primarily derived from the phytol present in the chlorophyll molecule and in petroleum products. Among them, the most commonly found are Pristane and Phytane. Whereas Pristane can be from both natural and anthropogenic sources, Phytane represents a pollution that is strictly anthropogenic (Gaven, 1982; Jones, 1993). It appears that if the Pristane/Phytane ratio is smaller or equal to 1, the source is mostly anthropogenic, and if the ratio is greater than 1 the source is mostly natural (Albaigés, 1984; Jones, 1993).

Also, as Pristane and Phytane are more resistant to bacterial actions than the *n*-alkanes C_{17} and C_{18}, the C_{17}/Pristane and C_{18}/Phytane ratios give information on the level of biodegradation. If the ratios are greater than 1, the entry of the hydrocarbons in the environment is considered to be recent (Jones, 1993).

First, the Pristane/Phytane ratio shows that the source of pollution is mostly anthropogenic in both cases, as both results are equal to 1.

The calculated C_{17}/Pristane ratios are 1.27 and 1.52 and the C_{18}/Phytane ratios are 1.16 and 1.70 for Ramallah and for Paris respectively.

Both studies show the same patterns. The aliphatic pollution in both cities has an anthropogenic source, such as traffic, with a recent pollution-entry that is also characterised by traffic.

The reasons for higher "traffic pollution" in Ramallah have already been discussed in chapter 5.2.

6. Conclusion

The classification of the compounds into different chemical families together with their specific physical properties gives some insight of how each chemical family tends to behave in water.

The aliphatic hydrocarbon family is characterised by generally high water solubilities and vapour pressures. This indicates a tendency to evaporate easily, that is confirmed by low Henry's Law Constants. The Soil Adsorption Constant is mostly low, which correlates well with the three previous observations. This family seems to be the most "volatile" of all. Nevertheless, although a trend is extracted, the compounds should always be considered individually, as exceptions exist (e. g.: Methylcylopentane whose Soil Adsorption Constant is estimated close to 600).

The aromatic hydrocarbons monocyclics are characterised by lower water solubilities and vapour pressures, compared to the aliphatics. Consequently, the Henry's Law Constants here are higher than in the previous group. This family is characterised by high Soil Adsorption Constants, and does not tend to volatilise as easily as the aliphatics.

The aromatic hydrocarbons polycylics are all semi volatile organic compounds. Because of the lack of information concerning the physical properties of these compounds, no particular trend can be extracted. Nevertheless, because of the high molecular weight of these compounds, it is known that they do not tend to volatilise as easily as the aromatic hydrocarbons monocyclics.

The chlorinated hydrocarbons are, just like the aliphatic hydrocarbons, characterised by high water solubilities and vapour pressures. Yet, this is the only chemical family for which the densities are greater than water density.

Because of the lack of information about the physical parameters of oxygenated alicyclic hydrocarbons, no clear conclusions about their behaviour are possible to extract. Nevertheless, the fairly high water solubility and vapour pressures tend to indicate that these compounds evaporate easily.

Although trends are extracted for each family, the compounds that are used for the description of the behaviour in stormwater are all analysed specifically.

The investigation of the hydrological situation shows that the runoff is mainly generated by the roads for small events, whereas the more important runoff events have an additional generating area, probably buildings. The additionally quantified runoff generating areas are estimated to be 0.006 km^2 and 0.016 km^2 for the Luthery and for the Womens Association stations respectively. The results correlate well for both stations, so much so that it can be concluded that the quantified generating areas are the main runoff generating areas at least for the small events.

The load calculation for the different families illustrates the volatility of the compounds, except for one family: the chlorinated hydrocarbons, which show an accumulation throughout the sampling period that is explained by the high density of these compounds.

The MTBE loads are calculated separately. This compound does not behave in the same way as the chemical family to which it belongs. An accumulation of the compound throughout the sampling period is observed. This accumulation can be explained by lateral inputs that probably occurred on the way to the Kiswani station. Although some authors hypothesized that urban air can be an important source of MTBE (Lopes, 1998), (which can explain the accumulation of the compound), this possibility is not taken into consideration, as MTBE is not detected on the roof station in Ramallah and is therefore not present in the atmosphere.

