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ISSUES TO BE CONSIDERED IN PASSIVE WATER SAMPLING

Case of chlorophenols

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Abstract

A wide distribution of biocides in the industrial activities and households around the world has become the reason for the ecological anxiety due to the high toxicity of these chemicals even in low concentrations; therefore it is necessary to control the presence of hazardous substances in the environment. In this regard, environmental monitoring is an effective tool for establishing the baseline quality and defining environmental trends that will be used for policy and plan development and its implementation. Passive sampling is one of the most effective methods of environmental monitoring discussed in the thesis.

This thesis was dedicated to identifying possible factors influencing passive sampling in water based on a literature review that provided the basics of passive sampling and identified possible factors that need to be considered in this monitoring method. The practical work involving the use of available polymers to test their ability to adsorb chlorophenol compounds and define issues encountered in practice.

In this study, the following factors influenced the result: the need to derivatize chlorophenols before GC/MS analysis, careful pipetting of solutions into water samples, and selection of appropriate solvents for the extraction of chemicals that do not dissolve the materials. Most of the faced issues can be minimized or eliminated by following sampling standards and care operations. In future, it could be recommended to conduct more research if studied polymers are planned to use in qualitative sampling.

Keywords

Environmental monitoring, passive sampling, water sampling, chlorophenols, biocides, GS/MS

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INTRODUCTION

The use of biocides in industrial activities has steadily increased in recent decades. Pesticides, herbicides, insecticides and others products that are intended to destroy, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means are widely distributed in industrial and daily usage. Many of the biocides are the sources of ecological anxiety as they are toxic and potential carcinogens at concentrations of only a few µg/L. Therefore, it is necessary to monitor the potential discharge of hazard compounds for preventing negative consequences to the environment and all living beings. In this regard, environmental monitoring is used as a tool to establish baseline quality, uncover environmental trends, and identify any variations, support policy development and its implementation.

Passive sampling is one of the most effective techniques of environmental monitoring that is proving to be a reliable, robust and cost-effective way establishing an accurate, early picture of the risk, making it possible to respond appropriately. This technique is widely used in monitoring pollutants in air, soil and water in areas, where contamination results from domestic and industrial discharges, and the use of agrochemicals.

In this thesis, reliable literature will be reviewed for analyzing of passive sampling methods and their working principles, and finding factors that can affect the sampling process and therefore should be considered beforehand. In addition, laboratory work will be done with available polymers to find out practical complications of the process.

The aims of the research are the following:

a) To test if commonly used polymers can adsorb chlorophenols from water.

b) Collect literature information on the facts that have to be considered when using passive sampling in water.

c) Define what issues to consider in practice when using passive water sampling.

1 THEORETICAL PART

Before the description of the experiments, it is essential to provide an insight into passive sampling and describe its working principle, as well as present the general information about chlorophenols along with its impact on the environment.

1.1 Passive sampling

Passive sampling is an environmental monitoring technique involving the use of a collecting medium, such as biotic or abiotic devices to accumulate chemical pollutants in the environment over time. Passive sampling was used for the first time for the semi-quantitative determination of CO in 1927 (Gordon & Lowe, 1927). Truly quantitative passive sampling was introduced in 1973 for determination of NO_2 (Palmes & Gunnison, 1973) and SO_2 (Reiszner & West, 1973) in the air. Since then, passive sampling has been used for monitoring contaminant concentrations in the water column, soil and sediment interstitial waters, and air at sites around the world. However, passive sampling is less sensitive to accidental extreme variations of the organic pollutant concentration thus giving more adequate information for long-term monitoring of contaminants in an environmental compartment. This method has many advantages in monitoring since it vastly simplifies sampling and sample preparation, eliminates power requirements, and significantly reduces the costs of analysis. One of the advantages of using passive samplers for long periods is the potential to detect episodic events such as spills or run-off or other sporadic chemical releases to the environment that may be missed in traditional sampling methods.

Passive sampling is based on a free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potentials. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is stopped.

(Górecki & Namieśnik, 2002). The process of passive sampling does not require any energy sources other than this chemical potential difference. The process of analytes capturing and retaining from the sample in a suitable medium within the passive sampler has been described as simple diffusion and partitioning between two compartments of the receiving phase and external environment.

The principle of analytes adsorption from the studied environment into passive sampling systems shown in Figure 1. The exchange kinetics between a passive sampler and water phase can be described by a first-order, one compartment mathematical model:

$$C_s\,(t) = C_w\,\frac{k_1}{k_2}\,(1 - e^{-k_2 t})$$

where C_S (t) is the concentration of the analyte in the sampler at exposure time t, C_W is the analyte concentration in the aqueous environment, and k_1 and k_2 are the uptake and offload rate constants. Two main accumulation regimes, either kinetic or equilibrium, can be distinguished in the operation of a sampler during field deployment.

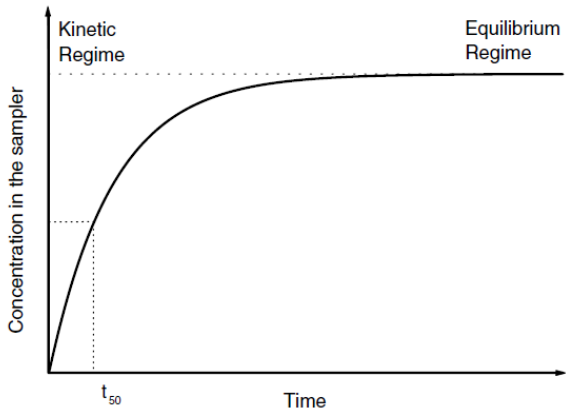

Figure 1. Two main regimes (kinetic and equilibrium) of passive samplers (Vrana et al, 2005)

Many passive samplers have been operated at the equilibrium regime when the sampler is deployed long enough so that thermodynamic equilibrium is established between the chemicals in the environmental medium and receiving phase.

In the kinetic regime, it is assumed that the rate of mass transfer to the receiving phase is linearly proportional to the difference between the chemical activity of the contaminant in the environment media and that in the receiving phase. (Vrana et al., 2005).

1.1.1 Passive sampling of water

Passive sampling is used for sampling from solid, liquid and gaseous media using various types of samplers. Passive samplers can have many different designs, depending on the sampling principle and the sampled medium. There are two categories of passive devices used for water sampling:

- Membrane-based passive samplers that are divided into types: semi-permeable membrane (**SPM**), including semi-permeable membrane devices (**SPMDs**) and supported liquid membrane (**SLM**).

    - **SPM** is a bag or a tube made of a suitable material and filled with a liquid collecting medium. Non-porous films made of hydrophobic synthetic polymers such as polyethylene or polypropylene can be used as suitable materials since they are more resistant to solvents and biodegradation, so they are generally more advantageous for SPM applications. These sampler types are generally solvent-filled that means the use of solvents as collecting media. It must be taken into account that if the solvent is allowed to reach equilibrium with the analyte dissolved in water, no more net flow of the analyte occurs between the two phases and the amount of analyte collected in the solvent may not reflect the true time-weighted average concentration of the analyte in water.

