

BABES BOLYAI UNIVERSITY - CLUJ-NAPOCA, ROMANIA

PhD THESIS IN PHYSICS

(SUMMARY)

**CONTRIBUTIONS TO DEVELOPMENT OF THE NOVEL EXTRACTION AND
ANALYSIS METHODS TO
PHYSICOCHEMICAL AND ECOTOXICOLOGICAL
CHARACTERIZATION OF THE VOLATILE ORGANIC COMPOUNDS (VOC) IN
SURFACE WATERS**

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2010

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*Literature review***Chapter 1**

Background regarding volatile organic compounds and their analysis from aquatic environmental samples

It is difficult to imagine our modern life style from every day without using and profit of products stocked by chemical industry such as pharmaceuticals, petrochemicals, agrochemicals and consumer chemicals (*Bhandari et al, 2008*). Unfortunately together with the rise of chemical manufacture and use, has come increasing public awareness and concern regarding presence of this chemicals in the surrounding environment due to the possible negative consequences of this chemicals linked to human health and biota. Owing to the more increased attention conferred to environmental pollution by mass media, has made a clutter regarding the terms like contamination and pollution, terms that tend to be used as synonym (*Hansen, 1993; Neuzil et al, 1996*). Hereby in scientific area has made an agreement in that the term contamination should be used where a chemical is present in a given sample with no evidence of harm and the term pollution to be used in cases where the presence of the chemical caused harm.

Doubtlessness any chemicals can become a pollutant in any kind of environmental media (water, soil, air, etc.) causing negative effects if it is present at a high enough concentration. Despite the fact that any chemical can be a pollutant, certain chemicals have been identified in regulation or by international agreement as being priority chemicals for control (*Harrison, 2001*). These chemicals have been selected based on their frequency found in environment and their persistence, their toxic effects at low concentration and carcinogenesis and not in the last case based on their bioaccumulativity (*Peirce et al, 1998*).

1.1. Source of pollution in surface water

Generally over the history, the quality of surface water as source of drinking water has been a factor in determining human welfare. Unhealthful surface waters, polluted by natural or manmade sources has caused great hardness's for people being under the necessity of use it as drinking water sources or to other types of usages such as washing or irrigation. Nowadays toxic chemicals presence in water body detain the most important hovering considering the safety of water supplies (having as mint: rivers, ground water, lakes, etc.) in industrialized countries. In order to develop a good strategy in protection or remediation of polluted water is important first of all to know the possible source of the specific pollutant that was highlighted in the media and not at last to know the behavior pattern of these pollutants in the specific media and also their possible interaction between different environmental compartments.

Characterizing the VOCs presence in aquatic system we can talk about natural and anthropogenic origins:

- a. As first source is considered the *natural sources* represented by snow and rainwater that could contain small amounts of this pollutants collected from atmospheric particulate matter or atmospheric gases. Behind sagging, they gain on the earth surface and flows over and through the soil, where have a thousand and one opportunities to enter into the surface or ground water (*Laws, 2000*).

- b. *Human-caused sources (anthropogenic)* – in most of the time were demonstrated that human activities could cause serious aquatic environment contaminations. The main sources of human-caused pollution could be summarized as: industrial waste discharges and spills; effluents from industries and waste treatment plants; petroleum leaks and spills from storage tanks, pipelines, tankers and trucks; leachate from landfills, septic tanks, treatment lagoons and mine tailings; agricultural applications of chemical fertilizers, herbicides and pesticides; urban storm water runoff; fallout from atmospheric pollution (*Tata et al, 2003*).

Sources of volatile organic compounds in aquatic environment, same as any kind of pollutants, could be sketchily onto two groups as point source pollution and non-point source pollution:

1. *Point source pollution* are specificities as localized and identifiable sources of contaminants from which they are discharged, including industrial and municipal wastewater outfalls, septic tanks discharges, hazardous spills, pipe, ditch, factory smokestack, etc (*Chin, 2006*). Main characteristic of this type of pollutants source is that they discharge pollutants into receiving waters at geographically clearly identifiable locations. Usually the most concerning point source in managing surface waters are represented by domestic wastewater discharges, industrial discharges and spills.

Point source pollution could be divided in some category as follows:

- a. *Domestic wastewater discharges,*
- b. *Combined sewer overflows,*
- c. *Stormwater discharges,*
- d. *Industrial discharges,*
- e. *Animal feeding operations,*
- f. *Spills.*

From the beginning, industrial developed countries tried to control these point sources pollutants, so that, today a high percent from them are well regulated and their control is mandated, requiring license for any type of discharges. By this reason point, sources are monitored and appraised using statistical and mathematical models stated for a specific condition as regards geographically and meteorically condition as well properties of the specific industrial contaminants defined by own physicochemical properties. The most artless balance equation conveyed in a point source pollution probabilistic model so as determine the completely mixed pollutant concentration downstream of the effluent is (equation 1.1):

$$C_d = \frac{Q_u \cdot C_u + Q_e \cdot C_e}{Q_u + Q_e} \quad (\text{equation 1.1.})$$

In this relation C_d indicate the completely mixed pollutant concentration downstream of the effluent, expressed usually in $\text{mg} \cdot \text{L}^{-1}$, Q_u represent the stream flow upstream of the effluent, $\text{m}^3 \cdot \text{s}^{-1}$, Q_e is flow of the effluent expressed in $\text{m}^3 \cdot \text{s}^{-1}$, C_u constituent concentration of upstream flow, $\text{mg} \cdot \text{L}^{-1}$ and C_e is the strength of the effluent, $\text{mg} \cdot \text{L}^{-1}$ (*Lin et al, 2007*).

2. *Nonpoint source pollutants* are considered pollutants whose sources are distributed over large area or could be conditioned by a large number of point sources such as runoff from agricultural sites, the atmosphere or from urban discharges. So, this pollution is a result of the direct land-use pattern.

Generally non-point source pollutions in aquatic systems are owing to rainwater or snowmelt that contains chemical pollutants. Rainwater or snowmelts are collected at a watershed and once with the water body they arrive in surface water systems as river, lake, etc. from there they could recommence the complete cycle. Follow-up the complete water cycle the pollutants could arrive in different environmental compartments.

Contaminants related to non-point source are called also *diffuse loads*. Contaminants derived from non-point sources usually are impossible to detect exactly due to their diffuse nature and large area that they cover. This fact made them very hard to control even for developed countries. Discharges that results from precipitation as snowmelt or rainfall is know also with name wet-weather discharges and usually this include stormwater runoff (that collect pollutants as it travels across land), combined sewer overflows and wet-weather sanitary-sewer overflows (that contain a mixture of raw sewage, industrial wastewater and stormwater).

Many studies on different situation showed that discharge from urban and agricultural sites are the principal sources that pollute surface waters while septic tanks, leaching underground storage tanks and waste injection wells are the main source of groundwater pollution.

Nonpoint source pollutants could be ranged as:

- a. *Agricultural runoff*,
- b. *Urban runoff*,
- c. *Landfills*,
- d. *Recreational activities*.

1.1.1. Physical transport of volatile organic compounds in aquatic media

In aquatic environment occurs the most physical transport of chemical pollutants, transport that could be delineate by two main physical process as bulk movement of fluids from one location to another (*diffusion* or *Fickian transport*) and as random mixing process within the fluids (*advection*). Is know that rivers flow downstream due to gravity advection, hereby chemical pollutants movement in river are in progress most in the case horizontally, while vertically movement is limited due to water body stratification bring about differences in temperature, density or depth limitation. In case of any kind of chemical pollutant, is consistent the natural tendency of molecule to move from regions of higher concentration to regions of lower concentration by the random movement of contaminant molecules (*Manahan, 2005*).

Insofar diffusion as advection are characterized one the one hand by equation of *mass balance expression* (see figure 1.1) that is stated for any type of chemicals in soever volume during whatever time expressed in terms of rates, namely mass per time $M \cdot T^{-1}$. Hence, the equation will be:

Rate of change in storage of mass

$$= (\text{mass transported rate in} - \text{mass transported rate out}) \\ + (\text{mass produced rate by sources} - \text{mass eliminated rate by sinks})$$

(equation 1.2).

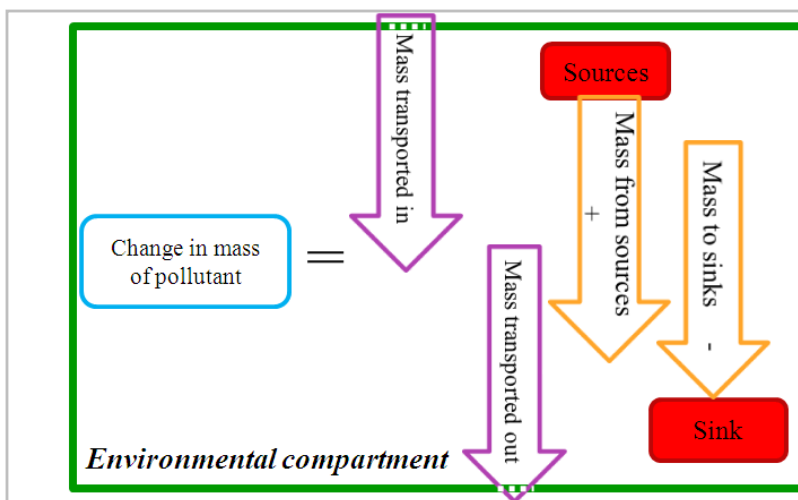


Figure 1.1. Illustration of mass balance relationships for chemical pollutants, with respect to a specific environmental compartment (Manahan, 2005).

1.1.2. Distribution processes of volatile organic compounds among different environmental matrices

The unique and principal characteristic of all VOCs in the environment is their volatility which makes the study of these compounds more challenging than all other types of contaminants. In addition volatile organic compounds studies involve complex questions such as their distribution sources, transport and fate in the environment, questions whose answers respond inquiries regarding ecological and health risk assessment, control and environmental remediation strategies (Wang *et al*, 1996).

Every part of all environmental media is continually changing once with essential ecosystems as well as unwelcome contaminants. The time whereat these changes may occur depends on the properties of the contaminant and the environmental media. Usually the modification of chemical pollutants in any kind of environmental media is induced by: physical forces, chemical changes or biological activity (Wang *et al*, 1996).

Physical forces transfer the chemical contaminants from a given location to new locations. Commonly this displacement takes place without significant change in chemical properties of pollutants. Almost in all cases the chemical contaminants released in a specific environmental media, let it be water or soil, can be transferred into regions far from their original source due to the forces of wind, gravity or water flow (Lister *et al*, 2000).

Chemical changes are induced fundamentally in facts by oxidation and reduction reactions, chemical reactions which break and make chemical bonds admitting atoms to rearrange into new

compounds (Miller *et al*, 2008). These new formed compounds will have different properties in comparison with the original molecules. The benefit facts of chemical changes are that it often has the ability to destroy the chemical contaminants through transformation of them into less deleterious compounds (Bailey, 2002).

Biological activity takes place through the medium of microorganisms, which owing to their constant search for survival energy decompose varied types of contaminant molecules into atoms and return it to environmental cycles that circulate these elements together with many others through our ecosystems (Moncmanova, 2007). Biological processes represent a special nature of chemical transformation (Whitacre, 2007; Ware, 2006; Ware, 2007; Howard *et al*, 1991).

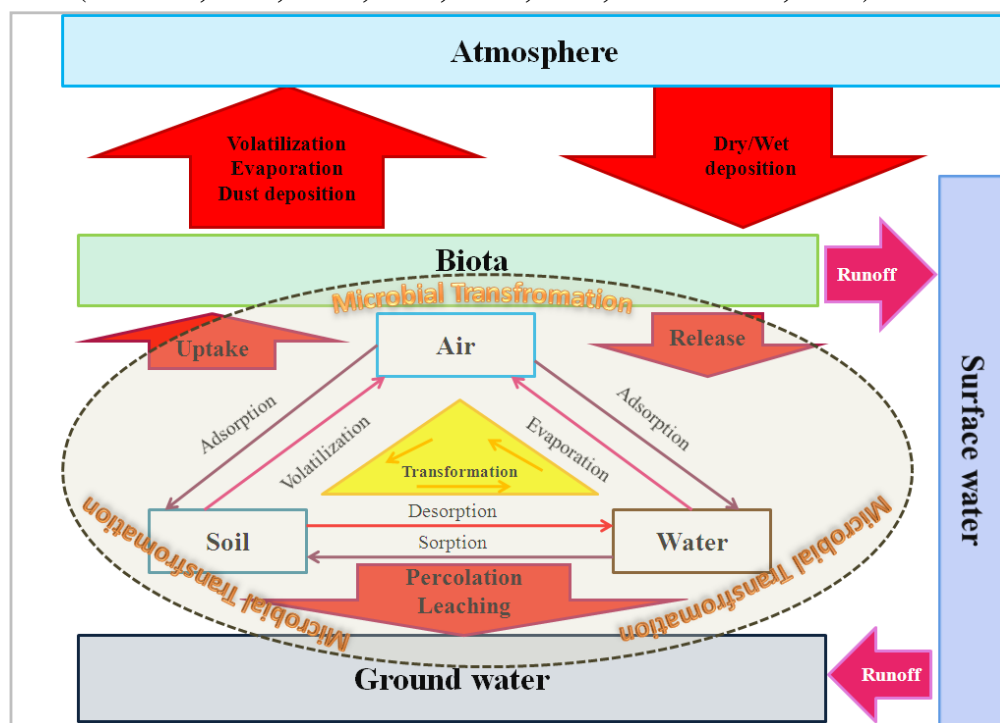


Figure 1.2. Environmental inter-media pathways of volatile organic compounds (adapted after Y. Cohen, 1986).

It's important to understand the processes that are involved in transport of chemical pollutants or in changes of them in nature. These processes depend on chemical properties of the pollutants and characteristics of water and soil environment where they are present (Nikolelis *et al*, 1997). While all chemical pollutants has its certain physicochemical properties, it is difficult to establish exactly their behavior and fate in a specific environmental media because all properties of media are always different from each other's and depends on site long term geologic history and its more recent anthropomorphic disturbances (Clayton *et al*, 2003). Because of this it is important to determine again all the times in every environmental sites the properties of the water and soil in which the pollutants reside.

Usually the main properties that affect the behavior of contaminants in aquatic environment are: temperature; water quality (chemical composition, pH, oxidation-reduction potential, alkalinity,

hardness, turbidity, dissolved oxygen, biological oxygen demand, fecal coli forms, etc.); flow rate and flow pattern (*Poston et al, 1986*). The bottom soil properties in contact with water can be summarized as: mineral composition; percentage of organic matter; sorption coefficients for contaminants (attractive forces between solids and contaminants); mobility of solids (colloid and particulate movement); porosity; particle size distribution; hydraulic conductivity (*Weiner, 2008*). According with all presented before, these physicochemical properties of any kind of environmental media are always site specific and must be measured for all sampling field.

Habitually could be sum up three possibilities in fates of contaminants in environment (*Alloway et al, 1997*) – see figure 1.2.:

- a. All or a percentage from the contaminant amount might remain unchanged in their present location.
- b. All or a part from the contaminant could be moved in other part location through the medium of transport processes. This movement can occur between different phases through volatilization, dissolution, adsorption and precipitation or can occur within the same environmental compartment under gravity, diffusion or advection.
- c. All or just an allotment from the chemical contaminant might suffer transformation into other chemical species through natural, chemical or biological processes. In case of transformation induced by biological processes, called biodegradation (aerobic or anaerobic) the chemical contaminants are changed structurally mainly by reason of microorganisms presence in an aquatic or soil environments. Usually this process might have as consequence bioaccumulation – process within the contaminants is accumulated in plant or animal tissues (*Rand, 1995*).

Even as, the contaminants go through a series of environmentally induced non-biological changes – through processes such as oxidation-reduction, hydration, hydrolysis, complexation or photolysis reactions – processes that could be classified as weathering process.

For example in case of volatile or gaseous contaminants, increase of temperature conduces to increases of rate of evaporation of these contaminants from water or soil into the atmosphere. For compounds with less evaporation capacity, the electrostatic attraction might generate dissolved substances and small particles there upon to be adsorbed to solid surfaces where may leave the water flow and become immobilized in soil or filters. Water flows can erode soils and transport once with sediment the sorbed pollutants over long distances (*Westrich et al, 2007*).

So, as in any kind of pollutants, volatile organic compounds presence in surface water is affected by innumerably processes as advection, dispersion, volatilization, microbial degradation, sorption, hydrolysis, aquatic photolysis, chemical reaction and bioconcentration.

1.2. Review of volatile organic extraction from environmental water samples

Until any kind of analysis of an analytes from an environmental sample it is very important to perform some steps that ensure the possibility to analyze the target analytes and in the same time

assure the reliability, quality and accuracy of the obtained results after analysis. In this manner when is necessary to determine qualitatively and measure quantitatively chemical compounds at very low concentration from any kind of environmental sample it is needed to follow a series of procedures like: isolation (extraction and separation) of the target compounds from the environmental sample matrix; separation and purification of the target chemicals from co-extracted non-target chemicals – this procedures is called sample clean-up); and finally their measurement by highly selective and sensitive analytical instrument like gas chromatography or mass spectrometry (Dean, 1990; Tomar, 1999).

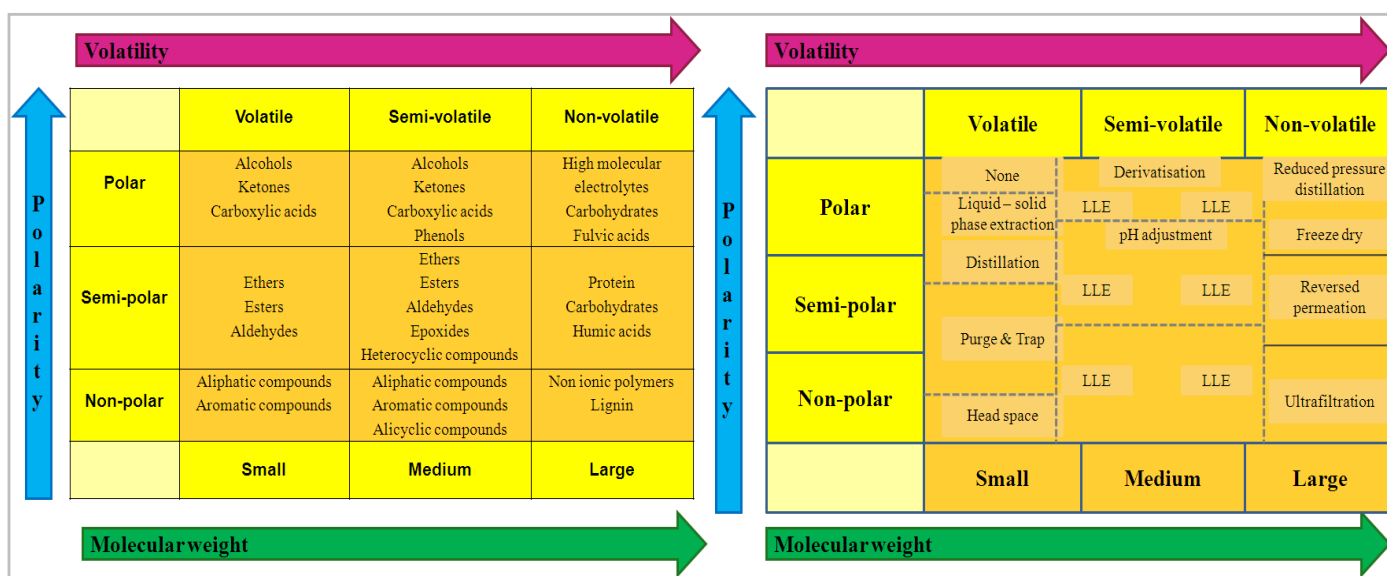


Figure 1.3. Chemicals classification based on their physicochemical properties (adapted after Meyer et al, 2001).