The description of the ten most frequently detected VOCs in the urban runoff shows that all BTEX compounds (gasoline related compounds) occur in the "top-ten". This suggests that the pollution in Ramallah is mostly derived from anthropogenic petroleum sources.

The description of the SVOCs (also mainly used in gasoline) indicates that emissions from vehicles are not the only source. Here, the noticeable delay in the occurrence of the concentration-peak in the different stations is explained by atmospheric fallout.

Therefore, emissions from vehicles along with atmospheric fallout constitute the main part of pollution in Ramallah.

The investigation that is done for the Ein Mazbah spring indicates that the concentrations measured here are probably directly linked with the city pollution. Knowing that the aquifer in question is a karst aquifer means that a lot of compounds can enter it in a direct way, without undergoing sorbtion.

The measured concentration of MTBE (0.1µg/L) is within the range of the second frequency of detection (21%) of MTBE detected in groundwater in Germany. The latter concentrations range from 0.10 to 0.49µg/L.

No increase of concentration is observed for the VOCs, whereas a significant increase of concentration is observed for the SVOCs, as the measured concentration in 1999 is 12µg/L and 36µg/L in 2000. The concentrations have tripled from one year to the next. Nevertheless, the short period of time makes the extraction of a trend difficult.

The comparison of the mean concentrations of 7 VOCs detected in Ramallah and in16 cities in the United States shows that the same mean concentration values occur for three compounds: Ethylbenzene, Dichloromethane and Tetrachloroethene measured with 0.3µg/L, 0.3µg/L and 0.6µg/L respectively. Ramallah has smaller mean values for two compounds: MTBE and Chloroform with 0.1µg/L and 0.4µg/L respectively, whereas the mean concentrations in the United States are 1.5µg/L and 0.7µg/L respectively. The two compounds for which the mean concentrations are higher in Ramallah are Toluene and Total Xylenes with 0.6µg/L and 1.1µg/L respectively. The concentrations of these compounds in the United States are estimated at 0.3µg/L and 0.4µg/L respectively. Here, the higher concentrations of Toluene and Benzene (gasoline related compounds) in Ramallah are probably linked to higher vehicle emissions due to older car models, for example. The higher MTBE (that replaces lead as an octane enhancer) detection in the United States is associated with the regulations concerning the use of oxygenates that are still inexistent in Ramallah.

The behaviour and the concentration of two compounds Toluene and Benzene are compared to those estimated in a parking lot in Brooklyn. No difference occurs in the compounds' behaviour in the runoff. Benzene behaves in a fairly constant way in both cases, with no noticeable fluctuations, and Toluene undergoes the so called "dilution effect" in both cases. The difference resides in the compounds' concentrations. Whereas the mean concentrations of Benzene and Toluene are 0.02µg/L and 0.06µg/L in the parking lot, the mean concentrations range from 1.09 to 1.24µg/L for Benzene and from 1.20 to 2.22µg/L for Toluene in Ramallah. Here, the measured concentrations are significantly higher in Ramallah.

The last comparison study case does not show any major differences in the range of the mean concentrations between Ramallah and Paris, as they range from 2.0 to 12.6µg/L for Ramallah and from 2.2 to 10.1µg/L for Paris. Nevertheless, the total aliphatic concentration is estimated to be 128.5µg/L in Ramallah – almost twice as high as Paris, where it is estimated to be 68.1µg/L.

The Carbon Preference Index CPI is estimated to be 0.87 in Ramallah and 0.93 in Paris, and both values (close to 1) indicate that the aliphatic pollution in both cities is due to traffic.

Again, the calculated C_{17}/Pristane ratios are 1.27 and 1.52 and the C_{18}/Phytane ratios are 1.16 and 1.70 for Ramallah and Paris respectively. As the ratios are greater than 1 in both cities, one can conclude that the entry of the hydrocarbons in the environment is recent (Jones, 1993). Also, the Pristane/Phytane ratios are equal to 1 in both cases, which indicates that the source of pollution is mostly anthropogenic.