    - **SPMDs** is an important class of membrane-based passive samplers for water developed by Huckins, Tubergen & Manuweera (1990) or studying the bioavailability of hydrophobic organic chemicals to aquatic organisms. They comprise a tubular low-density polyethylene lain-flat membrane filled with about 1 g of high molecular

weight lipid. SPMDs sampling is based on lipid–water partitioning. SPMDs have many advantages, including ease of deployment, standardized character, the possibility of using long sampling times without approaching equilibrium, and accurate representation of the freely dissolved fraction of the analyte in water. (Górecki & Namieśnik, 2002).

- **SLM** devices are based on porous polytetrafluoroethylene membranes impregnated with an organic solvent and separating the sample from a stripping solution. These devices do not relate to true passive samplers because the sample and the stripping solution are most often forced through channels in a special device.

- Diffusion-based passive samplers typically consist of solid sorbents as a collection medium that is directly exposed to water. Unlike the membrane samplers, these are less widespread applications in the water analysis.

  - Solid-phase microextraction (**SPME**) can be used as a diffusion-based passive sampling method used in gas, liquid and solid medium sampling. SPME method is based on the partition equilibrium of analytes between the sample matrix and the extraction phase. This extraction tool consists of a length of fused silica fiber coated with various stationary phases (for example, polyacrylate, polydimethylsiloxane or carbon). The fiber is attached to a stainless steel plunger in a protective holder. The fiber is exposed to the water sample of the headspace for a specified time, then retracted into the needle and inserted into a GC injection port. (Shoemaker et al., 1999). Then the analytes are thermally transferred onto the chromatographic column for separation and measurement. Afterwards, the SPME fiber is retracted into the needle and removed from the injection port for subsequent sample analysis. SPME is a unique technique that requires no solvents or complicated extraction apparatus. Because of the relatively short time required to reach equilibrium,

SPME is particularly suited for passive grab sampling. (Górecki & Namieśnik, 2002).

1.1.2 Passive sampling of groundwater

Passive groundwater sampling is defined as the collection of a water sample from a well without the use of purging by a pump or retrieval by a bailer (Interstate Technology and Regulatory Council, 2004). Over the past 51 years, knowledge of groundwater flow and transport processes has increased along with the development of innovative tools, techniques, and methods. The groundwater sampling has changed from the simple bailing and standard purging methods to passive sampling. (Imbrigiotta & Harte, 2020). The purpose of the groundwater sampling is to retrieve a water sample that represents the characteristics of water below the ground surface.

The idea behind the passive sampling is that a passive sampler is lowered into the screened or open interval to sample the water flowing through it owing to natural groundwater gradients instead of purging a well and drawing water into a well in purging method. In passive sampling, chemical compounds are collected in the sampler by the process of diffusion. Thus, passive samplers allow sampling pollutants in monitoring wells without creating active transport of groundwater and without any external energy sources. The identification and quantification of the pollutants are done by the chemical analysis after retrieval of the sampler.

1.2 Chlorophenols as studied chemicals

Chlorophenols (CPs) are a group of chemicals in which chlorines (between one and five) have been added to phenol. Phenol is an aromatic compound derived from benzene, the simplest aromatic hydrocarbon, by adding a hydroxy group to carbon to replace hydrogen. (Toxicological profile for chlorophenols, 1999). Nineteen congeners are possible, ranging from monochlorophenols to the fully chlorinated pentachlorophenol (PCB) including 5 basic types of chlorophenols: mono[one]chlorophenols, di[two]chlorophenols, tri[three]chlorophenols, tetra[four]chlorophenols, and penta[five]chlorophenols. Most chlorophenols are

solids at room temperature, except 2-chlorophenol, which is a liquid. The chlorophenols have a strong medicinal taste and odour, even small amounts (at parts per billion to parts per million concentrations) can be tasted in water and fish. (Agency for Toxic Substances and Disease Registry, 1999).

The chlorinated phenols are manufactured by chlorination of phenol, or for the higher chlorinated phenols, the chlorination of lower chlorinated phenols at high temperatures. The manufacture of the tetrachlorinated phenols requires a catalyst (e.g., iodine, ferric chloride). 2,4,5-TCP, 2,3,4,5-TeCP, and 2,3,5,6- TeCP have also been produced by the alkaline hydrolysis of hexachlorobenzene Both processes of the chlorophenol production result in the formation of impurities. The impurities include polychlorinated dibenzo-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated phenoxy phenols, polychlorinated diphenyl ethers, polychlorinated benzenes, and polychlorinated biphenyls. As the higher chlorinated phenols are produced at higher temperatures, the contamination of the higher chlorinated phenols is greater than that of the lower chlorinated phenols. (Agency for Toxic Substances and Disease Registry, 1999).

All the chlorophenols have been used as biocides. Generally, the monochlorophenols have been used as antiseptics, such as 4-CP that have been used as a disinfectant in households and hospital uses. The principal use of the monochlorophenols has been as intermediates for the production of higher chlorinated phenols. 2,4-DCP has been used for mothproofing and as a miticide, while the higher chlorophenols have been used as germicides, algaecides, and fungicides. (World Health Organization, 1989).

2,4,6-TCP and the tetrachlorophenols have also been used directly as wood preservatives and are generally used as a mixture and are applied to lumber in an aqueous solution (World Health Organization, 1989). Commercial pentachlorophenol, which is used as a wood preservative, contains about 4% tetrachlorophenols and 0.1% trichlorophenols. North America and Scandinavia are the main regions of the world where chlorophenols have been used as wood preservatives.

The use of these compounds has been banned in Sweden since 1978, and production was banned in Finland in 1984. (Kalliokoski & Kauppinen, 1990).

Chlorophenols are the major group of pollutants of environmental concern because of their toxicity and widespread uses (Häggblom & Bossert, 2004). Among 19 possible congeners of CPs, 2,4,6-trichlorophenol and pentachlorophenol are listed in the Priority Pollutant List of the US Environmental Protection Agency (CERCLA Priority List Of Hazardous Substances, 2007).

Chlorophenols are introduced into the environment as effluents waste from several industrial processes, through its use as biocides or as by-products of other industrial operations, such as pulp bleaching with chlorine, water disinfection or even waste incineration (Murialdo et al., 2004). Chlorophenols enter the atmosphere through volatilization, with mono- and dichlorophenols being the most volatile. Releasing to the environment, chlorophenols are subject to a series of physical, chemical, and biological transformations. Sorption, volatilization, degradation, and leaching are the primary processes governing their fate and transport. The pH in water, in soil and sediment, is a major factor affecting the fate and transport of CPs in these media, since the degree to which the compounds ionize increases with increasing pH.