Figure 1.4. Methods of chemical separation in water sample analysis (adapted after Meyer et al, 2001).

The first step that need to be take in consideration under their monitoring from aquatic environmental samples is the sample pretreatment and the target compounds extraction from it. Although are many types of extraction procedures in analytical and environmental chemistry, it is important to choose the most agreeable techniques when we monitoring volatile organic compounds from aqueous environmental samples. Chose of a specific extraction procedure often depends by physicochemical properties of the target compounds and by the physicochemical properties of the sample matrices (Harwood et al., 1999; Fifield et al, 2000-(a)).

When we analyze volatile organic compounds from aquatic environmental samples our attention must be intensive due to physicochemical properties of these types of compounds as their high grade volatility (Mitra, 2003).

Due to this is necessary to categorize the target compounds as their solubility in water based on their simplest physicochemical properties (e.g. molecular weight, boiling point, polarity) – see figure 1.3. Procedures for extraction of the target chemicals from water sample matrices based on these broad chemical categories are presented in figure 1.4. The most important conformation in

volatile organic compounds analysis from an aqueous environmental sample is that generally the target chemical compounds are firstly transferred to a gas-vapor phase and then subjected to instrumental analysis like gas chromatography. Normally, the analysis of VOCs is not awkward and can be realized through direct injection of the analyte into the instrument after that equilibrium was compassed (*Bloeman et al, 1993*). Based on this idea it was discovered the headspace extraction.

While almost in all cases the aquatic environmental samples contain a highly complex organic matrix, usually this asks special preparation (like isolation of analytes from primary matrix and removal of interfering chemicals) before to undergo to instrumental analysis. But introduction of secondary steps in sample preparation process might induce additional loss of the target volatile compounds and in the same time could become a source of additional contamination. Thus is important that the isolation of the enrichment process to be limited at a single step as possible.

1.2.1. Short theory of liquid-liquid extraction

Solvent extraction imply the selective transfer of the substance from a liquid phase to another, hereby the interested analytes from a sample is extracted using an immiscible organic solvent. This procedure is managed by the Nernst partition known also as distribution law which claims that at equilibrium a given solute will always be distributed between two immiscible liquids in the same proportion (*Harwood et al, 1999*). Terms that describe this apportionment of analyte between two immiscible solvents are the distribution coefficient and the distribution ratio, where the distribution coefficient is equilibrium constant that describe the apportionment of the analyte between the immiscible solvents that might be an aqueous and an organic phase. Distribution ratio represent a measure that characterizes how well was extracted an analytes, so that is equal with the concentration of solute in the organic phase divided by its concentration in the aqueous phase (*Yizhak et al, 2004*).

Mathematically we can express this extraction technique as follows:



where A symbolize the analyte and $aq.$, and $org.$, are the aqueous and the organic phases, respectively.

The distribution coefficient (K_d) that is the ratio of the activities of A in the solvent is constant:

$$K_d = \frac{A_{org}}{A_{aq}} \quad (\text{equation 1.4.})$$

Expressing the fraction of extracted analyte (E) as percentage, we obtain:

$$E = \frac{C_0 \cdot V_0}{C_0 \cdot V_0 + C_{aq} \cdot V_{aq}} = \frac{K_d \cdot V}{1 + K_d \cdot V} \quad (\text{equation 1.5.})$$

where C_0 and C_{aq} are the concentration of the analyte in the two phases (organic and aqueous phase, respectively). Also V_0 and V_{aq} are the volume of the two phases and V represents the phase ratio

$\left(V = \frac{V_0}{V_{aq}} \right)$ (*Rydberg et al, 2004; Loconto, 2006*).

1.2.2. Short theory of headspace analysis

A headspace analysis technique is reliable in terms of volatile organic compounds analysis and could be described in a couple of words as follows: the sample (that could be solid or liquid) is placed in a headspace vials and closed well with a Teflon lined screw cap. After that is heated at a certain temperature for a given time. So, the volatile analytes that are soluble in the condensed phase will distribute between liquid/solid and headspace phase of the vials pursuant to the thermodynamically controlled equilibrium as shown in figure 1.5. (Kolb *et al*, 2006).

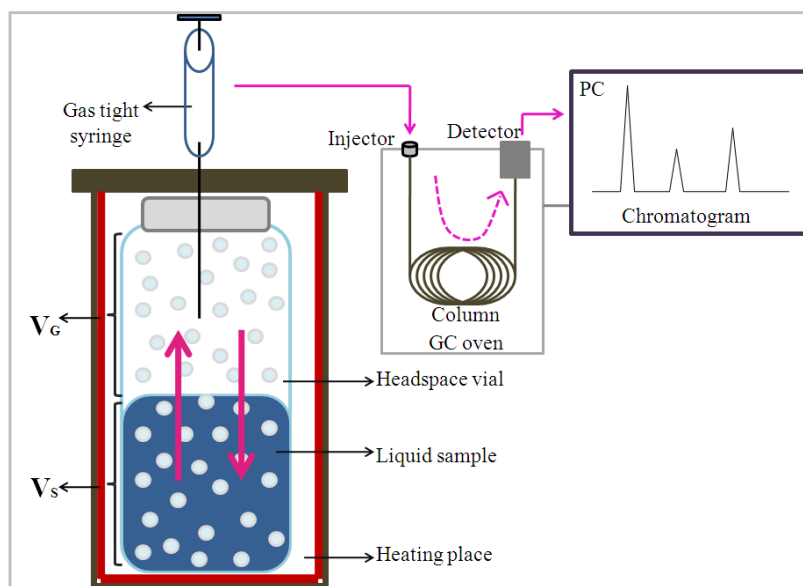


Figure 1.5. Headspace analysis of a liquid sample on GC
(V_G – volume of the gas phase, V_S – volume of the liquid sample).

According with the supposition that our sample is liquid, mathematically the following equation characterizes the volume of the two phases from the vials (equation 1.6):

$$\beta = \frac{V_G}{V_S} = \frac{V_V - V_S}{V_S} = \frac{V_G}{V_V - V_G} \quad (\text{equation 1.6.})$$

where β represent the relative volumes of the gas and liquid phase and V_V is the volume of the vials that is the sum of the volume of the sample phase (V_S) and the volume of the gas phase (V_G), so $V_V = V_S + V_G$ (Grob *et al*, 2004).

Hereby the volume of the liquid phase is given by equation 1.7., and the volume of the gas phase is assigned by equation 1.8.:

$$V_S = \frac{V_V}{1 + \beta} \quad (\text{equation 1.7.})$$

$$V_G = V_V \cdot \frac{\beta}{1 + \beta} \quad (\text{equation 1.8.})$$

The concentration of the analyte transferred in the gas phase during heating process (equilibration) is the same with the concentration from the liquid sample volume (*Oonk et al, 2007*).

Hereby $C_0 = \frac{W_0}{W_S}$, where C_0 represent the original concentration of the analyte from the liquid sample, W_0 is the original amount of the analyte in the sample. Behind equilibration process the volume of the analyte in the gas phase (W_G) and liquid phase (W_S) with their corresponding concentration C_G , respectively C_S , are as follows:

$$C_S = \frac{W_S}{V_S} \quad (\text{equation 1.9.})$$

$$C_G = \frac{W_G}{V_G} \quad (\text{equation 1.9.})$$

The formula of the original amount of analyte in the liquid sample is given by the following mathematical expression:

$$W_0 = W_S + W_G \quad (\text{equation 1.10.})$$

This equilibrium between the two given phases is stated by the thermodynamically controlled equilibrium constant known also in gas chromatography as partition coefficient (K), which is expressed mathematically as show equation 1.11.:

$$K = \frac{C_S}{C_G} = \frac{\frac{W_S}{V_S}}{\frac{W_G}{V_G}} = \frac{W_S}{W_G} \cdot \frac{V_S}{V_G} \cdot \beta \quad (\text{equation 1.11.})$$

This partition coefficient (K) helps us to indicate the mass distribution in the gas-liquid system. This hangs on the solubility of the analyte in the condensed phase (*Hachenberg et al, 1977*). Therefore in case of high solubility compounds C_S will be much higher than C_G so in this case K will have a high value. In the other case when the analytes is less soluble in the condensed phase C_S will be almost equal with C_G or might even be less than its value so K will be very small (*Kolb et al, 2006*).

According to these relations, the material balance equation ($W_S + W_G = W_0$) will become:

$$C_0 \cdot V_S = C_G \cdot V_G + C_S \cdot V_S = C_G \cdot V_G + K \cdot C_G \cdot V_S = C_G (K \cdot V_S + V_G) \quad (\text{equation 1.12.})$$

Therefore C_0 will be given by equation 1.13.:

$$C_0 = C_G \cdot \left[\frac{K \cdot V_S}{V_S} + \frac{V_G}{V_S} \right] = C_G \cdot (K + \beta) \quad (\text{equation 1.13.})$$

and C_G will be represented by equation 1.14.:

$$C_G = \frac{C_0}{K + \beta} \quad (\text{equation 1.14.})$$

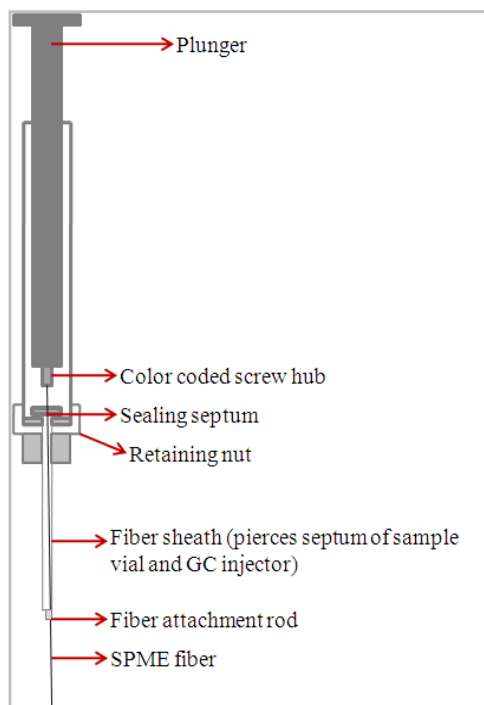
For a specific system under specific condition K and β are constants (*Kolb et al, 2006*). Below we can conclude that in a specific system the concentration of the analytes from the headspace is proportional to the original sample concentration. In this manner the basic canon of gas

chromatography is that the peak area of a specific analytes is proportional to the concentration of the analytes in the analyzed sample. So, an aliquot of the headspace is analyzed in which the analytes concentration is C_G , therefore we can express for the obtained peak area A after analysis through the follow statement: $A = ct \cdot C_G$, where ct represent the influence of several analytical parameters as the gas chromatograph detector response factor. Finally we can say that $A = ct \cdot C_0$ where ct is a combined constant and represent the influence of headspace extraction technique, gas chromatograph and the used detector parameter (Kolb, 1980).

Thus, the relationship between the peak area A obtained after analysis of an aliquot of the headspace and the concentration of the analytes in the headspace (C_G), the original sample concentration of the analytes (C_0), partition coefficient (K) and the phase ratio of the vial (β) could be expressed as in equation 1.15.:

$$A \cong C_G = \frac{C_0}{K + \beta} \quad (\text{equation 1.15.})$$

1.2.3. Solid phase microextraction theoretical consideration



These new technique allow to determine quantitatively chemical compounds from liquid or gaseous samples at ultra trace levels using a fused silica fiber coated with a polymeric phase where this polymeric phase have the function to extract the required analytes even if it is volatile, semi volatile or nonvolatile. The main idea of this extraction procedure could be described in a couple of words as: the analytes is concentrated onto a fused-silica optical fiber coated with a layer of a polymeric substances like that are used in chromatography as stationary phases. This fiber (usually with 1 cm length) is attached a special micro syringe, so that after concentration of the analytes from the sample into the coating by exposing it to the sample, that is subjected to analysis. After this step the needle with the fiber it is introduce in the injection port of the chromatograph on that is performed the analysis – see figure 1.6.

Figure 1.6. Solid phase microextraction devices with holder (Scheppers Wercinski, 1999).

The fiber after analysis is protected by a hollow stainless steel needle. This needle has also the aim to help the fiber to cross the septum from the vials as well from the chromatograph. After sorption of the analytes from the sample onto the fiber, they are desorbed thermally into the carrier gas stream (Fifield et al, 2000-(b)). The selectivity of the extraction is given by the polymeric coating on the fiber.

In solid phase microextraction case the sample preparation is grouped in two processes in that the first is represented by analytes extraction from the sample matrices and the second is represented by analytes desorption. In the first processes the fiber is exposed to the sample matrices and the target analytes partition between the coating and the sample until the equilibrium is achieved. In the second step, the fiber is introduced in the injection port of the analytical instrument where the analytes are desorbed to the instrument for analysis – see figure 1.7.

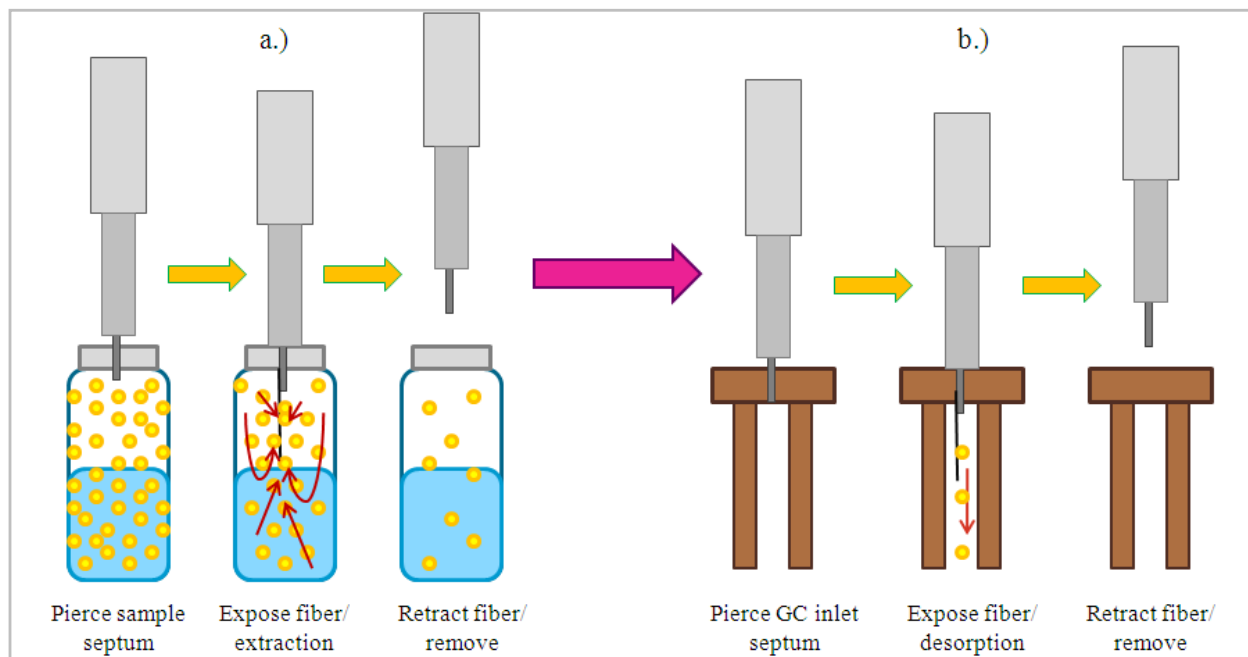


Figure 1.7. Schematic representation of SPME. a.) first step represented by extraction/sampling; b.) second step represented by desorption/injection (Robinson et al, 2005).

So, shortly we could characterize solid phase microextraction as the partition of the analytes between the sample matrices and the polymeric phase on the fiber. Quantitatively this process is described by Nernst's partition law.

1.3. Instrumental analysis of volatile organic compounds from aqueous samples

Gas chromatography – GC – was described for the first time in 1952 by Martin and James (James et al., 1952). Over the years this instrumental technique became one of the most used separation techniques for the analysis of gases and volatile compounds from different sample matrices. A fateful phase in GC evolution was the introduction of the open tubular column by Golay in 1958 (Golay, 1958) and enactment of fused silica capillary columns by Dandeneau and Zerrenner in 1979 (Dandeneau et al., 2005). In our days with using of capillary columns it is possible to solve a large scale analytical problems such as isomer separation and analysis of complex mixtures from natural products and biological sample matrices.

As a main idea, gas chromatography can be described in a couple of words by three steps: volatilization of the sample in a heated inlet port – injector, followed by the separation of the

component mixtures in a column and finally the *detection* of each compounds from the sample matrix by a detector.

As the procedures name showed, *gas chromatography-mass spectrometry* is a combination of two main separation processes as gas chromatography and mass spectrometry. Gas chromatography could be described very shortly as floating of the sample composite in mobile phase through the capillary column with a high length (usually 30 – 60 meter) whose inside walls are finely coated with the stationary phase where the components of the analyzing sample are separate and eluted one after another from the end of the column (*Niessen, 2001*). The detected components are enlisted as peaks in a chromatogram and based on the correlation between the peak area and retention time is given the information about the possible identity of the compounds from the solute and about their concentration in the sample. Anyway the identification of peaks is infrequently possible to determine exactly (*Honour, 2006*).

Opposite with gas chromatography, the mass spectrometer usually is useless for working with mixtures but in case when a single chemical compounds is analyzed on mass spectrometer the obtained spectrum (after a large variety of ionization method) help to identify the substance and to confirm its molecular structure (*Khandpur, 2006*).

Indeed if a mixture of chemical substances is analyzed through mass spectrometer the resulting mass spectrum is extremely complex and represents a summation of spectra of all the compounds presents in the analyzed sample. Therefore gas chromatographic instruments are very efficient for separation of chemical compounds from a sample in its components but it is inefficient for their identification, beside a mass spectrometer is extremely efficient in identification of the sample components (*Eidhammer et al, 2007*). So, combining these two analytical instruments was finding the gas chromatography-mass spectrometer instrument that is capable to separate, identify and quantify complex mixtures.

1.4. Ecotoxicological effects of volatile organic compounds

Living organisms including people are exposed to chemical pollutants, called also as environmental toxicants, via environmental media. The exposure might be occurred by breathing, ingestion by drinking or eating nourishments that contain these substances or through skin contact – see figure 1.8.

When living organisms as humans, plants or animals are exposed to environmental toxicants a cascade of biological as well biochemical events takes place in them. These effects intensity depends on exposure concentration if it is high enough and/or if the time duration of exposure if is long enough.