The results suggest that the contaminants are largely derived from petroleum anthropogenic sources. This correlates well with the fact that no industry is located in Ramallah. The generally higher concentrations that are measured indicate that Ramallah's stormwater is significantly more polluted than in the United States and Paris, for example. These higher concentrations can partly be explained by the fact that cars emissions are higher in Ramallah. The deficiency in rules and regulations should be improved, in order to increase controls. An example here can be the installation of emission standards. Public involvement and awareness also seems to be important, as this will lead to better decisions concerning the disposal of waste products, or repairing car leaks for example (Les, 1996). These points, together with a better knowledge of the compounds can possibly decrease the pollution level.

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ANNEX

ANNEX I: Physical properties of the compounds

Tab-A- 1 Aliphatic Hydrocarbons

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m^3/mole)	Soil Ads. Constant	Density (g/cm^3)	Use	MCL (mg/L)	Health Effects	Source
2 Methylpentene	C8H16	11.7	21.4	0.450	n.d.	0,6532	Gasoline additive	n.d.	n.d.	Traffic
MTBE	C5H12O	51000	250	0.000587	11,2	0.7404	Gasoline additive	0,013	n.d.	Traffic
4 methyl-2-Pentane	C6H12	102	207	0.423	n.d.	n.d.	Gasoline additive	n.d.	n.d.	Traffic
Dimethylsulfide	CH3SCH3	2.20E+04	502	0.00161	n.d.	0,8458	n.d.	n.d.	Eye and skin irritation, headaches	Industry
Cyclohexane	C6H12	55	96.86	0.195	482	0.779	Gasoline additive/ Solvent	n.d.	Eye and skin irritation	Traffic/ Industry
Methylcyclopentane	C_6H_{12}	42	137,5	0,363	559	0.7486	Gasoline additive	n.d.	Skin and eye irritation, breathing problems	Traffic
2,3-Dimethylpentane	C_7H_{16}	5,25	69	1,730	n.d.	0,6951	Gasoline additive	n.d.	n.d.	Traffic

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 2: Aromatic hydrocarbons

Name	**Formula**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**Henry´s Law Constant (atm-m³/mole)**	**Soil Ads. Constant**	**Density (g/cm³)**	**Use**	**MCL (mg/L)**	**Health Effects**	**Source**
m-Xylene	C_8H_{10}	161	8,29	0,00718	166	0,86	Gasoline additive/ Solvent	10	Nervous system damage	Traffic/ Industry
o-Xylene	C_8H_{10}	162	8,84	0,0069	260	0,86				
p-Xylene	C_8H_{10}	178	6,61	0,00518	219	0,88				
Toluene	C_7H_8	526	28,4	0,00664	250	0,8669	Gasoline additive/ Solvent	1	Nervous system, kidney or liver problems	Traffic/ Industry
Benzene	C_6H_6	1790	94,8	0,00555	83	0,08786	Gasoline additive/ Solvent	0,005	Anemia; decrease in blood platelets; increased risk of cancer	Traffic/ Industry
Ethylbenzene	C_8H_{10}	169	9,6	0,00788	257	0,867	Gasoline additive/ Solvent	0,7	Liver or kidneys problems	Traffic/ Industry

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 3: Chlorinated hydrocarbons

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m³/mole)	Soil Ads. Constant	Density (g/cm³)	Use	MCL (mg/L)	Health Effects	Source
Tetrachloroethene	C_2Cl_4	206	18,5	0,0177	240	1,6226	Solvent	0,005	Liver problems; increased risk of cancer	Industry
Trichloroethene	C_2HCl_3	1286	69	0,00985	123	1,465	Solvent	0,005	Liver problems; increased risk of cancer	Industry
Chloroform	$CHCl_3$	7950	197	0,00367	45	1,489	Used in the production of HCFC-22/ Solvent	n.d.	Skin and eye irritation, central nervous system damage	Industry
Dichloromethane	CH_2Cl_2	13000	435	0,00325	28	1,326	Solvent	0,005	Liver problems; increased risk of cancer	Industry
Trans-1,2-Dichloroethene	$C_2H_2Cl_2$	4520	331	0,00938	35	1,2565	Solvent	0,1	Liver problems	Industry

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 4 Oxygenated alicyclic hydrocarbons