Chlorophenol groundwater contamination will occur if sufficient quantities of the chemical are present to exceed the sorption capacity of the vadose zone saturated soils (Scow et al., 1982). Contamination is most likely in soils with low organic carbon content or high pH. Once in groundwater, sorption of chlorophenols by the solid aquifer matrix may be estimated based on log Kow and organic carbon content, provided that the organic carbon content exceeds 0.1% and the aquifer pH is not sufficiently high for significant dissociation to occur (Schellenberg et al., 1984). However, low levels of chlorophenols in water, soil, or sediment are broken down by microorganisms and are removed from the environment within a few days or weeks.

Phenol toxicity is related to unspecified toxicity related to the hydrophobicity of the individual compound and formation of free radicals. Microbiological transformation of CPs leads to the formation of other toxic compounds – trichloroanisole and tetrachloroanisole (Gunschera et al., 2004). Therefore, phenol and its compounds are grouped as priority pollutants by the United States Environmental Protection Agency.

The general population may be exposed to chlorophenols through the ingestion of chlorinated drinking water and food contaminated with the compounds and inhalation of contaminated air. Short-term exposure to large amounts of PCP can cause harmful effects on the liver, kidneys, blood, lungs, nervous system, immune system and gastrointestinal tract (Fiege et al., 2000). Additional side effects may include elevated temperature, profuse sweating, uncoordinated movements, muscle twitching and coma. Contact with PCP (particularly in the form of vapour) can irritate the skin, eyes and mouth. Long-term exposure to low levels such as those that occur in the workplace can cause damage to the liver, kidneys, blood and nervous system. Also, exposure to PCP is also associated with carcinogenic, renal and neurological effects. The Environmental Protection Agency classifies PCP in group B2, as a probable human carcinogen. Since phenol is absorbed through the skin relatively quickly, systemic poisoning can occur in addition to the local caustic burns.

Only 3,5-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol will be evaluated in the work, as these are the most likely to occur in groundwater as possible contaminants from an anthropogenic activities.

1.2.1 3,5-dichlorophenol

3,5-Dichlorophenol ($Cl_2C_6H_3OH$) is a dichlorophenol in which the two chloro substituents are located at positions 3 and 5 (Figure 2). It belongs to the class of substituted phenol compounds, which are widely used in industrial applications such as synthesis of pesticides, dyes, drugs, plastics, etc. Due to their extensive usage, they are commonly found in environmental samples as pollutants.

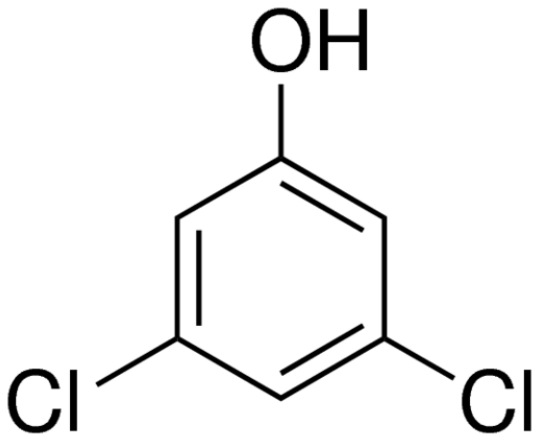

Figure 2. Molecular structure of 3,5- dichlorophenol (Sigma-Aldrich, No date a)

The compound exists as colourless crystals with a specific medical odour (International Programme on Chemical Safety, 2010). Limited amount of information available for study, mainly classification and labelling and basic physical and chemical properties.

1.2.2 2,4,6-trichlorophenol

2,4,6-trichlorophenol ($C_6H_3Cl_3O$ or $C_6H_2Cl_3OH$) is a trichlorophenol with phenolic substituents on positions 2, 4 and 6 (Figure 3). It is a synthetic, crystalline solid that is slightly soluble in water and soluble in organic solvents. 2,4,6 trichlorophenol is primarily used as a pesticide for wood, leather, and glue preservation; and as an anti-mildew treatment and antiseptic.

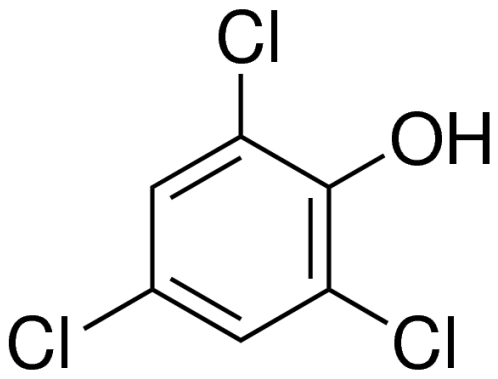

Figure 3. Molecular structure of 2,4,6,-trichlorophenol (Sigma-Aldrich, No date b)

2,4,6-trichlorophenol appears as yellow to pinkish-orange needles or orange fluffy solid and has the strong phenolic odour (Pubchem, 2020). When heated to decomposition, 2,4,6-trichlorophenol emits toxic and corrosive fumes of hydrochloric acid and other toxic gases. Exposure of humans to 2,4,6-trichrophenol via inhalation has been reported to cause respiratory effects, altered pulmonary function and pulmonary lesions. It is reasonably anticipated to be a human carcinogen.

1.2.3 Pentachlorophenol

Pentachlorophenol (C_6Cl_5OH) is a synthetic substance, made from other chemicals, and does not occur naturally in the environment; the most persistent of the chlorophenols (Agency for Toxic Substances and Disease Registry, 2001). Pentachlorophenol is a chlorophenol that substituted by 5 chloro groups (Figure 4). The purchase and use of pentachlorophenol have been restricted to certified applicators since 1984 and it is no longer available to the general public. PCP was widely used as as a wood preservative before restrictions. Nowadays, PCP is used industrially as a wood preservative for power line poles cross arms, fence posts, and the like.

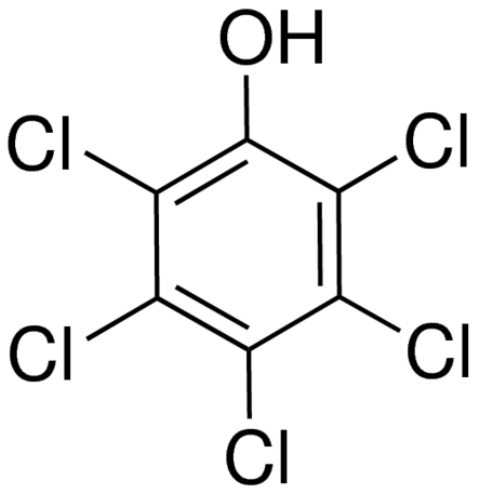

Figure 4. Molecular structure of pentachlorophenol (Sigma-Aldrich, No date c)

Pure PCP exists as colourless crystals with light specific smell at room temperature. In the case of heating, it has a sharp phenolic smell. Impure pentachlorophenol has dark colour from grey to brown and exists in fine fraction like dust and flakes. PCP exist in two forms: as pentachlorophenol or as the sodium salt of pentachlorophenol, which dissolves easily in water unlike the first form of the chemical.