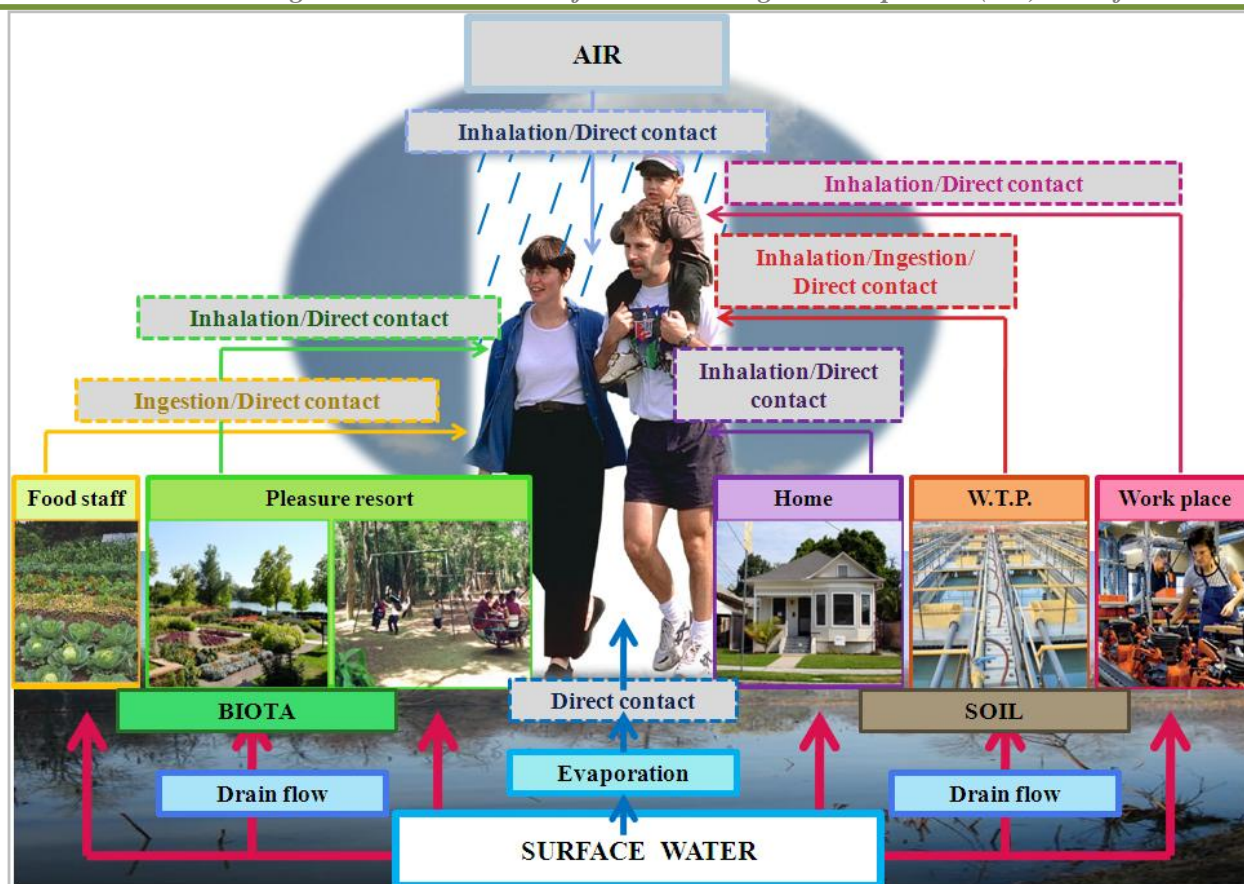


Figure 1.8. Potential pathways of human exposure to volatile organic compounds.

Certainly, when we talk about exposure we must take into account the dose (how much by the chemical substance are ingested, inhale or imbibe through skin contact), the period of exposure and the way where through the people get contact with them. Also is necessary to look at the other chemical contaminants hereat the people are exposed as well as their age, sex, diet, lifestyle, family trails and state of health. In the last decades many studies showed the compounds conspecific to volatile organic compounds result in different types of harmful effects on humans or other existences (Byers, 2006).

Due to the insufficient knowledge regarding additive effects of volatile organic compounds, is necessary to pay a special attention to detecting and eliminating the sources of this contaminants. However, in all cases is important to eliminate as possible the source of volatile organic compounds and contamination with them.

1.4.1. Outcomes of volatile organic compounds exposure

The adroitness of volatile organic compounds to cause harm for human beings varies greatly – see table 1.1. The effects of volatile organic compounds exposure depends on heterogeneous factors such as: the type of volatile organic compounds including its physicochemical properties as chemical substances and its interaction with the environmental media; the strength of volatile organic

compounds in environment hereupon the inhabitants and humans get contact and the period of time whereupon a person is exposed (*Davies et al, 1998*).

Table 1.1. General information regarding toxic effects of some volatile organic compounds classes.

Chemical compounds classes	Detrimental effects
<i>Volatile phenols</i>	Respiratory irritation, headaches, burning eyes, skin burns, irregular heartbeat, paralysis, damage of – lung, liver, kidney.
<i>Alcohols</i>	Lethargy, confusion, coma, damage of DNA cells, carcinogens.
<i>Volatile ketones</i>	Confusion, irritation of – nose, throat, eye, headaches, light headaches, increased pulse rate, nausea, vomiting, unconsciousness, damage of – liver, kidney, nervous system, lowered ability to reproduce, birth defects.
<i>Volatile alkanes</i>	Eye, skin, throat irritation, dizziness of headaches, neurotoxicity, carcinogenic effects.
<i>Volatile alkenes</i>	Low acute oral, dermal and inhalation toxicity, slight eye irritation, damage of liver and adrenals in low range.
<i>Volatile halogenated hydrocarbons</i>	Nose, throat, eyes, irritation, abnormal heart rhythms, damage of - kidney, liver, lung and nervous system, reproductive disorders, congenital malformation and tumors, spontaneous abortion, other teratogenic effects, carcinogen.
<i>Volatile monocyclic aromatic hydrocarbons</i>	Acute toxicity, mutagenicity, carcinogenic effects.
<i>Volatile polycyclic aromatic hydrocarbons</i>	Reproductive disorders, congenital malformation, other teratogenic effects.
<i>Volatile petroleum hydrocarbons</i>	Damage of lungs and nervous system, nerve disorders, headaches, dizziness, irritation of skin and eye, affects on the blood and immune system, carcinogenic.

As many scientific studies shows that display to “low” levels of volatile organic compounds may call irritation to the eyes, nose, throat and skin. In many cases was observed that these types of compounds might have as outcomes headaches, nausea or nerve problems (*Koenig, 2000*). Studies on animals have designates that exposure through ingestion, inhalation or in some cases through direct contact for a long period of time can increase the rate of disposal to cancer or could induce mutagenic anomalies. So, generally volatile organic compounds are suspected to be carcinogenic and having mutagenic or teratogenic effects on humans (*Ming-Ho et al, 2004*). Summaries of main harm effects of selected classes of volatile organic compounds are presented in table 1.1.

The great concern regarding volatile organic compounds is that they might enter in drinking water wells once that contaminated surface water are used as drinking water source and secondly after the reaction of disinfectant agents used in water treatment plant with the water matrices that most of the time results in formation of several volatile disinfection byproducts (VDBPs) (*Gottschalk et al, 2009; Xie, 2004; Speitel et al, 2006; Minear et al, 1996*). The inquietude connected with volatile disinfection byproducts formed during disinfection process in water treatment plant is based on the results showed by thousand and one studies that exhibit that these volatile byproducts posed some harmful effects, in particular cancer and reproductive disorders (*Clark, 2001; Karanfil et al, 2008*).

Chapter 2**2. Sampling program design to evaluate VOCs presence in surface waters**

Some river with its main tributaries were selected in order to evaluate the presence and quantities of volatile organic compounds. Extended presentation of sampling points is given in figure 2.1.

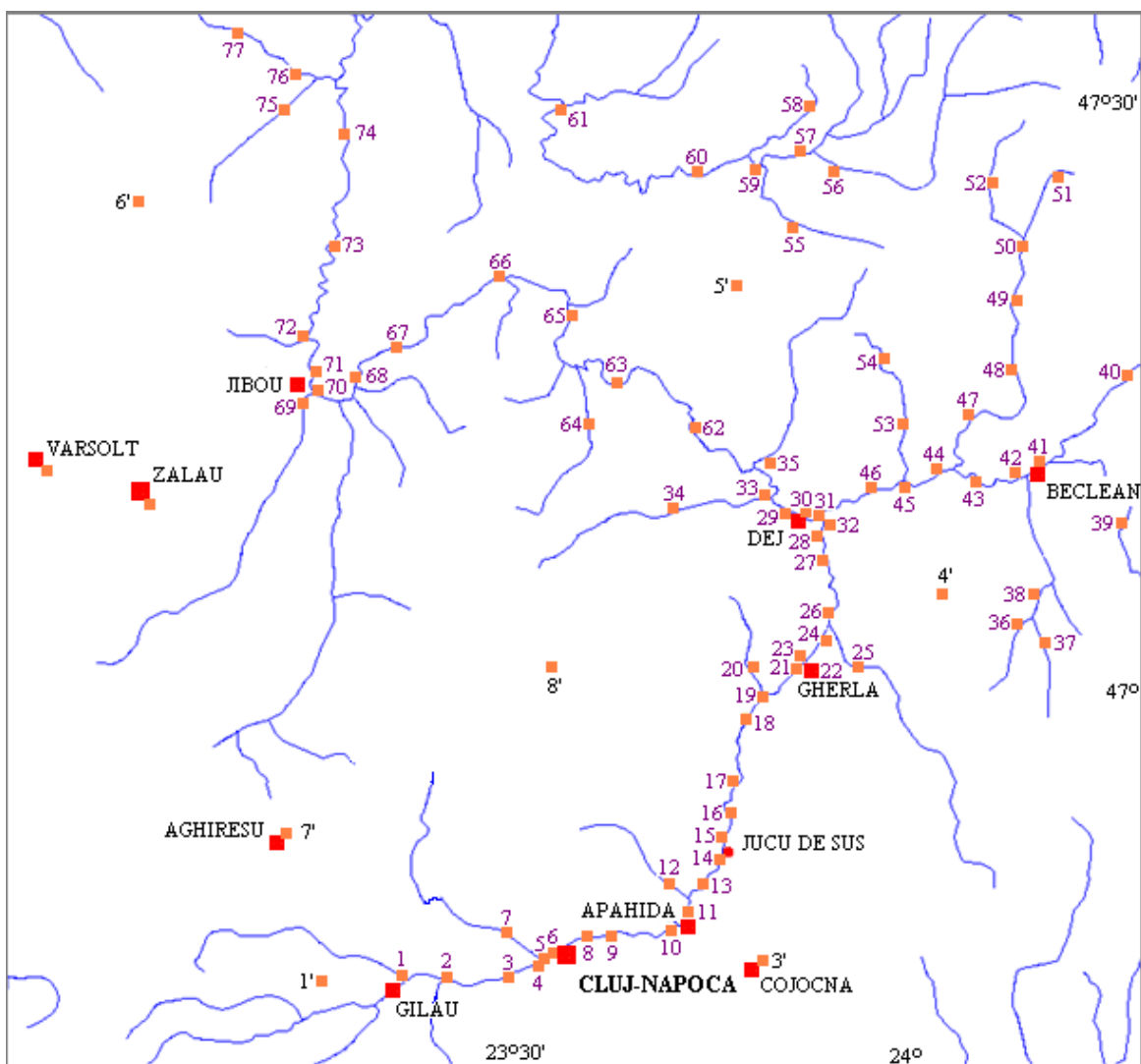


Figure 2.1. Extended presentation of the selected sampling points from Somes River (1'-8' represent the control sampling points).

Also five water treatment plants (Gilau WTP, Jibou WTP, Dej WTP, Beclean WTP, and Zalau WRP) with their corresponding distribution system were chosen to evaluate the volatile organic compounds that are presented in treated waters as well the volatile organic compounds that are formed after water treatment processes.

Chapter 3

Extraction and instrumental analysis techniques of volatile organic compounds from aqueous environmental samples

In case of these volatile organic compounds, the most befitting analytical method is gas chromatography with a suitable detector, whose choice usually depends by the target volatiles that are wanted to be analyzed (*Marriott et al, 2003; Huybrechts et al, 2003*) seconded by mass spectrometry usually engaged also with a chromatograph apparatus (*Aeppli et al, 2008; Sousa et al, 2006*). Beside these two major techniques of volatile compounds analysis, there are several additional methods as atomic emission detection (*Silgoner et al, 1997; Semb et al, 2002, Dietz et al, 2004*) or direct spectroscopic detection methods without using separation procedures (*Fujita et al, 2003*) or direct mass spectrometric techniques (*Lindingers et al, 1998; Ojala et al, 1999; Cowie et al, 1999; Harland et al, 1987*). Anyway, analysis of volatile organic compounds from environmental matrices doesn't involve just their separation or analysis, they ask also for several adjective steps as preconcentration, owing to their low levels from the sample matrices, or removing of the matrices component that disturb the instrumental analysis. Therefore sample preparation becomes the highest-toned and time consuming steps from the analysis procedures. Thus, the targets of researchers in this field become the development and optimization of steps as preconcentration or extraction until analysis followed by development of a slower time consuming instrumental analysis.

3.1. BTEX – volatile hydrocarbons

BTEX represent an acronym for the following chemical compounds: benzene, toluene, ethylbenzene and the three isomers of xylenes (as orto-xylene that is the single naturally occurring isomers of this compound, and meta-xylene with para-xylenes that are human-made forms of the xylene). They make part from the largest group of volatile organic compounds and usually are found in petroleum hydrocarbons as gasoline or other common environmental contaminants as household products (ex. synthetic rubbers, paints, plastics, dyes, detergents, cosmetics, resin-glues, etc.). Therefore, due to their characteristic of utility, these chemical compounds become widespread in the surrounding environment during the last decades, they being found in significant quantities even in surface waters (*Schmidt et al, 2004*). The necessity to monitoring of these compounds is motivated by their possible harmful effects on living things, most of them being suspected by carcinogenic effect (*Durmusoglu et al, 2010*). Thus their presence as quantity in different environmental matrices is regulated by several environmental and public health agencies from all over the world (*Coquery et al, 2005*).

3.1.2. GC-FID analysis of BTEX after HS extraction

In our days, development of new extraction and analysis technique of environmentally significant chemical compounds without using of any kind of solvents, as were required when it was performed liquid-liquid extraction (LLE), present more challenge. This avoidance is caused by the several disadvantages of LLE as: its performance in multiple steps that has as result the requirement for cleanup processes that has proved to be awkward, slow and less precise; the necessity of high

grade purity solvents that are expensive and hard to obtain but not in the last case are extremely unhealthful for analyst (Nollet, 2007; Bogusz, 2000). Thus, the attention was focused on the simplest and solvent less extraction of these compounds as static headspace extraction.

3.1.2.1. HS extraction working condition

Analysis of petroleum hydrocarbons could be extremely complex, it depending by the chemical properties of the sample matrix by which is wanted to do the extraction. As many studies presented before, presence of these compounds is often in our days. Unfortunately has been showed that their presence in large amount could damage significantly the environment and the ecosystem. Therefore their analysis becomes a challenge for any environmental analysts. Two procedures was applied in case if headspace extraction, once performed manually and the second performed automatically using a TriPlus HS autosampler provided by Thermo Electron Corporation, US.

a. *BTEX analysis by manual HS-GC-FID*: the optimization of this method was performed preparing several control samples with five different value of BTEX concentration – 5, 25, 50, 75 and 100 $\mu\text{g}\cdot\text{L}^{-1}$. The range of calibration curve was choose based on the level at that these compounds were founded in reality in monitored surface water samples. These controls were made in 20 mL clear glass vials, using ultrapure water spiked with BTEX stock solutions at selected concentration, after that they were hermetically closed by headspace metal screw cap magnetic (18 mm) with 3 mm thick blue/gray silicone/PTFE septum.

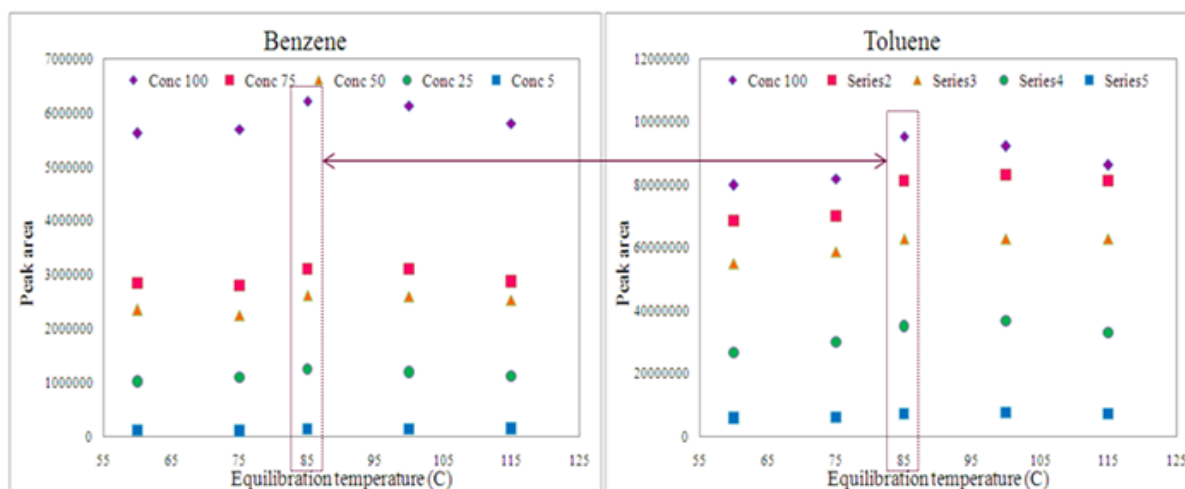


Figure 3.1. Vials equilibration temperature optimization for manual HS extraction in case of benzene and toluene.

Choice of the optimal temperature at that the vials to be exposed in oven as well the most relevant sample quantity was studied. Therefore the control samples for the selected concentration were prepared with three different volumes – 5 mL, 10 mL and 15 mL, respectively. The temperatures to that were exposed were: 60 °C, 75 °C, 85 °C, 100 °C and 115 °C. Also the equilibration was performed using three different procedures as follows, first using sand bath, second time with water bath and in the last case using an electric oven. The optimal equilibration time was

also studied; therefore four different times were choosing: 15 minutes, 30 minutes, 45 minutes and 60 minutes. 10 mL volume capacity gas tight syringe was used in order to perform the experiment, syringe that after and before injection it was held in oven at the working temperature condition.

Analyzing the results obtained after performing all these procedures has showed poorly temperature stability in case of water bath equilibration procedure than in case of sand bath but even in that case were observed temperature oscillations (that was monitored using a temperature electrode connected to an electrical multimeter). Thus, during the study it was observed that the most reliable method to perform the equilibration is using an electric oven; therefore fluctuations of the selected equilibration temperature were completely elided.

It was observed that the equilibration temperature present a great influence on the analytes extraction, therefore increasing the sample temperature induce changes in the analytes solubility conducting to the reaching of the equilibrium between the two phases – see figure 3.1.

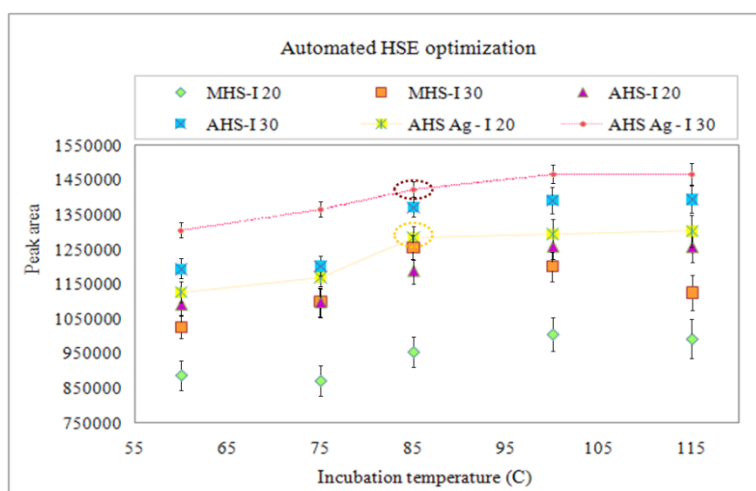


Figure 3.2. Benzene extraction optimization through different incubation temperature, different equilibration time and headspace mode (MHS-I 20: manual headspace mod with 20 minutes incubation; MHS-I 30: manual headspace mode with 30 minutes incubation; AHS-I 20: automatic headspace mode using TriPlus with 20 minutes incubation; AHS-I 30: automatic headspace mode using TriPlus with 30 minutes incubation; AHS Ag-I 20: automatic headspace mode using TriPlus with 20 minutes incubation and sample agitation during this time; AHS Ag-I 30: automatic headspace mode using TriPlus with 30 minutes incubation and sample agitation during this time;

Heighten of the vials at selected equilibration temperature resulted in higher vapor pressure of water and it was observed that BTEX analytes present a good pattern regarding their concentration in the gas phase at 85 °C, this temperature considered to be the most optimal for performance of HS extraction. After this temperature it was observed that the water vapor pressure has a great effect on the internal pressure from the vials that was maintained also in the gas tight syringe. This resulted in the dilatation of the pressurized gas from the headspace having as outcome the gas escapes in the atmosphere through the syringe needle at moment of its transportation to the chromatographic

apparatus. This effect could explain the loss of analytes concentration that is occurring after that the vials was equilibrated beyond 85 °C (Kolb et al, 2006; Camarasu et al, 2006; Snow et al, 2002).