Name	**Formula**	**Water Solubility (mg/L)**	**Vapour Pressure (mm Hg)**	**Henry´s Law Constant (atm-m³/mole)**	**Soil Ads. Constant**	**Density (g/cm³)**	**Use**	**MCL (mg/L)**	**Health Effects**	**Source**
2,5-Dimethylfuran	C6H8O	1470	25.9	0.00655	n.d.	0,8883	Solvent	n.d.	n.d.	Industry
2-Metylfuran	C5H6O	3000	72	0.00593	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
3-Methylfuran	C5H6O	3030	72.7	0.00593	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
2-Ethylfuran	C6H8O	1070	25.9	0.00788	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
2-Ethyl-5-methylfuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
2,3,4-Trimethylfuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
2,3,5-Trimethylfuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
2,4-Dimethylfuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
2.3-Dimethylfuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Solvent	n.d.	n.d.	Industry

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 5: Aliphatic Hydrocarbons (SVOCs)

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m^3/mole)	Soil Ads. Constant	Density (g/cm^3)	Use	MCL (mg/L)	Health Effects	Source
Pristane	$C_{19}H_{40}$	Insoluble	n.d.	n.d.	n.d.	0,7827	Gasoline additive	n.d.	Eye and skin irritation. Can cause aspiration pneumonia	Traffic/ Industry
Phytane	$C_{20}H_{42}$	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.		Traffic/ Industry
Pentadecane	$C_{15}H_{32}$	7.60E-05	0.00343	12.6	n.d.	0,7685		n.d.	Eye and skin irritation. Can cause aspiration pneumonia	Traffic/ Industry
Hexadecane	$C_{16}H_{34}$	9.00E-04	0.00143	0.473	47	0,7734		n.d.		Traffic/ Industry
Heptadecane	$C_{17}H_{36}$	2.94E-04	2.28E-04	38.5	n.d.	0,778		n.d.	n.d.	Traffic/ Industry
Octadecane	$C_{18}H_{38}$	0.006	n.d.	51.2	n.d.	0,7819		n.d.	n.d.	Traffic/ Industry
Eicosane	$C_{20}H_{42}$	0.0019	n.d.	90.2	n.d.	0,7787		n.d.	n.d.	Traffic/ Industry
Uncosane	n.d.	n.d.	n.d.	n.d.	n.d.			n.d.	n.d.	Traffic/ Industry
Docosane	$C_{22}H_{46}$	n.d.	n.d.	159	n.d.	0.778		n.d.	n.d.	Traffic/ Industry

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 6: Aliphatic hydrocarbons (SVOCs)

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m³/mole)	Soil Ads. Constant	Density (g/cm³)	Use	MCL (mg/L)	Health Effects	Source
Tricosane	C23H48	2.95E-07	n.d.	211	n.d.	n.d.	Gasoline additive	n.d.	n.d.	Traffic/ Industry
Tetracosane	C24H50	9.25E-08	n.d.	280	n.d.	0,7991		n.d.	n.d.	Traffic/ Industry
Pentacosane	C25H52	2.90E-08	n.d.	372	n.d.	n.d.		n.d.	n.d.	Traffic/ Industry
Hexacosane	C26H54	0.0017	n.d.	494	n.d.	n.d.		n.d.	n.d.	Traffic/ Industry
Heptacosane	C27H56	2.83E-09	n.d.	655	n.d.	n.d.		n.d.	n.d.	Traffic/ Industry
Octacosane	C28H58	8.84E-10	n.d.	870	n.d.	n.d.		n.d.	n.d.	Traffic/ Industry
a-terpineol	C10H18O	n.d.	n.d.	n.d.	n.d.	n.d.	Food additive	n.d.	n.d.	Household
15-crown-5 ether	C10H20O5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Industry
18-crown-6 ether	C12H24O6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Industry