PCP is released to the environment mainly from factories, chemical manufacturing plants, wood-treatment facilities, and hazardous waste sites. PCP mostly moves with water and generally stays in soil due to chemical and physical properties of the compound; an only small amount goes to the air by evaporation. In the air, surface water and soil PCP lasts from hours to days and breaks down by sunlight and microorganisms. The compound can be present in fish or other species used for food.

2 MATERIALS AND METHODS

The laboratory works were aiming to study the ability of different kinds of polymers to absorb chlorophenols from groundwater and estimate its efficiency. Water samples for analysis were collected at the beginning of October 2019 from the lake in the Mikkeli region a few days before the tests. All the measurements were conducted in the chemical laboratory at South-Eastern Finland University of Applied Sciences in Mikkeli Campus. The laboratory provided all the necessary equipment and reagents for the experiment.

2.1 Preparation of samples

Two water samples were prepared for the analysis: sample water 1 (containing chlorophenol standard) and sample water 2 (groundwater containing chlorophenols). Two replicates of both samples were prepared for accurate results. In total, there were twelve beakers: six with cholorphenol standard and six beakers with contaminated groundwater. Each beaker contains three polymer samples (Figure 5).

Figure 5. Sample preparation: Chlorophenol standard (left) and Ground water samples (right)

Sample water 1 contains tap water with a mixture of different phenols, shown in Table 1. 2,4,6-tribromphenol is an internal standard, and other chlorophenols are the analytes. Tests were done in the beakers containing 800 ml of chlorophenol water. All 12 beakers were labelled with abbreviated names, which are described in Appendix 1.

Phenol	Mass of added phenol (µg)
2,4,6-trichlorophenol	200
3,5-dichlorophenol	200
Pentachlorophenol	200
2,4,6-tribromophenol	20

Table 1. Phenols added in water sample 1

Bottles from polyethylene terephthalate, silicone tube, and polypropylene pipettes were used as samplers from commonly available polymers. The plastic bottle was cut into rectangular pieces which were fixed to the beakers with a metal wire so that the polymer samples were completely submerged in water. Small silicone tubes and polypropylene pipettes were also fixed with the wire to the beakers.

Figure 6. Preparing samples for 20 days soaking in water samples

Adsorbing materials were covered with foil and soaked in water for 20 days in the dark place to minimize environmental impact on the adsorption (Figure 6).

2.2 Chlorophenols extraction

After the soaking in the water samples, the samplers were dried in a stream of nitrogen for further analysis after that polymers were put into the beakers with 5 mL

Figure 10. Sonication of samples (left) and drying with nitrogen stream (right)

of ethyl acetate and sonicated with ultra wave for 15 minutes for each of 12 samples at room temperature. Ethyl acetate was used as extraction solvent because of its chemical function and ability to extract both polar and non-polar compounds.

Polymers were sonicated twice to extract all chemicals that presented in the materials. After the sonication, ethyl acetate solution was transferred to the test tubes and evaporated to dryness under a stream of nitrogen.

2.3 Preparation for GC/MS

After the drying, evaporation residues were taken into the test tube and dissolved in 1 ml of methanol. 2 ml of 5% K_2CO_3-solution and 200 µl fresh distilled acetic anhydride were added for acetylation process (Figure 8). Potassium carbonate was used as a weak base to form chlorophenol anion that reacted with acetic anhydride more easily than chlorophenols. Acetylation of CPs was carried to reduce the polarity and increase the volatility inside the GC column. The tubes were shaken for 1 minute. 1 ml of hexane was added and shook for 1 minute after that hexane layer was pipette out into the clean test tubes.

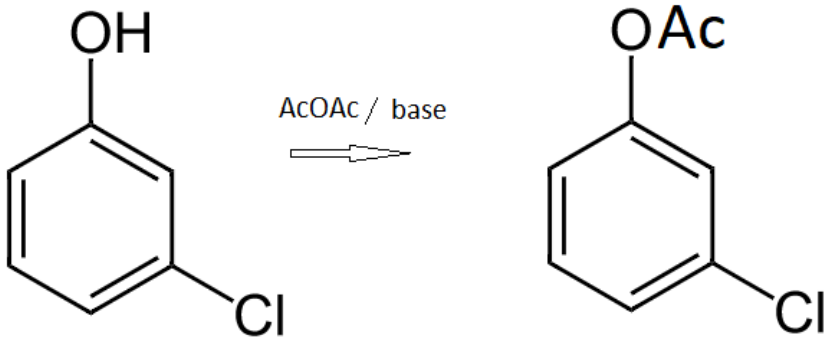

Figure 11. Acetylation of chlorophenols

The extraction procedure was repeated two times. A small amount of Na_2SO_4 was added to dry the hexane solution after that solution was evaporated under a stream of nitrogen to the volume of 1 ml and transferred into a GC sampling vial. A double extraction with ethyl acetate and hexane was performed to ensure that

all the chlorophenol was extracted. Finally, samples were analyzed with gas chromatograph-mass spectrometer.

3 GC/MS RESULTS AND ANALYSIS

The analysis was conducted with gas chromatography/ mass spectrometry (GC/MS) that is the most ubiquitous analytical method that combines the features of gas-chromatography and mass spectrometry to identify different substances within a test sample. GC/MS is recognized as the «gold standard» for identifying chemicals in simple and complex mixtures and this technique is indispensable in the fields of environmental science, forensics, health care, medical and biological research, health and safety, the flavour and fragrances industry, food safety, packaging, and many others.

The purpose of the method is to determine how many components are present in the samples, find out which components are (identify them) and find out how much of each compound is in the mixture. Gas chromatography is the best suited for combination with the ion detector of a mass spectrometer since the compounds are already in the gas phase in the column of the chromatograph.

The process of GC/MS analysis and the device is shown in Figure 9. The prepared sample solution was injected into GC injection port where it is vaporized at high temperature and transferred into GC column by the carrier gas. The sample flows through the column and the compounds comprising the mixture of interest are separated underf their relative interaction with the coating of the column (stationary phase) and the carrier gas (mobile phase). The latter part of the column passes through a heated transfer line and ends at the entrance to ion source where compounds eluting from the column are converted to ions. (Wu et al, 2012). After that, the ions enter a detector that sends information to a computer that records all of the data produced during the analysis.

The GC/MS analysis was performed with Scan and Sim methods to get mass spectra and identify unknown compounds. In the Scan method the MS device

monitors all the mass fragment and the SIM (Selected Ion Monitoring) method allows the mass spectrometer to detect specific compounds with very high sensitivity. The method also allows the collection of more points across a chromatographic peak, thus enhancing the accuracy and precision of quantitative results.