The time during is performed the vials equilibrium it was also an important parameter that has direct impact on the HS extraction performance. Therefore, after performing the experience through all four time it was observed high difference between the two group of time as 15 – 30 minutes and one hour, but a good equilibrium is obtained after 30 minutes. Also 10 mL sample volume has showed a better results than 5 or 15 mL of samples for all concentration from the working range (1 – 100 µg·L⁻¹).

According to Sakata et al, 2004, it was meet the requirements through the gas tight syringe as well its needle to be maintained at a lower temperature with a few Celsius grades (1 – 3 °C) during the vial equilibration process, thus avoiding the analytes condensation on the walls.

b. *BTEX analysis by automated static HS-GC-FID*: The automated extraction of the BTEX from water sample was obtained using a TriPlus HS autosampler purchased from Thermo Electron Corporation.

TriPlus HS

Incubation time: 30 minutes

Incubation mode: constant

Agitator temperature: 85 °C

Agitator on: 20 sec; Agitator off: 20 sec

Syringe temperature: 80 °C

Injection depth: 35 mm

Injection speed: 40 mL/mil

Filling volume: 1.2 mL/mil

Filling counts: 1; Filling delay: 0 sec

Post injection syringe flush: 1 minutes

The advantages of this method was introduced by the increased precision as regards time of sample incubation, keep on the disposed incubation temperature or of the amount of headspace gases that is introduced in the apparatus. All this betterment of intermediary steps has as result increasing in performance of method.

Another possibility to improve this method was represented by introduction of the agitation as intermediary step during incubation time of sample. Thus, better response of the target analytes was observed when sample agitation was introduced during the time of sample incubation – see figure 3.

Table 3.1. Working condition parameters of automated HS extraction.

With sample agitation through equilibration process the target compounds response increased significantly, therefore even for a shorter incubation time (20 minutes) the response were higher than case of equilibration for 30 minutes.

Several programming conditions of the automated HS extraction working parameters were tried in order to obtain a more suitable extraction and separation of these analytes from an aqueous environmental samples. HS program parameters with the optimum results that were obtained are presented in table 3.1.

Through this method was increased the method precision as regards maintenance perfectly the working temperature and timing. Therefore the method performance characteristics showed a better result for recovery that for the BTEX compounds was between the ranges of 96 – 104 %.

3.1.2.2. GC-FID working condition

Another great impact on the target analytes analysis has the analytical apparatus as well its detector that is used. In case of BTEX analysis Trace GC Ultra gas chromatographic apparatus (Thermo Electron Corporation) was used equipped with a flame ionization detector (FID).

In order to achieve a better separation of the BTEX compounds, two columns purchased from Thermo Electron Corporation was compared with different column temperature program.

The column used were TR 5 % phenyl methylsiloxane having 0.53 mm ID x 0.50 μm film thickness x 30 m length and TR-V1 Cyanopropylphenyl polysiloxane with 0.32 ID x 1.80 μm film thickness x 30 m length, both column purchased from Thermo Electron Corporation. Better sensitivity and capacity of separation was obtained in case of TR-V1 capillary column. With this column was separated the orto-xylene by para- and meta-xylenes, while with TR 5 column the three isomers of xylene were analyzed as sum of them (they wasn't separate). But even with TR-V1 column wasn't obtained a completely separation of this three isomers of the xylene.

Once with the capillary column checking, several temperature programs was tried in order to obtain the best program that permit a well separation of the BTEX analytes in a shorter analysis time as possible.

The performed temperature program were tried on both column, in idea to have a completely image on their performance when we done their comparison. In the follows are listed the temperature programs that were used and which presented relevant results:

1. The first temperature program used, started at 40 °C for three minutes, increasing directly to 200 °C with 10 °C·min⁻¹, then held for three minutes at the final temperature. This program showed a wily poor separation of ethylbenzene and xylene compounds in case of both columns, therefore it was completely abandoned.
2. The next program was: 50 °C and held for five minutes, then raised with 7 °C·min⁻¹ to 130 °C and held at this temperature for 2 minutes after that the temperature continue to increase at 220 °C with 10 °C·min⁻¹, where was kept for five minutes.
3. The most suitable temperature program with that was obtained the most relevant separation, including the separation of orto- isomers by the para- and meta- isomers of xylenes was started from 60 °C and increased rapidly with 7 °C·min⁻¹ to 180 °C where it was help three minutes. Using of this program with TR-V1 column, the separation of BTEX analytes was obtained after five minutes, whereas the poor separation through TR 5 column runs for almost 13 minutes.

In all cases the following parameters were disposed for flame ionization detector (FID): temperature 250 °C, as make-up gases were used nitrogen with a flow rate 20 mL·min⁻¹, hydrogen at a flow rate 35 mL·min⁻¹ and synthetic air at a flow rate 350 mL·min⁻¹, provided by a Hydrogen, Air and Nitrogen generator 2600 and 2381 HC generator, respectively. The injection port as well the detector operation temperature was set at 200 and 250 °C, respectively.

In case of BTEX analysis through HS-GC-FID, external calibration was used for quantification of these compounds. The main parameters of the method performance are summarized in table 3.2.

Table 3.2. HS-GC-FID analytical method parameters using TR-VI capillary GC column as well the working condition from point 3, below presented.

Substance	Limit of quantitation LOQ (µg/L)	Working range µg/L	Measurement uncertainty %	Recovery %	Retention time min
Benzene	0.3	1-100	± 10	98	2.96
Toluene	0.7	1-100	± 15	110	3.02
Ethylbenzene	0.5	1-100	± 10	105	3.75
o-xylene	0.5	1-70	± 13	105	4.38
m/p-xylene	0.8	1-70	± 20	110	4.51

3.1.2. SPME-GC-FID analysis of BTEX from water samples

This procedure involves the analysis of BTEX compounds from water samples using SPME devices in immersion mode (*Sokula et al, 2001*). The main characteristic of this procedure is given by idea that diffusion of the target analytes through the impounded water layer spot around the SPME fiber under known hydrodynamic condition proceed as the rate determining step of mass-transfer for a short time, usually less than 1-2 minutes, and hereby entails the extraction account (*Pasckhe et al, 2004*). This procedure has significant impact in making a comparison between a very short time and well extraction and analysis and less a contaminated sample (usually is used at the field sampling location); in evaluation and determination of the kinetics of a chemical reaction without troublesome of process and its performance through pulling casing of sample. Therefore this procedure could be characterized as a less invasive analysis method for water samples. But as in everything, there are some limitations as regards the basics of this procedure due to dissimilarities of heat and mass transfer that is considered by *Bird et al*, and *Levich*, as incommensurate comparing with the basic mode. Model of diffusion boundary layer reduce the hydrodynamic situation around the relatively acerb fiber surface which could result in formation of local turbulent flow with small eddies diffusions by way of standing water layer (*Pasckhe et al, 2004*).

3.1.2.1. Solid phase microextraction procedures and instrumental analysis procedures

SPME extraction was performed at 30 °C (room temperature) with water samples placed in 20 mL glass vials. The SPME needle was inserted through septum at 5 mm away from the axis of the vials according to results obtained by Pasckhe et al. The water samples were subjected to agitation by a Teflon coated stir bar (provided by Supelco) using a magnetic stirrer (Heidolph MR 2002). Through this building-up was obtained a tangential flow direction of the water sample to the PDMS SPME fiber. This is helpful for estimation of the linear velocity, u , of the sample and the thickness,

ρ , of the boundary layers, using the semi-empirical relationship enounced by Pawliszyn (Sokula et al, 2001; Pawliszyn, 2002; Pasckhe et al, 2004), see equation 3.2 and 3.3, respectively.

$$u = 1.05 \cdot \pi \cdot N \cdot r \cdot \left[2 - \left(\frac{r}{0.74 \cdot R} \right)^2 \right] \quad (\text{equation 3.2.})$$

$$\rho = 9.52 \cdot \left[\frac{b}{Re^{0.62} \cdot Sc^{0.38}} \right] \quad (\text{equation 3.3.})$$

where N express the magnetic stirred speed in revolutions per second, r is the distance between the fiber and the axis of the vial given in cm, R is the radius of the stir bar in centimeter, b is the radius of the SPME fiber also given in cm, Re represent the Reynolds number given by equation 3.4., and Sc is the Schmidt number given by equation 3.5.

$$Re = \frac{2 \cdot u \cdot b}{\nu} \quad (\text{equation 3.4.})$$

$$Sc = \frac{\nu}{D} \quad (\text{equation 3.5.})$$

where ν is the kinematic viscosity of the matrices medium (in this case water) and D is the diffusion coefficient of the target analytes molecule in the water sample matrices, in this case at “infinite” dilution.

During the experiment the PDMS SPME fiber was exposed between 10 and 180 seconds and the sample was stirred between 100 and 1250 rpm. In case of 60 seconds exposure and 120 seconds exposure the extraction was repeated some few times in order to determinate the reproducibility of the method.

The analysis was performed on Trace GC Ultra gas chromatographic apparatus (Thermo Electron Corporation) equipped with a flame ionization detector (FID) and a split/splitless injector. After desorption of target analytes 1 μL of the aliquots was injected in the injector with a constant 220 $^{\circ}\text{C}$ temperature. As column was used TR 5 % phenyl methylsiloxane column, provided by Thermo Electron Corporation, having as characteristics 0.53 mm ID x 0.50 μm film thickness x 30 m length. The oven temperature program has set as follows: 40 $^{\circ}\text{C}$ for 5 minutes, followed by increases with 5 $^{\circ}\text{C} \cdot \text{min}^{-1}$ at 150 $^{\circ}\text{C}$ and held at this temperature for 3 minutes, subsequent by an increases of temperature with 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ at 220 $^{\circ}\text{C}$ and kept at this temperature for 5 minutes. Nitrogen with 1 $\text{mL} \cdot \text{min}^{-1}$ as flow rate was used as carrier gas. The FID detector temperature was set at 300 $^{\circ}\text{C}$.

3.1.2.2. Method performance

During this study, were performed also experiments in order to establish the velocity dependence of the extracted amounts for 90 seconds as fixed extraction time.

After that calculations were performed using equations 3.2. – 3.5., it could be observed as showed also figure 3.6., that a plateau is obtained at 80 $\text{cm} \cdot \text{sec}^{-1}$ where redundant increases of velocity has no effect on the extracted mass. This showed that the mass transfer from sample liquid

to the PDMS SPME interface is nothing else but rate limiting steps as showed also previous researches of Levich et al, Plucinsky et al, and Schoner et al.

Therefore the diffusion of target analytes from sample matrices into the pores of SPME fiber is a limiting factor in this case. Same pattern was observed for the other BTEX compounds and the standard deviation for all components was established at 6 %, 8.2 %, 5 %, 7.8 % and 10 % for benzene, toluene, ethylbenzene, ortho-xylenes and para-,metha-xylenes, respectively.

$$C_w = \frac{m_f \cdot \ln(b + \delta)}{2 \cdot \pi \cdot D_w \cdot L \cdot t} \tag{equation 3.6}$$

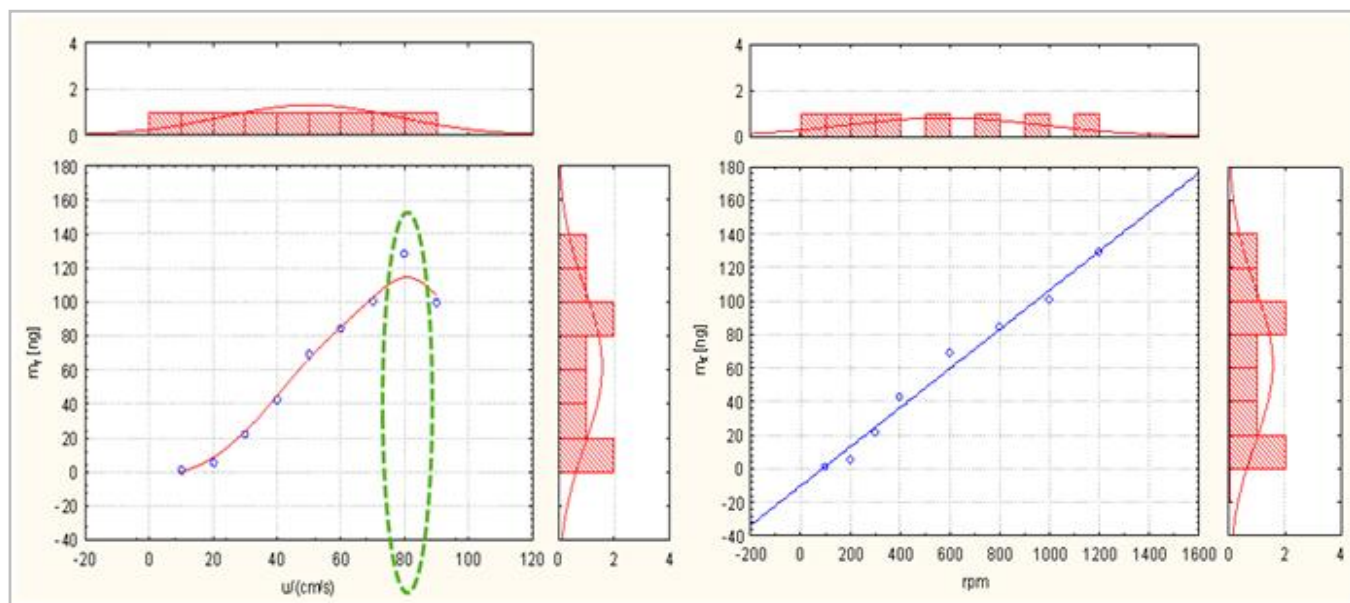


Figure 3.1. Extract amount of benzene with PDMS SPME fiber versus tangential sample velocity ($C_{w(0)} = 200 \mu\text{g}\cdot\text{L}^{-1}$, $t = 120 \text{ sec}$).

Table. 3.3. Average of concentration estimates C_w^{av} calculate empirically with equation 3.6., using m_f values determined for $u = 22 \text{ cm}\cdot\text{sec}^{-1}$ and $C_{w(0)} = 200 \mu\text{g}\cdot\text{L}^{-1}$ at sampling extraction times between 40 – 100 seconds, and their relative errors.

Substance	$C_w^{av} (\mu\text{g} \cdot \text{L}^{-1})$	E (%)
Benzene	182	-15
Toluene	193	-9
Ethylbenzene	228	+11
p-xylene	172	-19

Using equation 3.6., it was estimated the m_f value (the quantified absolute amount of the analyte trapped with the PDMS SPME fiber) for a specific exposure time, t , between 40 and 100 seconds at $u = 22 \text{ cm}\cdot\text{sec}^{-1}$. These results and their relative errors, E , with respect to $200 \mu\text{g}\cdot\text{L}^{-1}$ are presented in table 3.3.

It was observed that the predicted values of errors are usually analyte-specific as showed also Sokula et al, and Pasckhe et al. Therefore, these results show that the target analytes mass uptake of PDMS fiber depends linearly on the speed of sample stirring – see figure 3.1.

3.2. n-alkanes extraction and analysis from water samples

N-alkanes represent usually the dominant group of saturated and unsaturated hydrocarbons in the environmental media. Their distribution characteristics, most of the time is given by the predominance of carbon number, high molecular weight compounds with a maximum between n-C₂₅ and n-C₃₃ over a series of light n-alkanes in the range C₁₅₋₁₉.

3.2.1. HS-SPME GC-MS analysis of n-alkanes

Usually in any organic chemical contaminants analysis several intermediary steps are covered before to obtain the final results. This intermediary steps as extraction of target analytes from environmental sample or their pre-concentration, demand large time and in most of the case involve a significant number and quantities of toxic organic solvents (*Przvjazny et al, 2002*). As presented before, SPME is a relative new, simple and inexpensive sample preparation technique without implication of any kind of chemical solvents.

3.2.1.1. HS-SPME extraction procedures of n-alkanes from surface water

In order to perform and to improve the analytical method several spiked samples were prepared as follows: 10 milliliter distilled water were placed in headspace vials after that it was spiked with a specific quantities from the prepared diluted standard of n-alkane compounds, thus obtaining in the headspace vials a fixed concentration of $50 \mu\text{g}\cdot\text{L}^{-1}$. After that the vials were immediately sealed with caps equipped with PTFE-silicon septum, provided by Supelco.

The aims of this study were to evaluate the HS-SPME extraction applicability in case of n-alkanes analysis from surface water samples. In order to obtain an optimal extraction of n-alkanes through HS-SPME method, there are a wide range of parameters that could help to improve it.

As previous research has showed, water sample volume could influence positively or negatively the extraction efficiency through the magnitude of headspace (*Zanjani et al, 2006*). Method optimization was assessed for seven different sample volumes as follows 1 mL, 2.5 mL, 5 mL, 7.5 mL, 10 mL, 12.5 mL and 15 mL – see figure 3.2.

Analyzing the results obtained for different sample volume it was perceived that increasing of sample volume increase the response of target analytes till 10 mL, upon that the response showed a plateau. Subjecting a 10 mL sample volumes to different stirring rate (100, 200, 300, 600, 800, 1000 and 1250 rpm) the target analytes peak area increased up to 800 rpm stirring rate. Significant influences on the extraction procedures have the stirring rate and sample volume. But also a too much increasing of sample volume could damage the extraction performance. Thus according to

performed analysis results we considered that significant response was get for 10 mL sample volume and for an 800 rotation per minutes stirring rate.