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 7: Aliphatic hydrocarbons

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m^3/mole)	Soil Ads. Constant	Density (g/cm^3)	Use	MCL (mg/L)	Health Effects	Source
Limonene epoxide	C10H16O	n.d.	n.d.	n.d.	n.d.	n.d.	Food additive	n.d.	n.d.	Household
Caffeine	C8H10N4HO2O2	2.16E+04	15	1.90E-19	n.d.	1.2	Food additive	n.d.	n.d.	Household
Squalene	C30H50	n.d.	n.d.	n.d.	n.d.	n.d.	Food additive	n.d.	n.d.	Household
3,6,9,12,15-pentaoxanonadecane-1-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dehydroabietic acid	C20H30O2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3,6,9-trioxatridecan-1-ol	$C_{10}H_{22}O_4$	n.d.	n.d.	n.d.	n.d.	0,989	n.d.	n.d.	n.d.	n.d.
3,6,9,12-tetrahexadecane-1-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-cyclohexen-1-ol, 1-methyl-4-isopropyl	C10H18O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-cyclohexen-1-ol, 1-methyl-1-isopropyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 8: Aromatic hydrocarbons Polycyclics

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m³/mole)	Soil Ads. Constant	Density (g/cm³)	Use	MCL (mg/L)	Health Effects	Source
Benzene, (2-methyl-3-butenyl)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1H-Indene,1 ethylidene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dimethylnaphtalenes	$C_{12}H_{12}$	14.9	8.40E-03	6.41E-04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,3-Benzodioxide,4-methoxy-6-isopropenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Naphtalene,1,2,3,4-tetrahydro-6-methyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Naphtalene,1,2,3,4-tetrahydro-2,7-dimethyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Naphtalene,1,2,3,4-tetrahydro-1,5,7-trimethyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diisopropylnaphtalenes	$C_{16}H_{20}$	0.11	5.00E-04	1.27E-03	11031	n.d.	n.d.	n.d.	n.d.	n.d.

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

Tab-A- 9: Aromatic hydrocarbons Monocyclics

Name	Formula	Water Solubility (mg/L)	Vapour Pressure (mm Hg)	Henry´s Law Constant (atm-m³/mole)	Soil Ads. Constant	Density (g/cm³)	Use	MCL (mg/L)	Health Effect	Source
Trimethylbenzene	C_9H_{12}	Insoluble	n.d.	n.d.	n.d.	n.d.	Solvent	n.d.	n.d.	Industry
N-butyl-benzenesulfonamide	$C_{10}H_{15}N_1O_2S_1$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
a-isopropyl-2,4,6-trimethylbenzyl alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexa(methoxymethyl)melamine	$C_{15}H_{30}N_6O_6$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-di-t-butyl-4-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Sources: URL1; URL2; EPA (1994).
n.d.: no data.

ANNEX II: VOCs Concentrations (µg/L) in the stations

Tab-A- 10: VOC concentrations in the Luthery station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aromatic Hydrocarbons Monocyclics	**Benzene**	1.59	1.07	1.06	1.08	1.09
	p-Xylene+m-Xylene	4.27	0	0.7	1.04	0.79
	o-Xylene	2.51	0	0.52	0.63	0.48
	Ethylbenzene	1.26	0.14	0.61	0.62	0.59
	Toluene	4.82	0	0.41	0.6	0.57
Chlorinated Hydrocarbon	**Dichloromethane**	0.43	0.06	0	1.12	0.43
Aliphatic Hydrocarbon	**Dimethylsulfide**	0.86	0.06	0	0	0
Oxygenated Aliphatic Hydrocarbon	**MTBE**	1.64	0.08	0.2	0.02	0
Chlorinated Hydrocarbon	**Chloroform**	0.02	0	0	0	0.95

Tab-A- 11: VOC concentrations in the Womens Association station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aromatic Hydrocarbons Monocyclics	**Benzene**	1.1	1.09	1.09	1.08	1.18
	p-Xylene+m-Xylene	0.72	0.64	0.57	0.92	1.68
	o-Xylene	0.46	0.46	0.44	0.63	0.95
	Ethylbenzene	0.58	0.58	0.59	0.62	0.77
	Toluene	1.49	1.55	0.57	0.65	2.93
Chlorinated Hydrocarbon	**Dichloromethane**	0.37	0.03	0	0	0.27
Aliphatic Hydrocarbon	**Dimethylsulfide**	0.55	0	0.36	0.53	0.93
Oxygenated Aliphatic Hydrocarbon	**MTBE**	0.21	0	0	0	0.4
Chlorinated Hydrocarbon	**Chloroform**	1.14	0	0.96	1.27	1.06