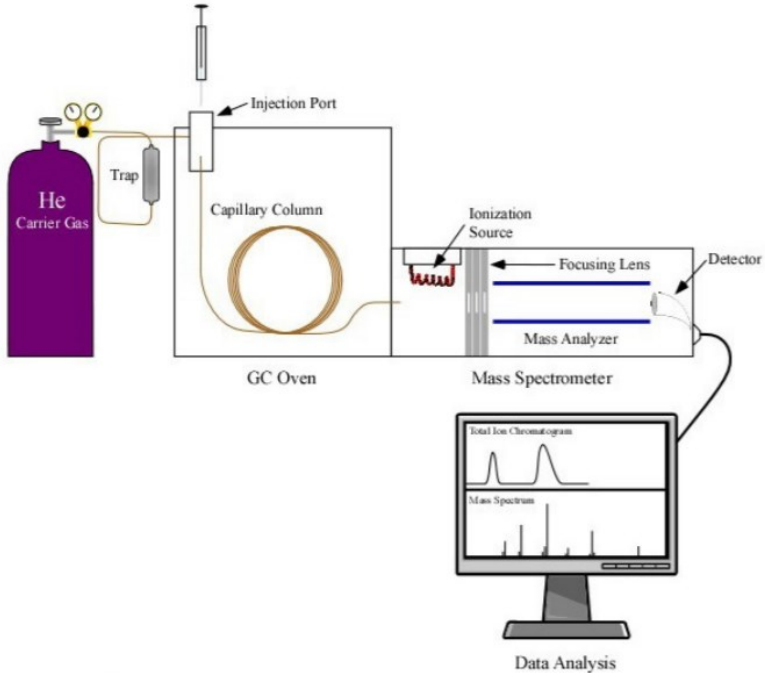

Figure 12. Schematic of a GC/MS system (Wu et al, 2012)

The results are presented in the chromatograms, a graph showing detector response as a function of elution of time. The x-axis of the gas chromatogram shows the amount of time taken for the analytes to pass through the column and reach the mass spectrometer detector. The peaks that are shown correspond to the time at which each of the components reached the detector. The y-axis, or the area of the peak, is a reflection of the amount of analyte that presents in the sample. The area is based on the number of counts taken by the mass spectrometer detector at the point of retention.

The identification of compounds in the samples is based on the retention times and mass spectra. The mass spectra of every peak are shown in the chromatograms. The mass spectra of samples are compared to the mass spectra in the mass spectrum library in the computer after what the computer defined what compound is in every peak.

There are two examples of chromatograms (SW1PET1 and SW2PP2) were shown in the results part for detailed analysis since other chromatograms looked the same.

3.1 Sample water 1 with polyethylene samplers

SW1PET1 contains tap water with chlorophenol standard with polyethylene samplers. The results of the GC/MS analysis of the sample are shown in Figure 10. The first chromatogram was done with the SCAN method, and the second one with more sensible SIM method. Chromatogram with SIM mode shows compounds in the view of several peaks in the polyethylene sample. Detailed information about these peaks (retention time, area etc.) is shown in Appendix 2.

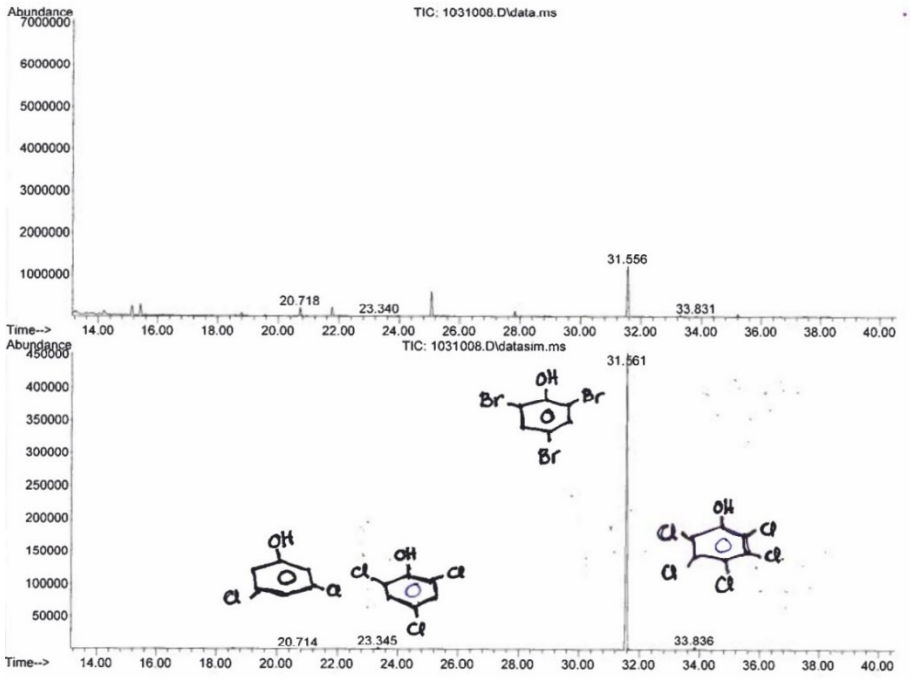

Figure 13. GC/MS chromatogram of polyethylene samplers (SW1PET1)

The computer compared the retention times and mass spectra of compounds in the sample water 1 and defined several chemicals: 3,5-dichlorophenol (retention time of 20,714 minutes), 2,4,6-trichlorohenol (retention time of 23,345 minutes), internal standard 2,4,6-tribromophenol (retention time of 31,561 minutes) and pentachlorophenol (retention time of 33,836 minutes). Chromatograms indicate

all chemicals that were added in the water sample at the beginning of the experiment.

3.2 Sample water 2 with polypropylene samplers

SW2PP2 contains groundwater from the Mikkeli region. The GC/MS results of this sample are shown in Figure 11. The lower chromatogram shows four clear peaks that were defined by a mass spectrum library as: 2,4,6-trichlorohenol (retention time of 23,345 minutes), 2,3,4,6-tetrachlorophenol (retention time of 28,893 minutes), 2,4,6-tribromophenol (retention time of 31,550 minutes) and pentachlorophenol (retention time of 33,827 minutes).

In this experiment with polypropylene samplers, all the analytes were detected except for 3,5-dichlorophenol. Moreover, GC/MS revealed the presence of 2,3,4,6-tetrachlorophenol, which was not used in the chlorophenol standard.