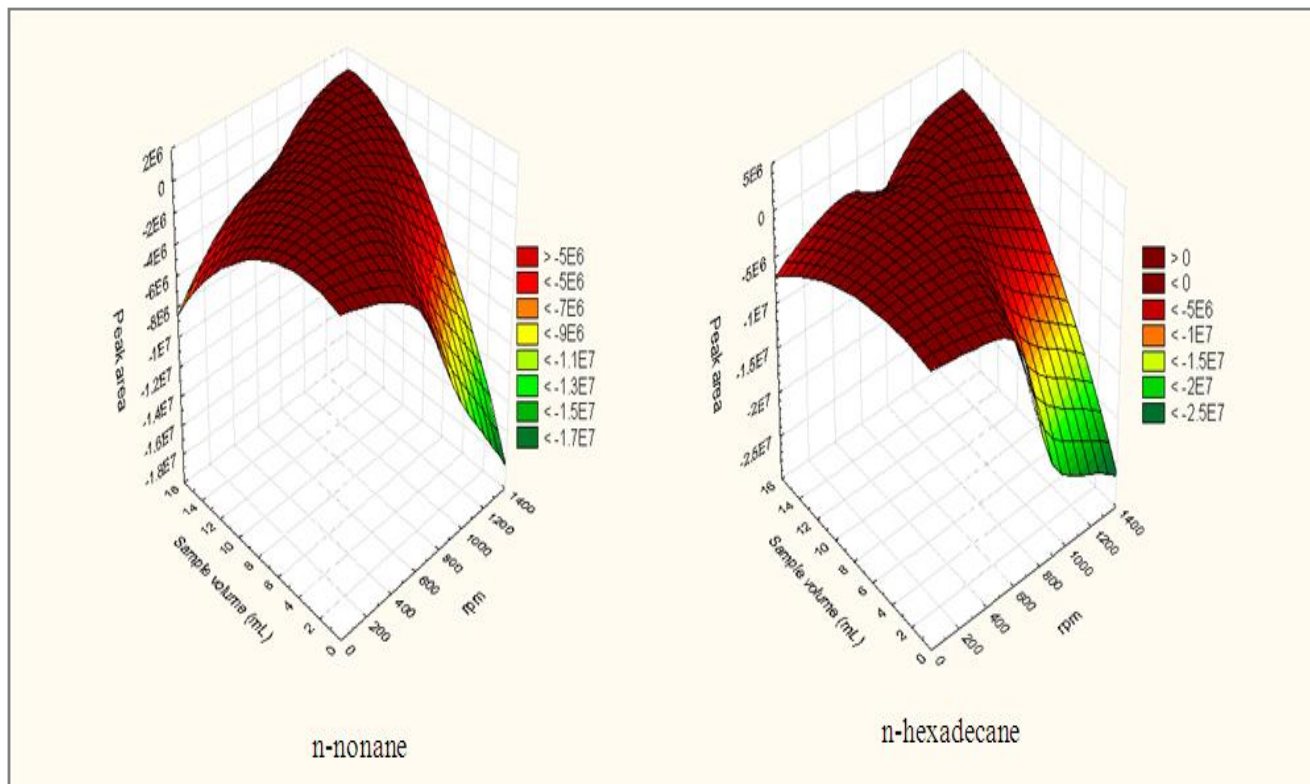


Figure 3.2. Effect of sample volume and stirring rate on the peak area of target analytes onto the following extraction conditions: needle temperature 98 °C, sample temperature 100 °C and 5 minutes extraction time without salt addition.

The impact of ionic strength of the sample on the HS-SPME extraction efficiency has shown no effect when increasing of NaCl concentration in water sample spiked with n-alkanes was performed. Therefore the analyses were done without changing the initial ionic strength of water samples.

Usually in order to increase the HS-SPME extraction efficiency, increasing of extraction time through that the equilibrium is reached between the aqueous sample and headspace, is a common strategies.

In this case the method performance was evaluated for several extraction times, as follows: 2 minutes, 5 minutes, 7 minutes, 10 minutes and 15 minutes. Analyzing picture 3.3., it could be see that peak area of n-nonane increase of the extraction time 1 to 10 minutes after that the target analytes response remain constant. Therefore 10 minutes was selected as optimum time through the target analytes molecules could diffuse from the aqueous phase onto gaseous phase.

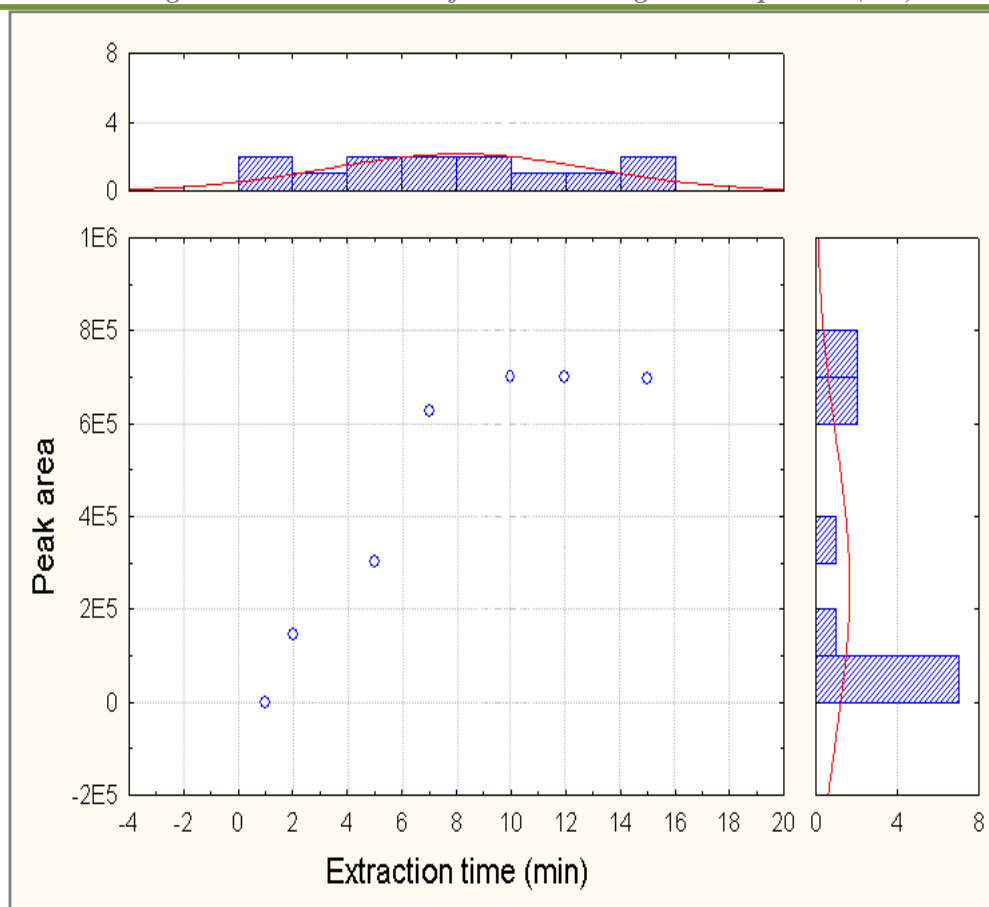


Figure 3.3. Effect of extraction time on the peak area of target analytes onto the following extraction conditions: needle temperature 98 °C, sample temperature 100 °C, 10 mL sample volume, 800 rpm stirring rate and no salt addition.

3.3. Chlorinated organic compounds

Among all the organohalogen compounds, chlorinated hydrocarbons class compounds are the most widespread chemical contaminants that are found in environment, they being detected in all environmental compartments. Chemically, chlorinated hydrocarbons consist by hydrocarbon molecules hereat one or more chlorine atoms are chemically bonded. Usually the number of chlorine atoms as well the number of carbon atoms and their three-dimensional arrangement determines in part the physicochemical properties of the molecule. Owing to the large number of possible forms of these compounds, the class of chlorinated hydrocarbon compounds has a broad range of applicability hereby a great practical and economical importance.

But their importance is not just due to their large usages in industry or to their widespread presence in nature, but also due to their toxic effects to plants, animals and humans. Therefore their analysis is a requirement for every environmental monitoring agency.

3.3.1. Headspace-solid phase microextraction-gas chromatographic-electron capture detector analysis vs. headspace-solid phase microextraction-gas chromatographic-mass spectrometer analysis of chlorinated organic compounds

As another technique of target compounds extraction from water sample matrices, solid phase microextraction was tried. The extract analysis were performed on gas chromatography equipped with ^{63}Ni electron capture detector and consecutively on gas chromatograph coupled to a quadrupole mass spectrometer, in order to compare their performance in case of chlorinated organic solvents analysis. As we know electron capture detector present an increased sensibility towards halogenated organic compounds but on the other side mass spectrometer as detector has the ability to distinguish exactly the particles according to their m/z ratio.

3.3.1.1. HS-SPME-GC-ECD procedures improvement for chlorinated organic solvents extraction and analysis from water samples

The challenge in analysis of volatile chlorinated organic solvents is to reduce as possible the loss of target analytes, the possible contamination through extraction procedures as well to find a sensitive, reliable and easily applicable instrumental technique. Considering these headspace extraction procedures and solid phase microextraction are one of the most “clean” analytical methods because in their procedures doesn't required any kind of organic solvents. Also another significant advantage of them is that they are easily applicable, not long time consuming and are capable to be automated.

Combining of these techniques with gas chromatography equipped with an electron capture detector given out that a sensible and straightforward method in case of volatile chlorinated organic solvents.

3.3.1.2. HS-SPME procedures improvement

There are several working parameter that could influence positively or negatively the sensitivity and selectivity of this procedures. In order to obtain a good response in case of volatile chlorinated solvents two different fiber were tested and compared in their ability to extract the target chlorinated solvents in order to choose the best - 100 μm thickness polydimethyl siloxane (PDMS) and 85 μm thickness polyacrylate fiber (PA). All the two fibers were conditioned in the gas chromatography injector port before their uses as the manufacturer recommended. For increasing of their extraction capacity the fiber desorption temperature, pH, equilibration time, salt concentration and desorption time was tried to be optimized in the following.

The HS-SPME procedures was performed through a TriPlus HS autosampler equipped with an automated SPME devices, all provided by Thermo Electron Corporation. Through the analysis of the two SPME fibers good responses were obtained from the PDME fiber – see figure 3.4.

In case of HS-SPME the sample exposure temperature as well exposure time could affect significantly the method performance. Owing to these the spiked water sample were subjected to five different temperature, 50 °C, 80 °C, 100 °C, 125 °C and 150 °C for different time period, 3, 5, 10, 15 and 30 minutes, respectively – see figure 3.5., a.

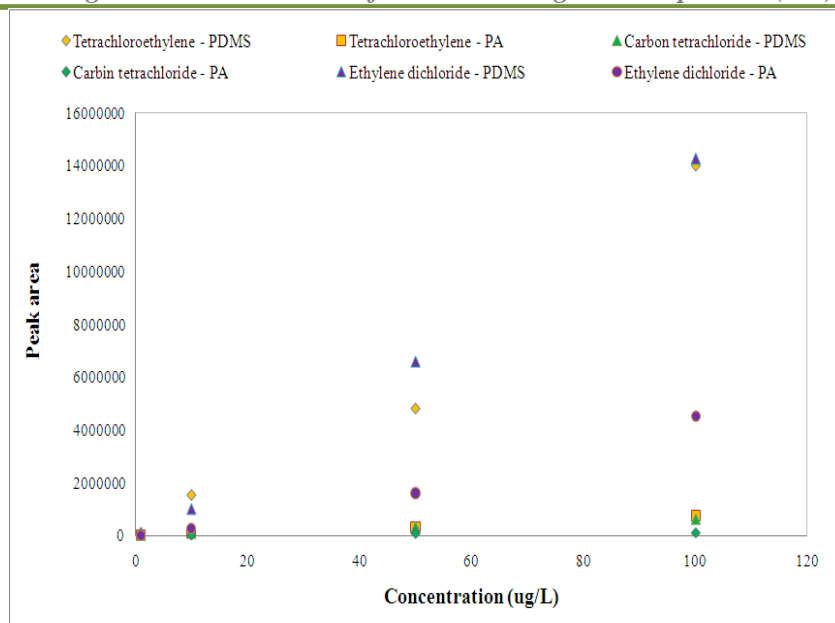


Figure 3.4. Comparison of PDMS and PA fiber response at different concentration of the target analytes ($1 \mu\text{g}\cdot\text{L}^{-1}$, $10 \mu\text{g}\cdot\text{L}^{-1}$, $50 \mu\text{g}\cdot\text{L}^{-1}$ and $100 \mu\text{g}\cdot\text{L}^{-1}$).

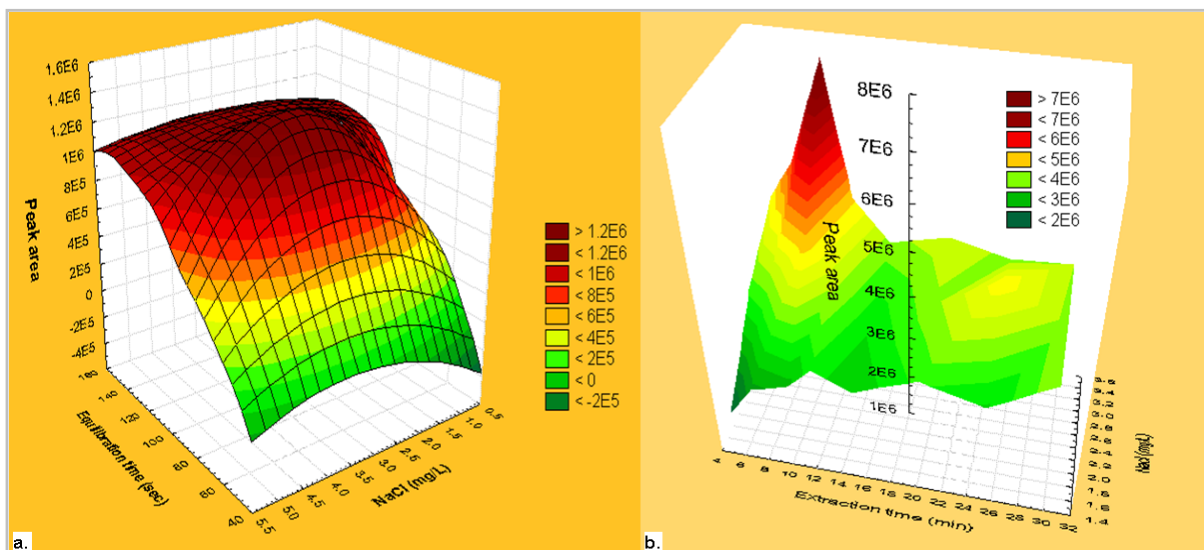


Figure 3.5. HS-SPME optimization: a. Target analytes response at different equilibration time (seconds) and NaCl ($\text{mg}\cdot\text{L}^{-1}$) amount; b. Target analytes response during different extraction time (minutes) and its exposure at different NaCl ($\text{mg}\cdot\text{L}^{-1}$) amount.

It was observed that three minutes of sample exposure at $150 \text{ }^\circ\text{C}$ is high enough for good response obtaining purposes. Also, desorption temperature could affect seriously the recovery of the target volatile chlorinated solvents from the SPME fiber, therefore the desorption temperature must

to be enough high to permit a quantitative reliable and rapid desorption of the analytes without to destroy through decomposition the thermally instable compounds.

Different extraction time were tried in order to choose the most convenience time as target analytes response as well operation time consuming, thus the chlorinated solvents from the spiked water samples was extracted during the following time moments: 1,5,10, 15, 20, 25 and 30 minutes, respectively – see figure 3.5., b. High response was observed at 5 minutes extraction time, time after that the target analytes response decreased dramatically.

After the performance of these extraction steps the PDMS SPME fiber was introduced in the heated gas chromatographic injector and permitted to desorb at the required temperature. In case of chlorinated solvent 2 minutes was proved to be enough for an acceptable response from the gas chromatograph detector. Also as desorption temperature 180 °C was considered to be optimal, after that incoherent response being obtained for a high number of target chlorinated solvents, fact that could be characterized by their thermally instability or a possible reaction of them with the fiber phase.

Many previous researches showed that addition of a salt, as NaCl, could bring forward the solubility of some analytes thus increasing the capacity of their extraction by the SPME fiber. In our working condition case it was observed that addition of 3.5 mg/L NaCl to the analysed sample is enough in order to obtain a suitable response after analysis – see figure 3.5., a., and b. In order to avoid the salt accumulation on the fiber or in injector port /liner and syringe needle, it was rinsed before all analysis.

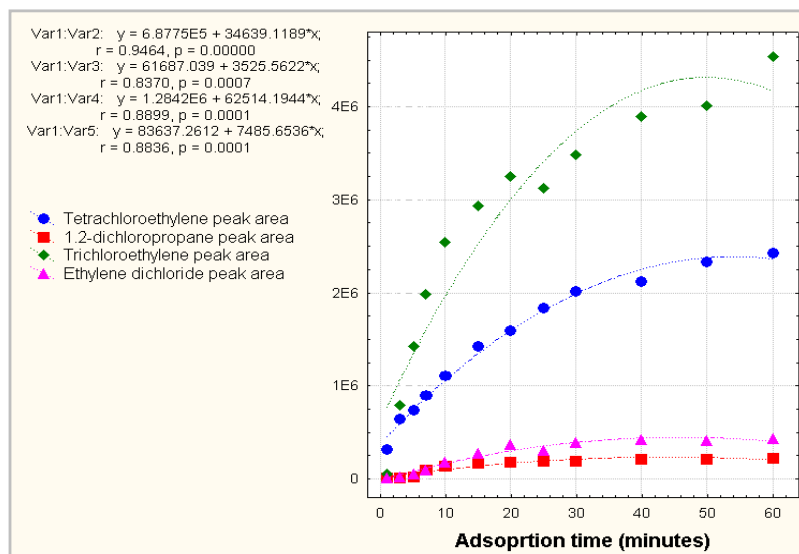


Figure 3.6. HS-SPME optimization: selection of optimal adsorption for some chlorinated solvents.

The chlorinated solvents quantities that were absorbed by the SPME fiber depends by the distribution constant between the fiber and analytes, the thickness of the fiber phase and the diffusion coefficient of the target analytes (*Jenkins et al, 1994*). Therefore the adsorbed quantities are different from one analytes to another, from fiber to fiber as well from working parameters to working parameters. So the fiber adsorption time must be determined over and over when even one of this parameter is changed or when new analytes are target of our analysis see figure 3.6.

3.3.1.3. GC-ECD analytical procedures improvement

Water samples were extracted through the best sensitive HS-SPME procedures, as presented previously. As analytical instrument a Trace GC Ultra gas chromatograph (Thermo Electron Corporation) equipped with a ^{63}Ni Electron Capture Detector (provided also by Thermo Electron Corporation) was used. Therefore in order to evaluate the best parameter set up for HS-SPME-GC-ECD analytical procedures in case of volatile chlorinated solvents, 10 mL of Milli Pure-Q water was placed in 22 mL clear headspace glass vials (provided by Supelco), and spiked with 1 μL from the standard solution mixture of chlorinated solvent in order to obtain 10 $\mu\text{g}\cdot\text{L}^{-1}$ amount of the 16th solvents. After that the vials were immediately sealed with caps equipped with PTFE-silicon septum, provided by Supelco. In the next, the sample was subjected to the most able HS-SPME working parameter (presented before). Towards to increase the method sensibility and selectivity the GC-ECD working parameter were improved. Significantly satisfying results in cases of the 16th target analytes separation was obtained using a TR-V1 Trace GC capillary column with cyanopropylphenyl polysiloxane phase type and with 0.53 mm I.D. x 3.0 μm film thickness x 30 m column length (Thermo Electron Corporation). The chromatograph oven temperature was set at 45 $^{\circ}\text{C}$ and held for 3 minutes after that was raised to 130 $^{\circ}\text{C}$ (kept for 1 minutes) at 9 $^{\circ}\text{C}\cdot\text{min}^{-1}$, than to 240 $^{\circ}\text{C}$ at rate of 18 $^{\circ}\text{C}\cdot\text{min}^{-1}$, and hold at 240 $^{\circ}\text{C}$ for another three minutes. As carrier gas high purity nitrogen was used with 7 $\text{mL}\cdot\text{min}^{-1}$ flow rate. Both the detector and injector temperature was set at 180 $^{\circ}\text{C}$. Results as regards method performance are presented in table 3.4.

Table 3.4. GC-ECD-HS-SPME method performance.