Tab-A- 12: VOC concentrations in the Kiswani station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aromatic Hydrocarbons Monocyclics	**Benzene**	1.08	1.07	1.09	1.08	1.08
	p-Xylene+m-Xylene	0.58	0.19	0.64	0.76	0.83
	o-Xylene	0.38	0.24	0.55	0.5	0.56
	Ethylbenzene	0.12	0.08	0.61	0.59	0.61
	Toluene	0.25	0.05	0.63	0.49	0.45
Chlorinated Hydrocarbon	**Dichloromethane**	0.39	0.11	0.02	0.3	0.56
Aliphatic Hydrocarbon	**Dimethylsulfide**	0.53	0.2	0.02	0.24	0.03
Oxygenated Aliphatic Hydrocarbon	**MTBE**	0.11	0.08	0.2	0	0.51
Chlorinated Hydrocarbon	**Chloroform**	1.03	0	0.98	1.08	0

Tab-A- 13: VOC concentrations in the Industrial station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aromatic Hydrocarbons Monocyclics	**Benzene**	1.06	0	1.06	0	0
	p-Xylene+m-Xylene	0.07	0	0.57	0	0.66
	o-Xylene	0.06	0	0.45	0	0.41
	Ethylbenzene	0	0	0	0	0.57
	Toluene	0.03	0	0	0	0
Chlorinated Hydrocarbon	**Dichloromethane**	0.29	0.26	0	0.32	0.36
Aliphatic Hydrocarbon	**Dimethylsulfide**	0.11	0.3	0	0	0.03
Oxygenated Aliphatic Hydrocarbon	**MTBE**	0.32	0	0	0	0
Chlorinated Hydrocarbon	**Chloroform**	0.94	0	0	0	0

Tab-A- 14: VOC concentration in the Khaled station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aromatic Hydrocarbons Monocyclics	**Benzene**	0	n.d.	1.09	0	0
	p-Xylene+m-Xylene	0	n.d.	0	0	0
	o-Xylene	0	n.d.	0	0	0
	Ethylbenzene	0	n.d.	0	0	0
	Toluene	0.07	n.d.			
Chlorinated Hydrocarbon	**Dichloromethane**	0	n.d.	3.08	0	0
Aliphatic Hydrocarbon	**Dimethylsulfide**	0	n.d.	0.27	0	0
Oxygenated Aliphatic Hydrocarbon	**MTBE**	0	n.d.	0	0	0
Chlorinated Hydrocarbon	**Chloroform**	0	n.d.	0	0	0

n.d.: no data.

ANNEX III: SVOCs Concentrations (µg/L) in the stations

Tab-A- 15: SVOC concentrations in the Luthery station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aliphatic Hydrocarbon	Pentadecane	n.d.	0	0	3	0
	Hexadecane	n.d.	0	2	7.5	3.5
	Heptadecane	n.d.	0	0	8.5	3.5
	Pristane	n.d.	0	0	5.5	1.5
	Octadecane	n.d.	0	0	7	2.5
	Phytane	n.d.	0	0	6	2
	Eicosane	n.d.	0	0	9	3.5
	Uncosane	n.d.	0	0	9	3.5
	Docosane	n.d.	0	0	6.5	3
	Tricosane	n.d.	0	0	5.5	4
	Tetracosane	n.d.	n.d.	0	2	0
	Pentacosane	n.d.	n.d.	0	2	0
	Hexacosane	n.d.	n.d.	0	0	0
	Heptacosane	n.d.	n.d.	0	0	0
	Octacosane	n.d.	n.d.	0	0	0
	a-Terpineol	n.d.	0	0	3	0
	Caffeine	n.d.				
	3-cyclohexen-1-ol-4-methyl-1-isopropyl	n.d.	0	0	2	0
	Cyclohexanol 2-methyl-5-Isopropyl	n.d.	n.d.	0	0	0
	3 cyclohexen-1-ol-1-methyl-4-isopropyl	n.d.	0	0	0	0
	Limonene	n.d.	1	0	0	0
	Eucalyptol	n.d.	0	0	0	0
	Ocimene	n.d.	0	0	0	0
	Borneol	n.d.	0	0	0	0
Aromatic Hydrocarbon Polycyclic	Benzene, (2-methyl-3-butenyl)	n.d.	n.d.	0	0	0
	Naphtalene, 1,2,3,4-tetrahydro-6-methyl	n.d.	0	0	0	0
	1H-Indene, 1-ethylidene	n.d.	0	0	0	0
	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl	n.d.	n.d.	0	0	0
	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl	n.d.	0	0	0	0
	Dimethylnaphthalenes	n.d.	0	0	0	0
	Naphthalene, 1,2,3,4-tetrahydro-1,5,7-trimethyl	n.d.	n.d.	0	0	0