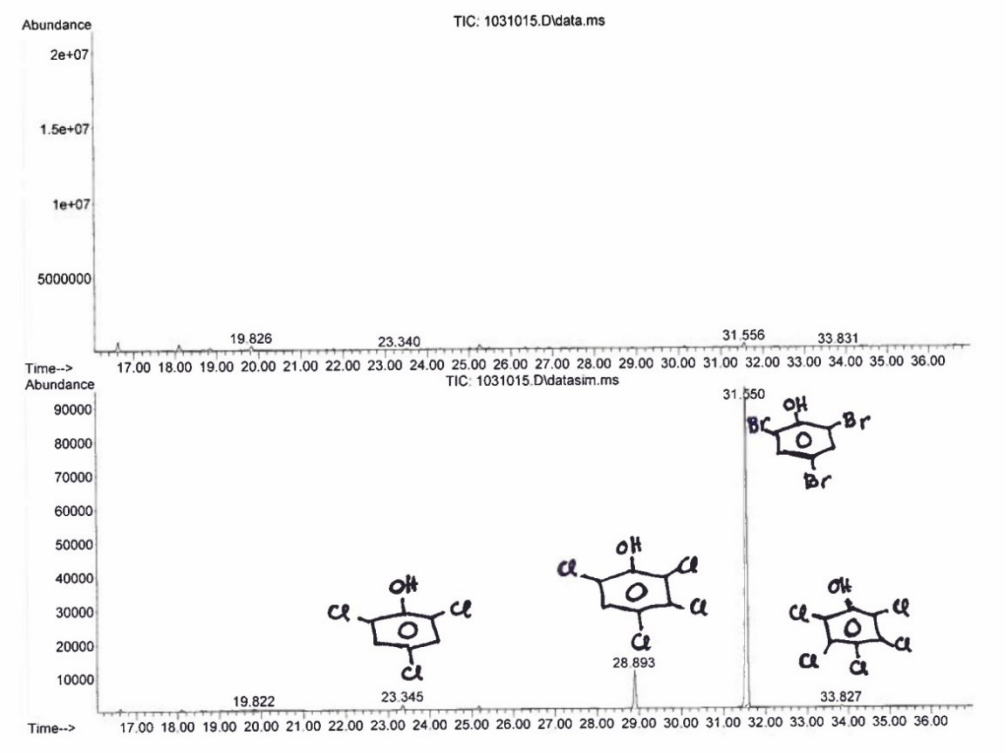

Figure 14. GC/MS chromatogram of polypropylene samplers (SW2PP2)

2,3,4,6- tetrachlorophenol ($C_6H_2Cl_4O$) belongs to the class of substituted phenol compounds, which are widely used in industrial applications such as synthesis of

pesticides, dyes, drugs, plastics, etc. (Sigma-Aldrich, No date d). Due to their extensive usage, it has become a common environmental contaminant and probable human carcinogen.

3.3 Ratio of internal standard and compounds

2,4,6-tribromophenol was used as the internal standard in this work, controlling the acetylation process. In the ideal situation, the areas of internal standard peaks should have been almost equal because the amount of the added standard was equal for each water samples, but we can see some variations in Table 2.

Water sample	Area
SW1PET1	37930522
SW1PET2	128429482
SW1PP1	59229722
SW1PP2	27901996
SW2PET1	169285
SW2PET2	51780180
SW2PP1	1125999
SW2PP2	9500771

Table 2. Peak's area of 2,4,6- tribromophenol in the samples

To determine the amount of a compound in the analysis, it is necessary to make calculations where the area of the internal standard peak is divided with the area of each compound's peak. The smaller the ratio is the more there has been the compound in the analysis.

In Table 3 we can see the ratio of internal standard and CPs in water sample 1, containing chlorophenol standard and in it replicate. Although the same amount of chlorophenols was added to this water sample, the ratio shows that the amount of 3,5-dichlorophenol is more than other chlorophenols in both samples and pentachlorophenol was the least in the samples.

Water sample	Peak #	Compound	Area	RATIO
SW1PET1	2	3,5 - dichlorophenol	6068720	6,25
	5	2,4,6- trichlorophenol	195941	193,58
	7	2,4,6-tribromophenol	**37930522**	1,00
	10	PCP	555117	68,33

Water sample	Peak #	Compound	Area	RATIO
SW1PET2	2	3,5-dichlorophenol	13094334	9,81
	6	2,4,6 –trichlorophenol	296394	433,31
	10	2,4,6 –tribromophenol	**128429482**	1,00
	15	Pentaclorophenol	579776	221,52

Table 3. Ratio of internal standard and CPs in chlorophenol standard with polyethylene samplers

Table 4 shows the ratio of internal standard and detected chlorophenols in groundwater samples. There are different amounts of chemicals in both sample and its replicate. Sample SW2PP1 contains the most pentachlorophenol and 2,3,4,6 - tetrachlorophenol, respectively. In sample SW2PP2, which contains the same water sample, the highest amounts of 2,3,4,6-tetrachlorophenol and 2,4,6-trichlorophenol were found. Detailed table of peak's area and the ratio of internal standard and compounds are presented in Appendix 3.

Water sample	Peak #	Compound	Area	RATIO
SW2PP1	4	3,5-dichlorophenol	13202	85,29
	6	2,3,4,6-tetrachlorophenol	50462	22,31
	9	2,4,6 –tribromophenol	**1125999**	1,00
	14	Pentaclorophenol	52306	21,53

Water sample	Peak #	Compound	Area	RATIO
SW2PP2	8	2,4,6 –trichlorophenol	138865	68,42
	9	2,3,4,6-tetrachlorophenol	749648	12,67
	10	2,4,6 –tribromophenol	**9500771**	1,00
	14	Pentaclorophenol	41935	226,56

Table 4. Ratio of internal standard and CPs in ground water with polypropylene samplers

3.4 Tests with silicone samplers

The results of the experiment with silicone samples as commonly available polymers capable of adsorbing chemicals from water samples were ignored since the solvent used in the CPs extraction stage from the samples dissolved the siloxanes in the sample. Siloxanes give very high background to the GC/MS analysis that disturbs the method.

4 DISCUSSION

4.1 Issues encountered in practice

During the conducting and analysis of the work, the following issues that could affect the results were identified. One of the issues encountered in practice is the need for standard compounds that certify the presence of certain chemicals in water samples. In this study, 2,3,4,6-tetrachlorophenol was found in a groundwater sample that was not added to chlorophenol standard. Thus, the existence of this compound in the groundwater is based on the scan analysis run with GC/MS and it is not certified with the standard compound. In addition, reliable identification of compounds using GC/ MS requires the use of pure standard substances.

The second issue was in the inappropriate solvent for the silicone sampler on the extraction stage. During the sonication of the samples, silicone tubes changed in size and consistency, causing siloxanes dissolving, which affected further analysis. Therefore, it is necessary to study thoroughly the extraction methods, and the effect of solvents and other chemicals on the samples.

Moreover, using an internal standard requires careful pipetting to ensure that all samples are equal to the standard. GC / MS results showed that the samples had completely different amounts of both the internal standard and the chlorophenols in the standard, even though the same amount of chemicals were added in the water samples. In this case, incorrect pipetting may have played a role in the outcome of the study.

It is also necessary to take into account that chlorophenols could not be analyzed directly and they had to be derivatized. In this work, we derivatized chlorophenols by acetylation with acetic anhydride. Acetylation has the following benefits in GC analysis: it improves analyte stability by protecting unstable groups; it can provide volatility on substances such as carbohydrates or amino acids, which have many polar groups that they are nonvolatile and normally decompose on heating; it assists in chromatographic separations which might not be possible with compounds that are not suitable for GC analysis; compounds are detectable at very low levels with an electron capture detector. (Orata, 2012).