Chlorinated solvents	Linearity range ($\mu\text{g/L}$)	Linear equation (a.)	Correlation coefficient - r^2 - (b.)	Linear equation for 0.95 C.I. (c.)	Correlation coefficient for 0.95 C.I. - r^2 - (c.)
Tetrachloroethylene	1-100	$y=26509x+1184$	0.996	$y=1.1284e5+26509.4524*x$	0.9960
1.1.2.2-tetrachloroethane	1-100	$y=1284x+8427$	0.982	$y=8427.5333+1284.0201*x$	0.9914
1.1.2.-trichloroethane	1-100	$y=1842x+14605$	0.990	$y=14604.8352+1842.6375*x$	0.9950
Carbon tetrachloride	1-100	$y=6725x+33134$	0.991	$y=33134.4609+6726.2493*x$	0.9955
Chloroform	1-100	$y=58825x-5932$	0.997	$y=-5932.2407+58825.3249*x$	0.9978
Methylene chloride	1-100	$y=19054x-66327$	0.992	$y=-66327.2158+19054.0445*x$	0.9929
Trichloroethylene	1-100	$y=14909x+42539$	0.998	$y=4.2539e5+1.4909e5*x$	0.9983
1.1.1-trichloroethane	1-100	$y=12825x-5246$	0.998	$y=-5246.6352+12825.3744*x$	0.9981
1.2.3-trichloropropane	1-50	$y=158.4x+684.6$	0.978	$y=684.6727+158.4043*x$	0.9782
Ethylene dichloride	1-100	$y=23891x+21584$	0.998	$y=21583.8777+23890.972*x$	0.9986
1.2-dichloropropane	1-50	$y=885.5x+3636$	0.990	$y=3635.9742+885.5846*x$	0.9908
1.2-dichloroethylene	1-100	$y=42772x-5416$	0.997	$y=-5416.8303+42771.5582*x$	0.9972
1.1-dichloroethane	1-100	$y=14007x-54602$	0.992	$y=-54603.3833+14006.9953*x$	0.9964

(a.) – calculated based on peak area given by ECD response after GC analysis of the HS-SPME extract.

(b.) – established from the linear regression analysis of ten (n) standards, using Microsoft Excel 2007 software.

(c.) – established based on peak area given by ECD response after GC analysis of the HS-SPME extract of ten (n) standards, using Statistica StatSoft 8.0 software.

3.4. Volatile disinfection byproducts

3.4.1. Development of alternative photometric method for mathematical prediction of trihalomethane strength in treated water

Monitoring of disinfection byproducts in finished water by Water Treatment Plants is often awkward to do mainly due to increased price of the required equipments such as gas chromatograph, especially in case of developing countries. Considering these, a more easily applicable and not so expensive methods was tried to be developed in order to help the workers from water treatment plants to estimate the levels of disinfection byproducts that are formed when a specific quantities of disinfectant agent is added to raw water. Therefore a mathematical formula based on multiple colorimetric methods was tried to be extended in order to could estimate the possible amount of formed disinfection byproducts after treatment processes. These formulas were expressed based on kinetically experiments of disinfection byproducts formation.

These formulas was estimates based on the data obtained after sampled water (from Gilau Water Treatment and Cluj-Napoca distribution system) analysis.

3.4.2. Experimental method description

500 ml of filtrated water collected after one of the sand filters from the WTP Gilau, was filled into a Schott bottle and the pH was adjusted to the desired value by addition of NaOH or H₂SO₄ (0.5 M and respectively, 0.1 M). For experiments under baseline conditions, the water was buffered with 12.5 ml of a Na₂B₄O₇ solution (0.5 M) to pH 7. A diluted chlorine solution was prepared and its concentration was determinate by the ABTS method and checked also with the DPD method. The respective chlorine dose was added to the filtrated water and well stirred for 40 seconds (*Ristoiu et al, 2009*). For each desired reaction time, two 8 ml water samples were taken with a dispenser and total chlorine, free chlorine and monochloramine concentration were determined. After chlorine addition, the headspace vials were filled with 10 ml of the chlorinated water, closed immediately with Teflon lined screw caps and put into the water bath. At each desired reaction time, one vial was removed and a thiosulfate solution was injected through the septum in order to quench chlorine and stop the trihalomethane formation. The vials were then stored at 4 °C and analyzed. In order to determine seasonal variations, experiments were conducted with raw filtrated water samples from March 2006 to February 2010. To determine the effect of chlorine dose on byproducts formation, two different initial chlorine doses were applied to each water samples. At the end of each of the predetermined time interval, chlorination byproducts as well total chlorine, free chlorine and monochloramine concentrations were measured by chromatographic (as described before) and spectrophotometric method (Hach Lange DR 2 800), respectively (*Kovacs et al, 2009-(c)*).

Chlorine ion concentration was measured through colorimetric method according to standard method 8 021 DPD method (powder pillow) for free chlorine determination and standard method 8 167 DPD method (powder pillows) for total chlorine determination using a Hach Lange DR 2 800 analyzer. A 25-ml cell was filled with samples and added DPDs free chlorine reagent (powder pillow). After mixing, chlorine ion concentration was read at 530 nm wavelength. Also the chlorine ion concentration was determined by the ABTS method (*Pinkernell et al, 2000*) at a

wavelength of 405 nm and ϵ has a value of $28\,500\text{ M}^{-1}\text{ cm}^{-1}$ using the same Hach Lange DR 2 800 spectrophotometer analyzer. Monochloramin, total and free chlorine were measured with these methods (Kovacs et al, 2009-(c)).

Monochloramin and HOCl react with ABTS to a green colored product, which can be measured at a wavelength of 405 nm. The concentration of free chlorine is calculated by subtracting monochloramine from total available chlorine fraction. In table 3.16., are showed the amounts ($\text{mg}\cdot\text{L}^{-1}$) obtained for total chlorine, free chlorine and NH_2Cl in laboratory kinetics experiment with both methods: ABTS and DPD. Analyzing the obtained results it was observed that low differences between these two methods. According to these small differences, in the followings ABTS method was used (owing to its simplicity in apply) in order to determine the levels of total chlorine, free chlorine and monochloramine (Kovacs et al, 2009-(c)).

3.4.2.1. Kinetics experiment conditions and their results

Chlorination experiments were conducted under two conditions: **base line condition** ($\text{pH } 7$; $21\text{ }^\circ\text{C}$ and $2.5\text{ mg}\cdot\text{L}^{-1}\text{ Cl}_2$) to gain information about the change of the organic matter in the raw water.

It was observed that in the warmer month like August, June, July, April the chlorine consumption was quicker as in the month when the temperature decreased, such as October, November, December or March. Because the kinetics experiment were done in the same condition during the months and because the consumption of $\text{KMnO}_4\text{ mg}\cdot\text{L}^{-1}$ – CCO Mn [$\text{mg KMnO}_4\cdot\text{L}^{-1}$] values are in the range $3.572 - 6.891\text{ mg KMnO}_4\cdot\text{L}^{-1}$ in winter season and $7.015 - 11.268\text{ mg KMnO}_4\cdot\text{L}^{-1}$ in summer season, we could concluded that the NOM presence in the water present a highest variability during the months because of the changes of the water temperature and light of the sun.

The second condition was: **seasonally variable condition** in order to simulate the actual process at the treatment plant – see figure 3.36. Experiments under seasonally variable conditions were carried out with the pH and temperature as measured in the pretreated water on the sampling day and the initial chlorine dose according to a free chlorine concentration after 12 minutes was the same as in the water treatment plant on the sampling day (Kovacs et al, 2009-(c)).

During the kinetics experiment in every month of the studied period (2006-2010) were observed that while the THM formation increases, chlorine concentration decreases with increasing time due to the chlorine reaction with organic precursors to form trihalomethanes – see figure 3.7. and 3.8.

For a given initial chlorine dose, the formation of THMs and consumption of chlorine were both completed at the same reaction time, however, the time period required for the completion of trihalomethanes formation varied with the applied chlorine dose and season.

The obtained results shows the reaction rates of chlorine are dependent on several factors such as source water characteristics including temperature, pH, total organic carbon content, treatment agent used at the water treatment plant as well its dose, contact time (both in the treatment

plant and the distribution system) and the characteristics of the distribution system (pipe material, pipe age, etc.).

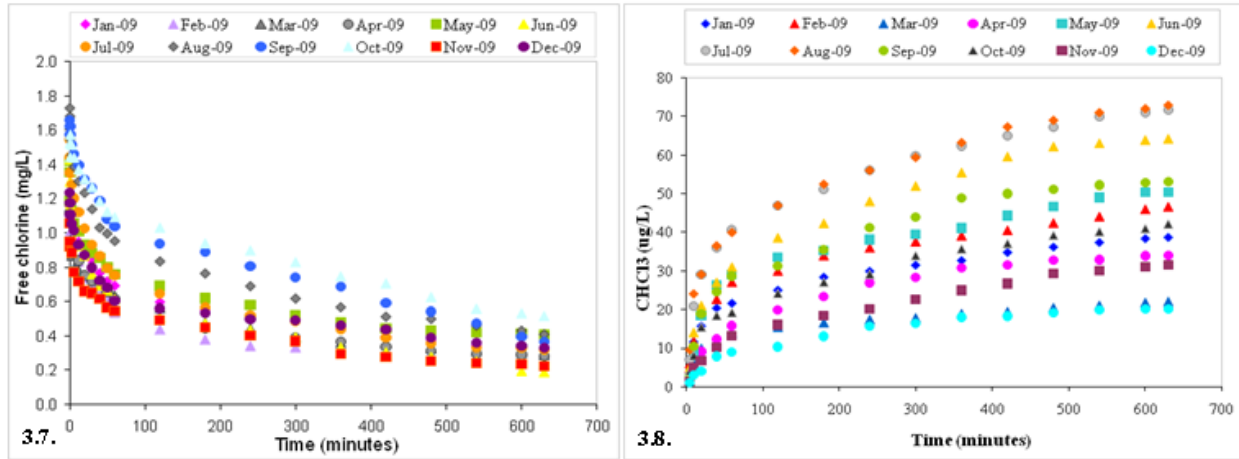


Figure 3.7. Free chlorine decay obtained after laboratory kinetic experiments under seasonally variable conditions in 2009. **Figure 3.8.** Chloroform ($\mu\text{g}\cdot\text{L}^{-1}$) after laboratory kinetic experiments under seasonally variable conditions in 2009.

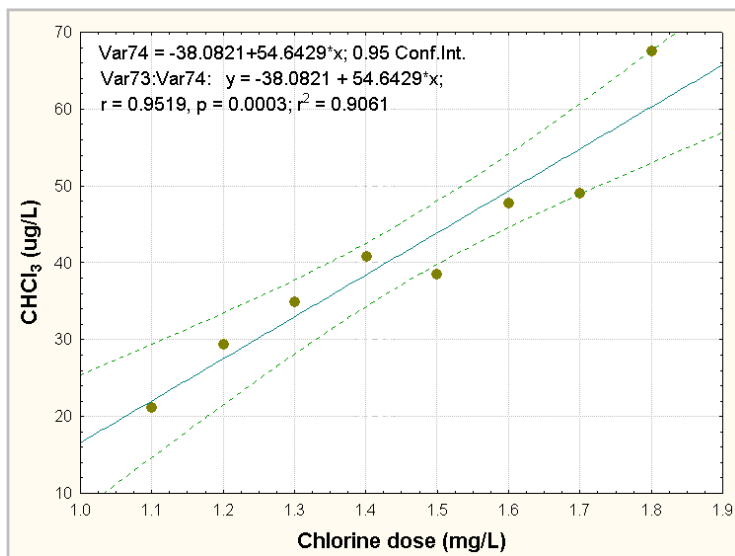
Therefore these factors influence rate on formation of disinfection byproducts was necessary to be determined in order to evaluated a good mathematical formula that to have the ability to predict the amount of formed disinfection byproducts.

As our results obtained after water sample analysis as well after laboratory simulation experiments many previous studies has showed that there are a large number of factors that affect the formation as well the amount of disinfection byproducts. Considering that the main factors that influence the amount of trihalomethanes formed in treated water are: water pH, chlorine dose, water temperature and natural organic matter content, in the following the influence rate of these factors

were studied carefully.

During the studies it was observed that one of the main important factor that affect the THMs formation in the distribution system in all water treatment plants that was subjected to these study, was the amount of chlorine that was added to water in order to treated it.

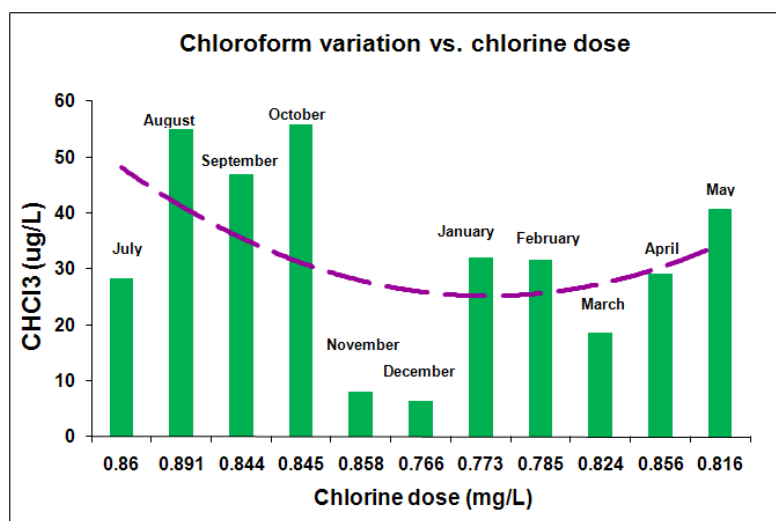
Figure 3.9. Influence of chlorine dose ($\text{mg}\cdot\text{L}^{-1}$) on chloroform ($\mu\text{g}\cdot\text{L}^{-1}$) formation.



In all the water treatment plants the amount of chlorine dose varies day-by-day according with the changes suffered by the water matrices that are subjected for treatment (temperature, pH, total organic carbon content). After several measurements, it was observed that in periods when higher chlorine dose are added to raw water the CHCl_3 concentration increased – as shown in figure 3.9. This characteristic was respected by all the other four Water Treatment Plants (*Ristoiu et al, 2008*).

In case of Gilau Water Treatment Plant, the company has set 2 different chlorine dose ranges, as function of season: for summer season the chlorine dose added to water in order to disinfect it was set between range of $0.7 - 0.9 \text{ mg}\cdot\text{L}^{-1}$ and for winter season the chlorine dose set was between the range of $0.5 - 0.7 \text{ mg}\cdot\text{L}^{-1}$.

Usually in warmer period, higher chlorine dose was necessary to be added at water in order to keep it disinfected through distribution system. Analyzing the added chlorine dose at Gilau Water Treatment Plant and the amount of chloroform that was formed in distribution system after chlorine addition, it was observed that once with increases of chlorine dose also the amount of chloroform formed in distribution system increased also – see figure 3.10.



This fact was proved also by a large numbers of laboratory kinetics experiment of CHCl_3 formation when different chlorine dose was added to decanted water, it was once again observed that with increasing of chlorine dose increased also the amount of CHCl_3 .

Figure 3.10. Chloroform amount ($\mu\text{g}\cdot\text{L}^{-1}$) formation influenced by the applied chlorine dose ($\text{mg}\cdot\text{L}^{-1}$) at Gilau Water Treatment Plant.

3.4.3. Prediction of potential trihalomethane formation through empirical formula established based on kinetic experiments

Besides the kinetics of THM formation, consumption of chlorine was also investigated. The concentration of chloroform obtained in chlorination experiments under seasonally variable conditions were linked to the chlorine that was consumed.

The resulting linear equation has showed good value for correlation coefficients, its value was between $R^2 = 0.8633$ – see figure 3.11. This could be explained by the changing in composition of organic matter and the varying ammonium concentration in the raw water: ammonia reacts rapidly with free chlorine to chloramine which shows much lower reactivity with organic substances (*Wong et al, 2007*). For the same chlorine consumption higher ammonium concentration therefore leads to lower trihalomethane yields. A slightly better correlation could be obtained by taking in account only

the free chlorine concentration. This was done by subtracting the monochloramine concentration from the chlorine consumption.

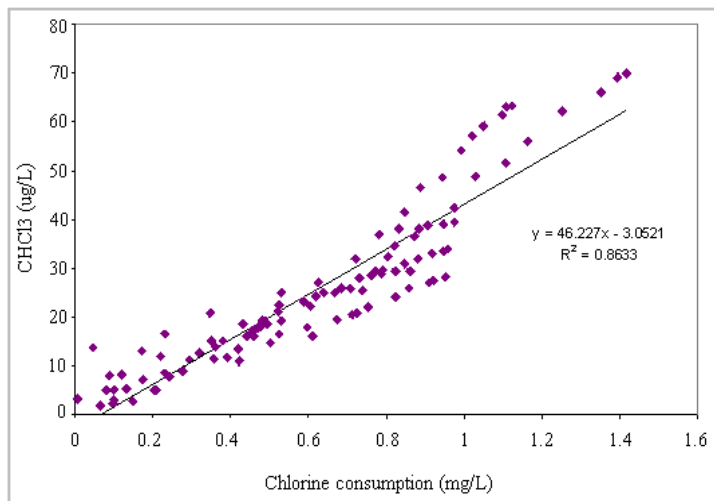
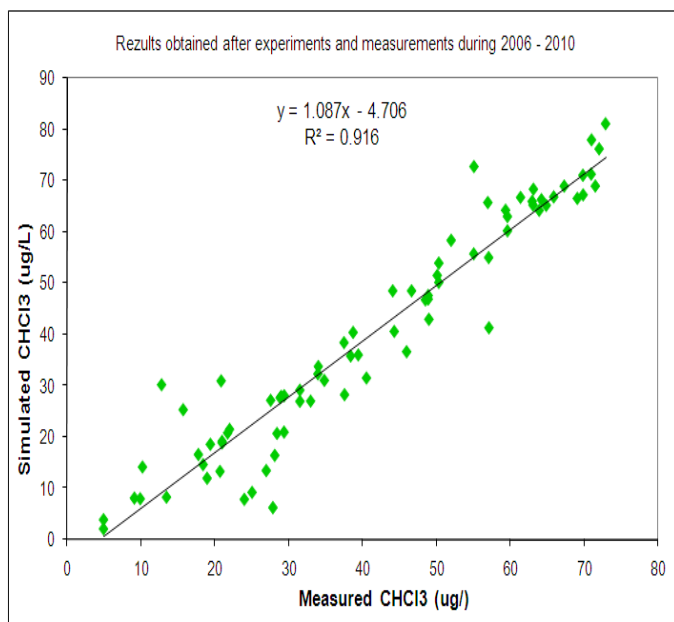


Figure 3.11. Relationship between chlorine consumption ($\text{mg}\cdot\text{L}^{-1}$) and formed chloroform amount ($\mu\text{g}\cdot\text{L}^{-1}$) for period of 2006 -2010.

Residual chlorine concentrations during THM formation are always higher for the high doses of chlorine because the residual concentrations are dependent on the applied doses (see Figure 3.39.). Furthermore, the overall yields (chloroform formed/total chlorine consumed during the entire reaction periods) as well as the average yield ($\mu\text{g}\cdot\text{L}^{-1}$ chloroform formed/ $\text{mg}\cdot\text{L}^{-1}$ chlorine consumed between two reaction times) differ through sampled months.



This can be attributed to the different unit chlorine demand of the treated water which can be explained by the differences in natural organic matter composition in the sampled month. Results of the kinetic laboratory experiments were compared with the measured value of CHCl_3 ($\mu\text{g}\cdot\text{L}^{-1}$) in the sampling points of the Cluj-Napoca distribution system for every month. The results are shown in Figure 3.12., with a good linear correlation ($R^2 = 0.916$) (Ristoiu *et al*, 2009).

Figure 3.12. Relationship between observed and predicted chloroform amount ($\mu\text{g}\cdot\text{L}^{-1}$) in Gilau Water Treatment Plant and distribution system for period of 2006 -2010.

Chlorine decrease in the bulk phase is characterized by a first-order kinetic model as follows:

$$\frac{dC}{dt} = -k \cdot t \quad (\text{equation 3.7.})$$

where C is the chlorine concentration ($\text{mg} \cdot \text{L}^{-1}$), k is the first order decay constant (minutes^{-1}) and t is the time (minutes).