n.d.: no data.

Tab-A- 16: SVOC concentrations in the Womens Association station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aliphatic Hydrocarbon	Pentadecane	n.d.	0	n.d.	25.5	7
	Hexadecane	n.d.	4	n.d.	41	1
	Heptadecane	n.d.	2	n.d.	43	16.5
	Pristane	n.d.	3	n.d.	38.5	11.5
	Octadecane	n.d.	3	n.d.	41	16
	Phytane	n.d.	0	n.d.	31.5	13.5
	Eicosane	n.d.	3.5	n.d.	35.5	15
	Uncosane	n.d.	3.5	n.d.	34	15
	Docosane	n.d.	3	n.d.	29.5	12.5
	Tricosane	n.d.	2	n.d.	22.5	10.5
	Tetracosane	n.d.	n.d.	n.d.	15.3	7
	Pentacosane	n.d.	n.d.	n.d.	11.5	8
	Hexacosane	n.d.	n.d.	n.d.	7	3
	Heptacosane	n.d.	n.d.	n.d.	2	0
	Octacosane	n.d.	n.d.	n.d.	9	5
	a-Terpineol	n.d.	0	n.d.	114	14
	Caffeine	n.d.	0	n.d.	0	9
	3-cyclohexen-1-ol-4-methyl-1-isopropyl	n.d.	0	n.d.	7.5	0
	Cyclohexanol 2-methyl-5-Isopropyl	n.d.	0	n.d.	18.5	3
	3 cyclohexen-1-ol-1-methyl-4-isopropyl	n.d.	0	n.d.	21.5	0
	Limonene	n.d.	0	n.d.	0	0
	Eucalyptol	n.d.	0	n.d.	0	0
	Ocimene	n.d.	0	n.d.	20	2.5
	Borneol	n.d.	0	n.d.	12.5	3
Aromatic Hydrocarbon Polycyclic	Benzene, (2-methyl-3-butenyl)	n.d.	n.d.	n.d.	0	0
	Naphtalene, 1,2,3,4-tetrahydro-6-methyl	n.d.	n.d.	n.d.	0	0
	1H-Indene, 1-ethylidene	n.d.	n.d.	n.d.	0	0
	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl	n.d.	n.d.	n.d.	0	0
	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl	n.d.	n.d.	n.d.	3	0
	Dimethylnaphthalenes	n.d.	n.d.	n.d.	1	0
	Naphthalene, 1,2,3,4-tetrahydro-1,5,7-trimethyl	n.d.	0	n.d.	1	0

n.d.: no data.