4.2 Issues to be considered in passive sampling

Despite its relatively long history of application, passive sampling is still developing. This method has many significant advantages, including the simplicity of use, low cost, no need for expensive and specific equipment, unattended operation, and the ability to obtain accurate results. Some factors that can ambiguously influence the results:

- Passive sampling provides information about average contaminant concentrations and all possible concentrations over the sampler deployment time are included in this average value. If high and low concentrations of pollutants are required throughout the sampling period, other sampling methods in combination with passive sampling should be used. (National Water Quality Monitoring Council, 2019).

- The effect of environmental conditions on analytes uptake can complicate the sampling process. Chemicals uptake also depends on temperature and flow conditions. In this case, compared diffusion of lower temperatures indicated lower sampling rates and higher temperature contrariwise higher rate (Vermeirssen, 2012). To avoid such deviations, it is necessary to bring the temperature during sampling closer to the real environmental conditions.

- An excessive concentration of compounds in the studied environment can lead to a decrease in the ability of the sampler to adsorb or retain contaminants for further analysis (Vermeirssen, 2012).

- A sampling time can adversely influence the results. In most cases, the studied liquid medium is a mixture of various compounds. Some substances take less time to accumulate than others do. In contrast with slowly accumulating substances, those that amass relatively faster the overall toxicity will tend to be underestimated in passive sampling extract, even if both mixtures would be equally toxic to aquatic organisms. (Lohmann et al., 2007).

5 CONCLUSION

The passive samplers soaked in the water samples for 20 days had positive results in adsorbing different types of chlorophenol that could be seen in the GC/MS results. The main results show, that even a commonly available polymer that can be found in any households or purchased at local markets can effectively adsorb chemical compounds and serve as a passive sampler. In this case, the three polymers available, including polyethylene, silicone and polypropylene were used as passive water monitoring devices. Polyethylene and polypropylene have shown their effectiveness in the study, therefore they can be successfully applied in water passive sampling but more research should be done if these polymers are planned to use in quantitative sampling.

Despite all the concerns, passive sampling is an excellent alternative to more conventional sampling procedures and widely used in many fields. To prevent the aforementioned problems, all instructions and recommendations for sampling with this method must be followed.

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7 APPENDICES

Appendix 1

Sample abbreviation and description

Sample abbreviation	Description
SW1PET1	Sample water 1, polyethylene samplers
SW1PET2	Sample water 1, polyethylene samplers (replication)
SW1PP1	Sample water 1, polypropylene samplers
SW1PP2	Sample water 1, polypropylene samplers (replication)
SW1Sil1	Sample water 1, silicone samplers
SW1Sil2	Sample water 1, silicone samplers (replication)
SW2PET1	Sample water 2, polyethylene samplers
SW2PET2	Sample water 2, polyethylene samplers (replication)
SW2PP1	Sample water 2, polypropylene samplers
SW2PP2	Sample water 2, polypropylene samplers (replication)
SW2Sil1	Sample water 2, silicone samplers
SW2Sil2	Sample water 2, silicone samplers (replication)

GC/MS results: Sample water 1 (Polypropylene samplers)

IC: 1031002.D\data.ms
SW1PP1

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	20.558	BV	0.056	754818	20.485	20.672
2	20.728	VV	0.052	548178	20.672	20.819
3	23.347	BV	0.050	381195	23.292	23.418
4	31.559	VB	0.052	59229722	31.440	31.655
5	33.539	BV	0.031	294314	33.484	33.607
6	33.670	PV	0.040	451007	33.607	33.712
7	33.763	PV	0.039	388250	33.712	33.792
8	33.832	VV	0.044	299238	33.792	33.871

(SW1PP1)

Peak 2: 3,5-dichlorophenol
Peak 3: 2,4,6 –trichlorophenol
Peak 4: 2,4,6 –tribromophenol
Peak 8: Pentaclorophenol

IC: 1031003.D\data.ms
SW1PP2

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	20.558	BV	0.061	554460	20.492	20.670
2	20.732	VV	0.052	704323	20.670	20.827
3	20.863	PV	0.046	194731	20.827	20.909
4	20.950	VB	0.044	522332	20.909	21.037
5	23.349	BB	0.043	135207	23.292	23.441
6	31.560	VB	0.054	27901996	31.436	31.670
7	33.669	VV	0.047	377099	33.630	33.715
8	33.763	PV	0.049	493369	33.715	33.801
9	33.831	VV	0.039	275753	33.801	33.869

(SW1PP2)

Peak 2: 3,5-dichlorophenol
Peak 5: 2,4,6 –trichlorophenol
Peak 6: 2,4,6 –tribromophenol
Peak 9: Pentaclorophenol

GC/MS results: Sample water 1 (Polyethylene samplers)

TIC: 1031008.D\data.ms
SW1PET1

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	20.566	BV	0.051	257825	20.492	20.641
2	20.726	VV	0.047	6068720	20.641	20.801
3	20.869	VV	0.058	246963	20.801	20.904
4	20.945	VV	0.048	277922	20.904	21.003
5	23.346	BV	0.052	195941	23.285	23.425
6	25.075	BB	0.046	17559685	24.980	25.181
7	31.564	BB	0.050	37930522	31.416	31.670
8	33.656	BV	0.060	52337	33.566	33.708
9	33.733	VV	0.054	36810	33.708	33.775
10	33.836	VB	0.051	555117	33.775	33.940
11	50.682	VB	0.345	925120670	50.068	51.217

(SW1PET1)

Peak 2: 3,5-dichlorophenol
Peak 5: 2,4,6 –trichlorophenol
Peak 7: 2,4,6 –tribromophenol
Peak 10: Pentaclorophenol

TIC: 1031009.D\data.ms
SW1PET2

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	20.569	BV	0.061	626730	20.485	20.626
2	20.731	VV	0.047	13094334	20.626	20.817
3	20.867	VV	0.046	626781	20.817	20.907
4	20.947	VB	0.043	788659	20.907	21.022
5	21.781	BB	0.043	26028732	21.657	21.866
6	23.349	BV	0.042	296394	23.292	23.409
7	25.077	BB	0.047	28509979	24.987	25.189
8	27.836	BB	0.042	15899448	27.757	27.921
9	28.839	BV	0.045	26262754	28.735	28.917
10	31.571	BB	0.050	128429482	31.423	31.692
11	33.580	BV	0.000	-2768	33.544	33.599
12	33.614	PV	0.015	11165	33.599	33.626
13	33.684	VV	0.055	163934	33.626	33.702
14	33.746	VV	0.045	194807	33.702	33.788
15	33.831	VB	0.048	579776	33.788	33.925

(SW1PET2)

Peak 2: 3,5-dichlorophenol
Peak 6: 2,4,6 –trichlorophenol
Peak 10: 2,4,6 –tribromophenol
Peak 15: Pentaclorophenol

GC/MS results: Sample water 2 (Polypropylene samplers)