Plot of the integrated form of equation 3.7., is presented in Figure 3.13. The slope of the straight line, represent the first-order decay constant. It can be seen that the chlorine decrease follows almost first order. The results obtained with water collected from Gilau Water Treatment Plant showed that the first order decay provide a good correlation ($R^2 = 0.9788$) with a k value of 0.0015 min^{-1} . However, looking more carefully at the data, it could probably be better described by a two-phase behavior (see discussion above) (Ristoiu et al, 2009).

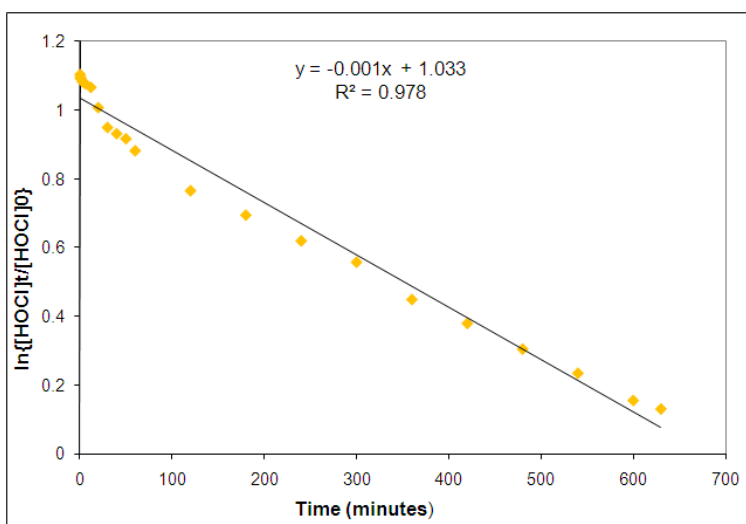


Figure 3.13. First order approximation of the chlorine decreases in sand-filtered water collected from Gilau Water Treatment Plant under seasonally variable conditions.

Chlorine consumption was very rapid during the first hours with higher resulting decay rate constants (between 0.06681 and 0.1743 min^{-1}) than in the next hours.

Trihalomethanes formation depends on temperature of water, nature and concentration of organic matter from water, applied chlorine dose at the water treatment plant, water pH, reaction time and inorganic ions like bromide and ammonia (as showed before) (Ristoiu et al, 2009).

By including these factors, USEPA developed an empirical simulation model for predicting the trihalomethanes levels that could be formed after treatment process (Golfinopoulos et al, 1998). We adapted this model to characteristics of our water matrices, therefore we considerate the following multiple power function:

$$THMs = k \cdot (\text{temp})^a \cdot (\text{Cl}_2)^b \cdot (\text{pH})^c \cdot (\text{time})^d \quad (\text{equation 3.8.})$$

where the independent parameters such as: temp (temperature) – correspond to the water temperature, Cl_2 – chlorine dose that was applied to water at water treatment plant, pH – water pH at chlorination time, and time correspond to the reaction time (h); k , a , b , c , d are empirical constants (Ristoiu et al, 2009).

This equation was used to predict the formation of THMs in the experimental part of this study. It can help to see if there is a risk for high trihalomethanes amount formation in the water treatment plant and distribution system after that a certain chlorine dose was applied for disinfection purposes. As seen in the 3.14., the simulation model shows a quite good value for correlation coefficient (R^2) using the following values for constant parameters: $k = 0.00441$, $a = 3.172$, $b = 0,538$, $c = 0,722$ and $d = 0.309$. These constant parameters were determined using a Levenberg-Marquardt statistical method (Fischer et al, 2008; Fan et al, 2009; Kanzov et al, 2005). The linear relationship between the predicted and measured chloroform concentration shows a reasonable correlation with some significant deviations for certain sampling events.

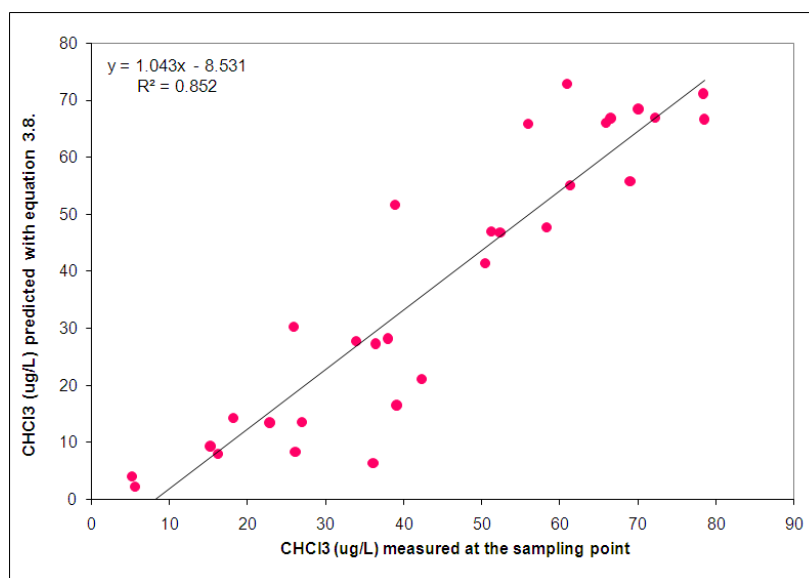


Figure 3.14. Comparison between observed and predicted values for chloroform concentration in water samples collected from Gilau Water Treatment Plant and Cluj-Napoca distribution system.

Chapter 4

Summarize of volatile organic compounds presence and behavior in surface waters from Cluj District

The results of detected volatile organic compounds showed that usually their levels were higher in urban and especially at the exit from cities than in rural sites far from big towns. Also higher amount of volatile organic compounds were measured near industrial sites (case of Dej and Gherla city). The main detected volatile organic compounds were from groups of chlorinated solvents (having as pollution source the cellulose and paper factory from Dej industrial platform that discharge its waste water in Somes River) and BTEX compounds.

Summarizing the results obtained for volatile organic compounds from all sampling points during the studied period it was observed that usually their level were higher with almost 30 % in winter period than in summer period, fact that could be explained by the fact that in summer period due to increased temperature they volatilized more easily from the surface water, as well by the fact

that in summer period the microbiological activities from surface water is more increased than on winter period.

Summarizing the amount of all volatile organic compounds detected from all sampling points (located in A.-J. sectors), their presence were in significantly higher levels in sectors E., D. and B. sectors. The centralized results including all detected volatile organic compounds from surface waters located in N-W part of Transylvania are presented in figure 4.1. Usually critical increased values were detected in the following sampling points: 8., 9., 23., 29., 30., 31., 32., 42., 47., and 48.

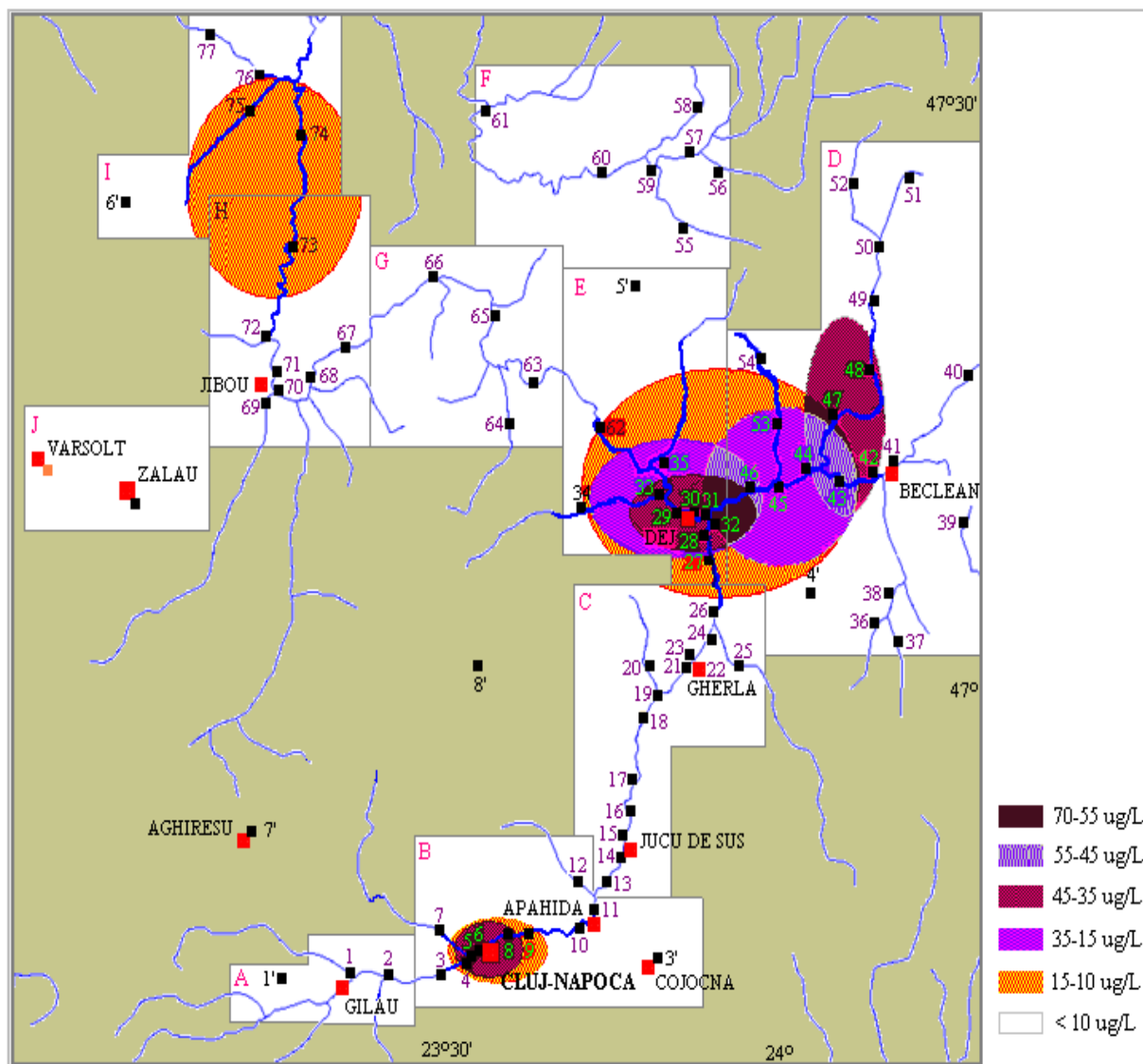


Figure 4.1. Summary of the main increased values of total volatile organic compounds from all sampling locations.

As regards volatile organic compounds presence in treated waters collected from the five water treatment plants as well from their corresponding distribution systems, trihalomethanes

were the most detected volatile byproducts, but its value never exceeded the maximum permissible value settled by the Romanian government ($150 \mu\text{g}\cdot\text{L}^{-1}$). From trihalomethanes, chloroform was the most prevalent compounds as frequency and amount while brominated volatile byproducts were less detected and in significantly lower levels, fact that could be explained by low bromine levels in water matrices. In case of all volatile byproducts it could be observed a great seasonally variability as regards their amount. This seasonal dependence was observed also in case of a large number of volatile compounds detected in surface waters, whereas in summer period their levels decrease owing to volatilization process induced by increased ambient temperature and also due to increased biochemical processes that take place in this period (increased microbiological activities) comparing with their amount detected in winter seasons.

In case of separation layer and combiner layer simulation experiments from laboratory it was observed that once that the volatile organic compounds were added through the port injection located at same level with water (combined layer experiment) it was observed that some pollutants are slightly adsorbed by soil, they remaining at the surface from there they could easily volatilized once that are transported by water flow. On the other hand heaviest chemicals that are not so volatile, they slowly tend to adsorb onto soil almost completely where they could remain and participate to different biochemical reaction or could be transported slowly by infiltrated water in soil porosity.

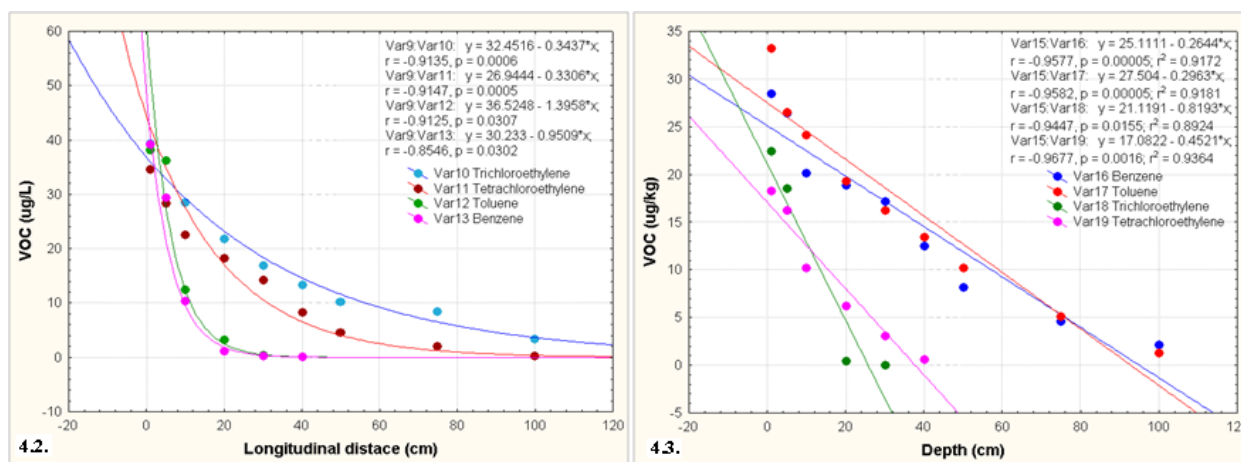


Figure 4.2. Longitudinal distribution profile of selected volatile organic compounds obtained after laboratory simulation experiments. **Figure 4.27.** Selected volatile organic compounds adsorption (depth profile) profile obtained after laboratory simulation experiments.

As regards volatile organic compounds behavior in water column usually chlorinated solvents present easiness in their dissolving capacity in water and tend to diffuse over a longitudinal profile (see figure 4.2) while in case of some hydrocarbons as benzene or toluene, this pattern is lowered, therefore they tend to remain more time in the same place where they enter, showing a low diffusion capacity through the water column (see figure 4.2).

When soil and water layer was jointed together, in case of volatile chlorinated solvents almost a half from the amount added to water is spread through water matrices, therefore usually just

50 % from the initial value arrive to the soil (this could be explain also by their low molecule density). In case of heavier molecules as benzene and toluene, almost all their quantity arrive into the soil surface from where they are graduated sorbed – see figure 4.3.

Comparing these chemicals behavior in all tested soil type usually these pollutants are easily absorbed in clay followed by ground but in sandy soil they present a lower sorption capacity. Therefore in case of chlorinated solvents they are adsorbed in clay soil in 48 % and in sandy soil in 18 % while in case of hydrocarbons as benzene or toluene, they are sorbed into the clay soil in 67 % while in sandy soil in 24 %.

Chapter 5

Indentation of volatile organic compounds on inhabitants and surrounding environment

In table 5.1. are presented the mean value of detected volatile organic compounds in the collected vegetables sample from all monitored sampling sites. These results represent5 the average value of the selected pollutants in the selected plant species.

Table 5.6. Volatile organic compounds concentration in vegetables samples collected from the described studied sites.

Vegetable species	No. of samples	Mean (µg/kg)		Range (µg/kg)		Standard error	
		Total chlorinated organic solvents	Total BTEX compounds	Total chlorinated organic solvents	Total BTEX compounds	Total chlorinated organic solvents	Total BTEX compounds
Carrot	488	4.2	3.4	0.2-18.2	0.2-17.1	± 0.25	± 0.41
Potato	324	5.6	2.8	1.1-22.8	0.5-16.7	± 0.32	± 0.39
Bean	241	2.5	1.8	0.5-10.9	0.3-14.2	± 0.27	± 0.51
Wheat	56	3.2	3.5	0.3-14.2	0.8-12.5	± 0.84	± 1.05
Maize	89	2.2	3.1	0.4-11.6	0.6-14.5	± 0.71	± 0.95

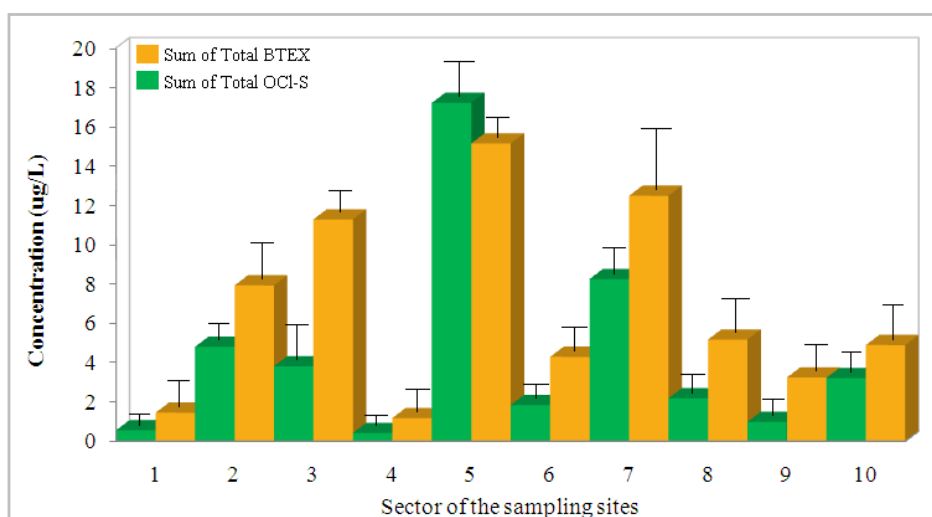


Figure 5.1. Average values of the selected pollutants in studied plant species collected from the studied sites.

Analyzing figure 5.1., that represent the average value of the sum of hydrocarbon compounds and sum of chlorinated compounds in all plant species detected it was observed that increased values of them were measured in case of sector 3., 5., and 7., sectors that if we analyze figure 5.1., we could see that its correspond for industrial sites (Dej city cases) and to exits of a big cities as Cluj-Napoca city or Gherla city cases.

The uptake capacity of pollutants through contaminated soil by the studied plant species was evaluated based on their bioconcentration factor (BCF) that represent the ration of the contaminated level in plant species to that in soil interstitial water (Zhang et al, 2005). In order to evidence the influence of plant lipids on pollutants uptake capacity of plants the normalized level of pollutants from the plant species based on the plant lipid content was determined through the following methods described by Zhang and Chiou (Zhang et al, 2005; Chiou et al, 1983; Chiou et al, 2001):

$$BCF_{lip} = \frac{BCF}{f_{lip}} \tag{equation 5.1.}$$

$$BCF = \frac{C_{pt}}{C_w} \tag{equation 5.2.}$$

$$C_w = \frac{C_s}{f_{oc} \cdot K_{oc}} \tag{equation 5.3.}$$

Where BCF represent the symbol for bioconcentration factor, f_{lip} represent the weight fraction of lipid, C_{pt} represent the concentration of volatile pollutants in soil interstitial water, f_{oc} represent the fraction of the total organic carbon and K_{oc} the normalized sorption coefficient.