Tab-A- 17: SVOC concentrations in the Kiswani station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aliphatic Hydrocarbon	**Pentadecane**	n.d.	1	0	10.5	n.d.
	Hexadecane	n.d.	4	2.5	24	n.d.
	Heptadecane	n.d.	2	9	25	n.d.
	Pristane	n.d.	1.5	1.5	23	n.d.
	Octadecane	n.d.	2	1.5	24	n.d.
	Phytane	n.d.	2.5	2	21	n.d.
	Eicosane	n.d.	2	1.5	25	n.d.
	Uncosane	n.d.	2	1	23	n.d.
	Docosane	n.d.	1.5	0	23.5	n.d.
	Tricosane	n.d.	1	0	16	n.d.
	Tetracosane	n.d.	0	0	14	n.d.
	Pentacosane	n.d.	0	0	7.5	n.d.
	Hexacosane	n.d.	0	0	5.5	n.d.
	Heptacosane	n.d.	0	0	0	n.d.
	Octacosane	n.d.	0	0	0	n.d.
	a-Terpineol	n.d.	0	0	43	n.d.
	Caffeine	n.d.	0	0	0	n.d.
	3-cyclohexen-1-ol-4-methyl-1-isopropyl	n.d.	0	0	0	n.d.
	Cyclohexanol 2-methyl-5-Isopropyl	n.d.	0	0	0	n.d.
	3 cyclohexen-1-ol-1-methyl-4-isopropyl	n.d.	0	0	0	n.d.
	Limonene	n.d.	0	0	0	n.d.
	Eucalyptol	n.d.	0	0	0	n.d.
	Ocimene	n.d.	0	0	0	n.d.
	Borneol	n.d.	0	0	0	n.d.
Aromatic Hydrocarbon Polycyclic	**Benzene, (2-methyl-3-butenyl)**	n.d.	0	0	0	n.d.
	Naphtalene, 1,2,3,4-tetrahydro-6-methyl	n.d.	0	0	0	n.d.
	1H-Indene, 1-ethylidene	n.d.	0	0	0	n.d.
	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl	n.d.	0	0	0	n.d.
	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl	n.d.	0	0	0	n.d.
	Dimethylnaphthalenes	n.d.	0	1	0	n.d.
	Naphthalene, 1,2,3,4-tetrahydro-1,5,7-trimethyl	n.d.	0	0	0	n.d.

n.d.: no data.

Tab-A- 18: SVOC concentrations in the Industrial station

Chemical Family	Compound	20.01.00	26.01.00	27.01.00	31.01.00	13.02.00
Aliphatic Hydrocarbon	**Pentadecane**	0	40.5	0	0	1.5
	Hexadecane	0	52	9.5	1.5	5
	Heptadecane	0	49	8	3	4.5
	Pristane	0	34	6	2	4
	Octadecane	0	45	27	2.5	6
	Phytane	0	36.5	17	3.5	6
	Eicosane	0	37	8	3	7.5
	Uncosane	0	32	7	3	7.5
	Docosane	0	29	6	2.5	10.5
	Tricosane	0	26	4	2.5	11.5
	Tetracosane	n.d.	19	3	0	16
	Pentacosane	n.d.	9.5	2.5	0	20
	Hexacosane	n.d.	6.5	0	0	12
	Heptacosane	n.d.	3	0	0	0
	Octacosane	n.d.	0	0	0	5
	a-Terpineol	56.5	0	0	2.5	1
	Caffeine	454	0	0	0	0
	3-cyclohexen-1-ol-4-methyl-1-isopropyl	9	0	0	0	0
	Cyclohexanol 2-methyl-5-Isopropyl	4.5	0	0	0	0
	3 cyclohexen-1-ol-1-methyl-4-isopropyl	3.5	0	0	0	0
	Limonene	2	0	0	0	0
	Eucalyptol	1.5	0	0	0	0
	Ocimene	2.5	0	0	0	0
	Borneol	3	0	0	3	0
Aromatic Hydrocarbon Polycyclic	**Benzene, (2-methyl-3-butenyl)**	n.d.	4	0	0	0
	Naphtalene, 1,2,3,4-tetrahydro-6-methyl	n.d.	19	0	0	0
	1H-Indene, 1-ethylidene	2	27	0	0	0
	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl	n.d.	10	0	0	0
	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl	1	17.5	2	0	0
	Dimethylnaphthalenes	1	39	1	0	0
	Naphthalene, 1,2,3,4-tetrahydro-1,5,7-trimethyl	n.d.	5	0	0	0

n.d.: no data.

ANNEX IV: VOCs Concentrations (µg/L) in the Ein Mazbah spring

Tab-A- 19: VOC concentrations in the Ein Mazbah spring

	Methylene Chloride	**2-Butanone**	**Benzene**	**MTBE**	**Tetrachloro-Methane**	**Toluene**
14.09.99	0.2	0.1 (was<0.1)	0.1 (was<<0.1)	n.d.	0.1 (was<<0.1)	0.2
14.02.00	0.1 (was<0.1)	n.d.	0.1 (was<<0.1)	0.1	n.d.	n.d.

n.d.: no data.