TIC: 1031014.D\data.ms
9 SW2PP1

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	6.535	BB	0.049	567246967	6.417	6.611
2	11.524	BB	0.050	278262997	11.383	11.607
3	20.865	VV	0.032	113092	20.828	20.928
4	23.351	BV	0.020	13202	23.307	23.419
5	28.828	BV	0.010	6832	28.787	28.858
6	28.903	PV	0.034	50462	28.858	28.921
7	28.933	VB	0.015	24990	28.921	28.950
8	31.442	BV	0.027	26284	31.401	31.475
9	31.554	PB	0.057	1125999	31.475	31.632
10	33.543	BV	0.015	10992	33.484	33.609
11	33.625	PV	0.014	26187	33.609	33.642
12	33.702	PV	0.047	258122	33.642	33.778
13	33.793	VV	0.038	37737	33.778	33.862
14	33.883	VB	0.034	52306	33.862	33.925

(SW2PP1)

Peak 4: 3,5-dichlorophenol
Peak 6: 2,3,4,6-tetrachlorophenol
Peak 9: 2,4,6 –tribromophenol
Peak 14: Pentaclorophenol

TIC: 1031015.D\data.ms
10 SW2PP2

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	6.590	BV	0.056	795163808	6.462	6.634
2	11.561	BB	0.058	509206474	11.405	11.644
3	20.552	BV	0.052	265902	20.492	20.611
4	20.628	PV	0.032	71131	20.611	20.672
5	20.687	PV	0.013	34049	20.672	20.701
6	20.719	VV	0.035	94032	20.701	20.755
7	20.862	VV	0.037	183003	20.830	20.920
8	23.345	BV	0.042	138865	23.307	23.404
9	28.898	BB	0.047	749648	28.788	28.953
10	31.556	BB	0.054	9500771	31.408	31.655
11	33.584	BV	0.021	20154	33.536	33.628
12	33.717	PV	0.044	217830	33.628	33.732
13	33.744	VV	0.051	202154	33.732	33.813
14	33.829	VV	0.036	41935	33.813	33.863
15	33.898	VB	0.051	248713	33.863	33.969

(SW2PP2)

Peak 8: 2,4,6 –trichlorophenol
Peak 9: 2,3,4,6-tetrachlorophenol
Peak 10: 2,4,6 –tribromophenol
Peak 14: Pentaclorophenol

GC/MS results: Sample water 2 (Polyethylene samplers)

TIC: 1031011.D\data.ms
7 SW2PET1

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	6.519	BB	0.040	218579079	6.417	6.581
2	20.733	PV	0.052	217935	20.672	20.755
3	20.772	VV	0.027	127036	20.755	20.800
4	20.866	VV	0.063	308497	20.826	20.950
5	23.349	BV	0.026	16844	23.299	23.418
6	28.831	BV	0.036	104226	28.787	28.890
7	28.907	PB	0.036	31568	28.890	28.950
8	31.480	BV	0.027	27476	31.423	31.517
9	31.554	VV	0.036	169285	31.517	31.590
10	33.539	BV	0.009	1112	33.491	33.553
11	33.581	PV	0.030	30165	33.553	33.611
12	33.629	VV	0.029	37861	33.611	33.669
13	33.713	VV	0.042	112683	33.669	33.749
14	33.770	VV	0.021	20896	33.749	33.786
15	33.815	PV	0.032	40418	33.786	33.850
16	33.882	PV	0.032	35036	33.850	33.897

(SW2PET1)

Peak 5: 2,4,6 –trichlorophenol
Peak 6: 2,3,4,6-tetrachlorophenol
Peak 9: 2,4,6 –tribromophenol
Peak 15: Pentaclorophenol

TIC: 1031012.D\data.ms
8 SW2PET2

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	20.568	BV	0.058	624804	20.499	20.622
2	20.633	VV	0.072	365786	20.622	20.755
3	20.879	PV	0.042	203086	20.818	20.894
4	20.951	VB	0.047	1725884	20.894	21.045
5	23.353	BV	0.052	977067	23.285	23.426
6	25.077	BB	0.047	12872603	24.987	25.150
7	28.838	BV	0.051	46539030	28.750	28.954
8	31.564	BB	0.050	51780180	31.408	31.685
9	33.663	BV	0.041	293485	33.559	33.704
10	33.733	VV	0.055	199838	33.704	33.790
11	33.839	VB	0.048	153647	33.790	33.908
12	47.604	BB	0.032	36309194	47.544	47.671
13	48.778	BB	0.033	36580669	48.723	48.843

(SW2PET2)

Peak 5: 2,4,6 –trichlorophenol
Peak 7: 2,3,4,6-tetrachlorophenol
Peak 8: 2,4,6 –tribromophenol
Peak 11: Pentaclorophenol

Appendix 3

Tables containing peaks area and ratio of internal standard and compounds contained in water samples.

Water sample	Peak #	Compound	Area	RATIO
SW1PET1	2	3,5 - dichlorophenol	6068720	6,25
	5	2,4,6- trichlorophenol	195941	193,58
	7	2,4,6-tribromophenol	**37930522**	1,00
	10	PCP	555117	68,33

Water sample	Peak #	Compound	Area	RATIO
SW1PET2	2	3,5-dichlorophenol	13094334	9,81
	6	2,4,6 –trichlorophenol	296394	433,31
	10	2,4,6 –tribromophenol	**128429482**	1,00
	15	Pentaclorophenol	579776	221,52

Water sample	Peak #	Compound	Area	RATIO
SW1PP1	2	3,5-dichlorophenol	548178	108,05
	3	2,4,6 –trichlorophenol	381195	155,38
	4	2,4,6 –tribromophenol	**59229722**	1,00
	8	PCP	299238	197,94

Water sample	Peak #	Compound	Area	RATIO
SW1PP2	2	3,5-dichlorophenol	704323	39,62
	5	2,4,6 –trichlorophenol	135207	206,37
	6	2,4,6 –tribromophenol	**27901996**	1,00
	9	PCP	275753	101,18

Water sample	Peak #	Compound	Area	RATIO
SW2PP1	4	3,5-dichlorophenol	13202	85,29
	6	2,3,4,6-tetrachlorophenol	50462	22,31
	9	2,4,6 –tribromophenol	**1125999**	1,00
	14	Pentaclorophenol	52306	21,53

Water sample	Peak #	Compound	Area	RATIO
SW2PP2	8	2,4,6 –trichlorophenol	138865	68,42
	9	2,3,4,6-tetrachlorophenol	749648	12,67
	10	2,4,6 –tribromophenol	**9500771**	1,00
	14	Pentaclorophenol	41935	226,56

Water sample	Peak #	Compound	Area	RATIO
SW2PET1	5	2,4,6 –trichlorophenol	16844	10,05
	6	2,3,4,6-tetrachlorophenol	104226	1,62
	9	2,4,6 –tribromophenol	**169285**	1,00
	15	Pentaclorophenol	40418	4,19

Water sample	Peak #	Compound	Area	RATIO
SW2PET2	5	2,4,6 –trichlorophenol	977067	53,00
	7	2,3,4,6-tetrachlorophenol	46539030	1,11
	8	2,4,6 –tribromophenol	**51780180**	1,00
	11	Pentaclorophenol	153647	337,01