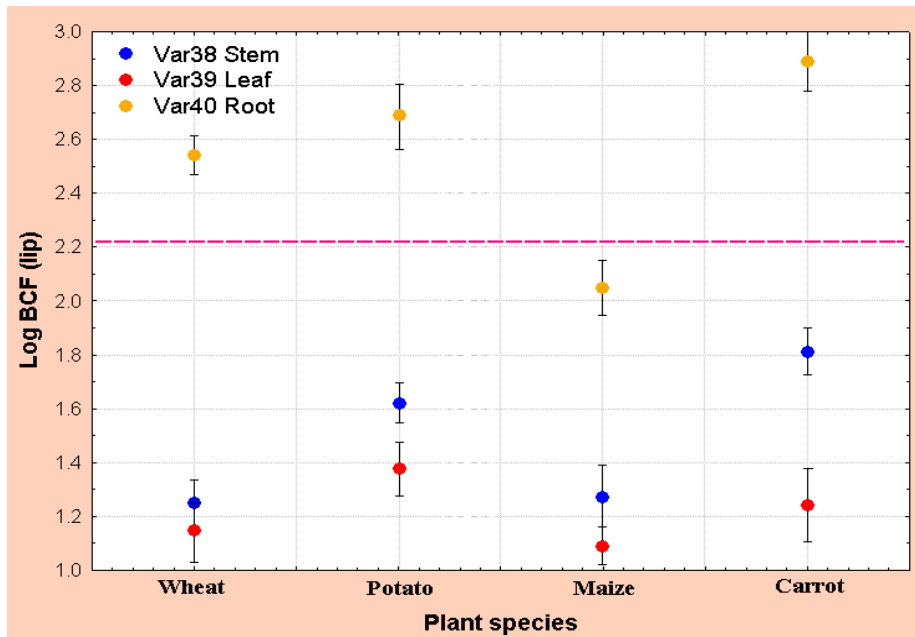


Figure 5.2. Log BCF (lip) of trichloroethylene in vegetables.

After determination of these parameters the results showed that in all plant cases the higher amount of lipid content was localized in the root part or the studied plant (except the maize cases when lower lipid content was detected in maize edible part and leaf). These showed that the main route through that the pollutants enter in the plant bodies is through its root – see figure 5.2.

5.1. Volatile organic compounds levels: reality vs. simulated situation

The correlation between the laboratory simulation experiments and the real pollutants level in plant species measured from sample collected from the specified sampling sites show good results in case of potato, carrot and wheat plant species cases, the corresponding correlation coefficient were 0.428, 0.512 and 0.622, respectively (*Kovacs et al, 2009-(a)*).

These results showed that through proposed simulation experiments is possible to estimate the contaminant level that are uptake by these species when there are grown in a contaminated sites with a specific amount of chemical pollutants.

5.2. Human intake fraction

As regards the intake fraction by human living in these regions, it was determinate that they intake more amount of these pollutants (in both pollutants class cases) consuming carrot and potato – see figure 5.3.

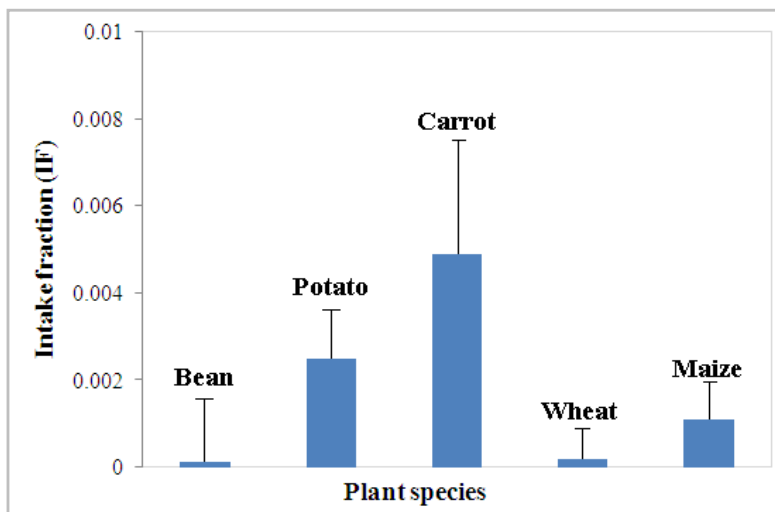


Figure 5.3. Pollutants intake fraction by humans.

5.3. Noninvasive human biomonitoring

As regards of chemical pollutants that were detected in hair samples they were increased with almost 20 % than in case of pollutants detected in milk samples. These could be explaining by a intensive external pollution through ambient air. Comparing the disinfection byproducts results measured in breast milk and human hair, higher values was determined in the hair than breast milk – see figure 5.4 (*Kovacs et al, 2009-(b)*).

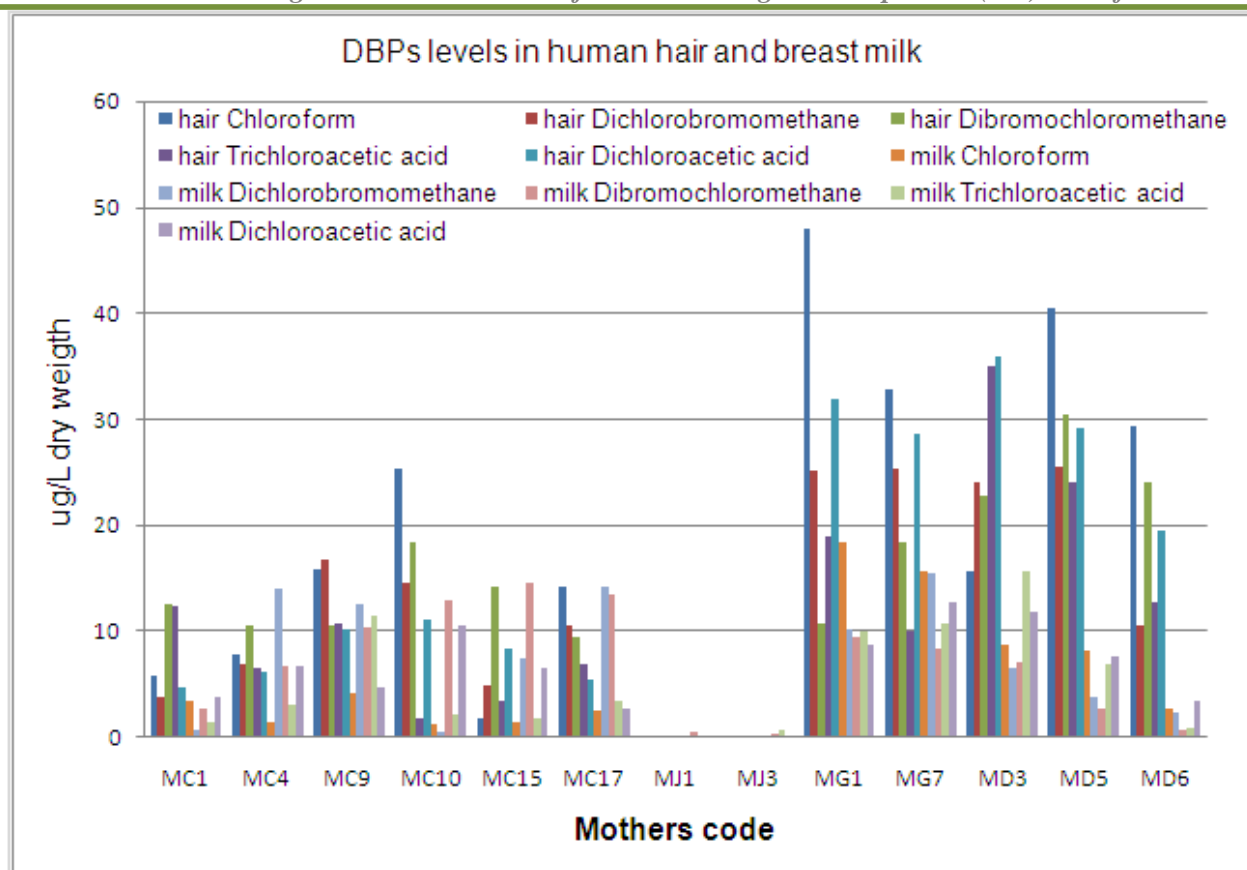


Figure 5.8. Results of disinfection byproducts accumulation in hair and breast milk samples.

Presences of these compounds in drinking water have effects on the human body, especially in the case of nursing mother. These compounds were detected in all human breast milk of the mother that lives in urban region. Absence of these compounds from mothers that live in rural area was explained by the situation that they used just fountain water that is not treated with any disinfectant agent.

Compounds with higher molecular weight masses were easily accumulated by human bodies than the easier compounds. Also it was observed that in human hair the concentration of these compounds was significantly higher that could be attributed to bodily care.

5.4. Limitation of noninvasive samples analysis and relevant research results

Main disadvantages of these techniques are the difficulty in making difference between external and internal contamination – as regards hair samples. Also in case of hair samples the results vary intensively once with color, age and gender without existing a good correlation between the same parameters.

The lack of a standardized procedure of analysis make more difficult to establish the reliability of results in order to estimate the method uncertainty and making real laboratory inter-

comparisons. Also a large number of studies showed that there are no correlation between the contaminant level from hair samples and blood samples in case of the same person.

Chapter 6

Conclusions

Surface water pollution is defined as any negatively change in water quality induced by biological, physical and chemical factors. Albeit the pollution could be caused also by natural source, in a high percent the surface water contamination is a consequence of human activities. Therefore, once with industrial development, pollution of the surrounding environment with chemical products or its byproducts becomes imminent. The biggest problem regarding water pollution is represented by the continuous movement of this as well its partition between all environmental media, phenomena that results in transport and diffusion of pollutants all over the world.

One of the main problem regarding surface water pollution with volatile organic compounds is that they affects unbenign the surrounding environment as well the living organisms causing on them teratogenic, mutagenic or carcinogenic effects. Thus, their continuous monitoring becomes a necessity. Considering the low maximum permissible limits established by selected agencies made from their monitoring a challenge for a large number of analysts.

Development of new extraction technique as well of new analysis instrumentation becomes a continuous necessity. In case of volatile organic compounds these advancement culminate in discoveries of gas chromatography and its combination with a large number of detector types as flame ionization detector, electron capture detector of mass spectrometer detector, differing as selectivity. Even in these cases the extraction of the target volatile organic compounds remains still a problem for scientist. Therefore introduction of new extraction as headspace extraction or solid phase microextraction those are solvent less methods and also easily to apply became great achievement of volatile organic compounds analysis from environmental samples. Even considering all of these developments new combinations of extraction and analysis for more and larger of environmental matrices remain still a requirement.

Summarizing all results obtained through all extraction as well instrumental analysis methods in case of volatile organic compounds determination from surface waters it were observed that:

- a. In case of BTEX compounds when headspace extraction method is performed the most reliable results are obtained when the water sample equilibration is done with help of an electric oven settled at 85 °C for a 30 minutes time period. In order to avoid the target analytes condensation on the needle and syringe walls both were maintained at a few °C lower than the equilibration temperature of the water sample. During methods performance evaluation it was observed that once that agitation was introduced in the time of equilibration process increased the response of the target analysis compounds and therefore a shorter equilibration time was high enough in order to perform well the surface water sample analysis, in this case achieving a recovery between 96 – 104 % in case of all BTEX compounds. When solid phase microextraction was used as extraction methods of BTEX compounds from surface water samples it was observed that once with using of a

100 μm thickness polydimethyl siloxane (PDMS) SPME fiber 2 minutes were enough as desorption time at 180 $^{\circ}\text{C}$ when the extraction was done at 30 $^{\circ}\text{C}$ for 20 minutes time period. Regarding BTEX compounds instrumental analysis gas chromatography joined to a flame ionization detector has proved to be the most suitable, especial when a TR-V1 Cyanopropylphenyl polysiloxane with 0.32 ID x 1.80 μm film thickness x 30 m length capillary column was used. Using this column has done the separation of orto-xylenes by meta- and para-xylenes, and the complete sample analysis was occurred in 5 minutes. Through this method good detection limits were obtained in case of these compounds: 0.3 $\mu\text{g}\cdot\text{L}^{-1}$ in case of benzene, 0.7 $\mu\text{g}\cdot\text{L}^{-1}$ in case of toluene, 0.5 $\mu\text{g}\cdot\text{L}^{-1}$ in case of ethyl benzene, 0.5 $\mu\text{g}\cdot\text{L}^{-1}$ in case of o-xylenes and 0.8 $\mu\text{g}\cdot\text{L}^{-1}$ in case of m- and p-xylenes.

- b. considering the results obtained after methods evaluation in case of n-alkanes it was concluded that through headspace extraction when water samples were equilibrated at 125 $^{\circ}\text{C}$ for 30 minutes a good extraction of them was achieved but in case of compounds that have a greater carbon number than 20 in their molecular structure they weren't detected. In case of solid phase microextraction method well extraction of n-alkanes was obtained when the water sample was exposed for a continuous stirring at 800 rpm. In this case 10 minutes was observed to be an optimum time through that the target analytes molecule could diffuse from the aqueous phase onto gaseous phase. Also no effect of salt addition was observed on the extraction performance in these target analytes cases. As regards instrumental analysis in case when a gas chromatograph equipped with flame ionization detector was used a good separation of the targets was achieved using a TR-V1 Cyanopropylphenyl polysiloxane with 0.32 ID x 1.80 μm film thickness x 60 m length capillary column.
- c. Considering the results in case of volatile chlorinated organic compounds when liquid-liquid extraction was performed suitable responses were obtained in case when hexane was used as extracting solvent and the water sample matrices pH was adjusted to 6.5 and to the sample volume was added 10 $\text{mg}\cdot\text{L}^{-1}$ NaCl and all these mixture was subjected to an 1400 rpm stirring rate in a centrifuge. In case of headspace extraction a longer exposure at heating time period as well as an increasing of the equilibration temperature has shown a good response as regards the analytes but just until to 70 $^{\circ}\text{C}$. After this temperature almost all analytes present a great instability. Concluding the results obtained after several instrumental methods analysis it was observed satisfying results when gas chromatograph apparatus equipped with an electron capture detector was used; therefore the limit of detection of the analyzed chlorinated solvents was between 0.29 and 1.2 $\mu\text{g}\cdot\text{L}^{-1}$ ($n = 10$) and the RSD was between 2.1 – 10.2 % in this case. In case when solid phase microextraction procedure was used to extract the volatile organic solvents from water sample matrices it was observed that the fiber exposure at 150 $^{\circ}\text{C}$ for three minutes and at desorption at 180 $^{\circ}\text{C}$ for two minutes has results a good recovery of these target compounds. Also adding a 3.5 $\text{mg}\cdot\text{L}^{-1}$ NaCl to the sample matrix increased the extraction capacity of the PDMS fiber. Analyzing of this extracts through GC-ECD good linearity

range was obtained between 1 – 100 $\mu\text{g}\cdot\text{L}^{-1}$ when the calibration curve correlation coefficient was between range of 0.978 and 0.998, excepting the cases of 1,2,3-trichloropropane and 1,2-dichloropropane when the linearity range showed a good pattern just between 1 – 50 $\mu\text{g}\cdot\text{L}^{-1}$ range. The recovery and the MDLs through GC-ECD analysis of volatile chlorinated solvents were between 93.8 – 110.8 (%) and 0.23 – 0.92 ($\mu\text{g}\cdot\text{L}^{-1}$), respectively. When the extracts were analyzed through GC-qMS in case of SPME procedure a higher amount (4.5 $\text{mg}\cdot\text{L}^{-1}$ NaCl) of salt addition was necessary in order to achieve a good extraction of these compounds from water sample matrices. In this case the recovery and the MDLs of volatile chlorinated solvents were between 88.1 – 118 (%) and 0.44 – 1.06 ($\mu\text{g}\cdot\text{L}^{-1}$), respectively. It could be observed that slower performances in GC-qMS case are obtained than in case of GC-ECD analysis.

- d. In case of alcohol analysis from water sample matrices when SPME extraction procedure was performed good results were obtained when the sample were equilibrated for 45 minutes at 100 °C and exposed to 2 500 rpm agitation in constant mode. Also addition of 6 $\text{mg}\cdot\text{L}^{-1}$ to the sample matrices increase the stability, resolution and sensitivity of the alcohol compounds but in the same time decrease seriously the life time of the SPME fiber. No evidence of improvement was obtained when the sample pH was adjusted.
- e. In case of volatile phenols extraction through liquid-liquid extraction procedure better results were obtained when dichlorobenzene or ethanol was used as extracting solvent, their choose depending on the analyst pleasure. In case of SPME procedure well response are obtained when PA fiber was used and the sample pH was adjusted at 4 and 2.5 $\text{mg}\cdot\text{L}^{-1}$ NaCl was added to the sample matrices. Regarding instrumental analysis most optimal performance were obtained through GC-qMS analysis.
- f. In case of volatile disinfection byproducts extraction through LLE procedure, n-hexane was considered to be the most suitable extraction agent, also introducing in extraction procedure the centrifugation step (1 200 rpm for 5 minutes) it was increased the performance of this extraction method. As regards brominated volatile byproducts, their extraction capacity increased when ultrasonication was introduced as additional extraction step. But even through these improvements, due to the extended sample handling the problems regarding the loss of these target compounds (owing to their volatility) wasn't eliminated. Using of HS extraction procedure it was increased the method sensitivity between 1.5 – 6.3 % in case of all target compounds; especially when during the water sample equilibration moment continuous agitation was introduced. As regards SPME procedure, using a 100 μm thickness polydimethyl siloxane (PDMS) fiber has proved to be suitable for our purposes. Also laboratory simulation and modeling experiments has showed that kinetic laboratory experiments could be used to predict chloroform formation in the Cluj distribution system. Furthermore, an empirical model allowed an estimation of the chloroform formation in the Gilau water treatment plant.

Analyzing results presented in this chapter it could be observed that a large number of subclasses pertaining to volatile organic compounds were detected in different levels in different surface water samples collected from a high number of sampling points covering a large geographical area.

Usually their amounts vary from one volatile organic compounds subclass to another, but significantly higher amounts were detected in case of volatile chlorinated organic compounds (usually in range of 20 – 80 $\mu\text{g}\cdot\text{L}^{-1}$) and in case of BTEX compounds (10 – 40 $\mu\text{g}\cdot\text{L}^{-1}$). As regards volatile organic compounds presence in treated waters collected from the five water treatment plants as well from their corresponding distribution systems, trihalomethanes were the most detected volatile byproducts. From trihalomethanes chloroform was the most prevalent compound as frequency and amount while brominated volatile byproducts were less detected and in significantly lower levels, fact that could be explained by low bromine levels in water matrices. In case of all volatile byproducts it could be observed a great seasonal variability as regards their amount. This seasonal dependence was observed also in case of a large number of volatile compounds detected in surface waters, whereas in summer period their levels decrease owing to volatilization process induced by increased ambient temperature and also due to increased biochemical processes that take place in this period (increased microbiological activities) comparing with their amount detected in winter seasons.

As regards their partition between different environmental layers (soil/water) it depends strongly by the volatile organic compounds physicochemical properties as well by the local; environmental conditions.

Vegetables growing on a soil material contaminated by former industrial activities may contain chlorinated or hydrocarbon pollutants in their tissues at significant concentrations. The PAHs in plants could be originated from the atmosphere and the soil, but the soil-to-root transfer was predominant in the range of concentrations tested. The leaves of the plant species tested in this study responded similarly to the soil contamination, but the PAH translocation from leaves to storage organs (i.e., potato tubers and, maize roots) was negligible. Germination of seed and growth of plants was not significantly affected by the presence of PAHs even at high concentrations in soil. Therefore, despite a significant soil-to-root transfer of PAHs, vegetables can grow in soils heavily contaminated without harmful effects on the biomass production or other signs of phytotoxicity.

Presences of these compounds in drinking water have effects on the human body, especially in the case of nursing mother. These compounds were detected in all human breast milk of the mother that lives in urban region. Absence of these compounds from mothers that live in rural area was explained by the situation that they used just fountain water that is not treated with any disinfectant agent.

Compounds with higher molecular weight masses were easily accumulated by human bodies than the easier compounds. Also it was observed that in human hair the concentration of these compounds was significantly higher that could be attributed to bodily care.

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