PL

POLITECHNIKA KOSZALIŃSKA

WYDZIAŁ INŻYNIERII LĄDOWEJ, ŚRODOWISKA I GEODEZJI

ROZPRAWA DOKTORSKA nt:

Badanie enkapsulacji supramolekularnej, jako potencjalnego narzędzia do analiz i usuwania wybranych mikrozanieczyszczeń z fazy ciekłej.

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Praca doktorska wykonana w
Katedrze Technologii Środowiskowych
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Koszalin 2018

KOSZALIN UNIVERISITY OF TECHNOLOGY

FACULITY OF CIVIL ENGINEERING, ENVIRONMENTAL AND GEODETIC SCIENCE

PhD THESIS

Investigation of supramolecular encapsulation as potential tool for analysis and removal of selected micropollutants from liquid phases

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Doctoral dissertation conducted at
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Koszalin 2018

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1. INTRODUCTION

1.1. KEY PROBLEMS OVERVIEW

1.1.1. Target micropollutants

Hormonal systems are considered to be essential elements of all living organisms. Many biogenic or synthetic chemicals that are present in our natural environment may affect hormone receptors, modulate hormone actions as well as significantly change their transport within multi-cellular organisms **[Wittliff 1995]**. The endocrine disrupting phenomenon was brought to the attention of the scientific community during the 1980s when deformities in fish were observed across the European rivers **[Aherne 1989].** Presently, the endocrine modulation is mainly related to the potentially dangerous consequences to human and wildlife, by reason of the presence of natural and anthropogenic endocrine disrupting compounds (EDCs) in the aquatic environment **[Stone 1994]**. It is noteworthy that endocrine disrupters are not defined by their chemical nature but by their biological effect **[Rivas 1997]**. Therefore, many different classes of common pollutants including: pesticides, polycyclic aromatic hydrocarbons, plasticizers, polychlorinated biphenyls, dioxins as well as natural steroids like phytoestrogens can be collectively referred as EDCs **[Clemons 1998]**.

One of the important group of chemicals regarded as endocrine disrupters are steroids **[Gomes 2003]**. This group of compounds is extensively used in modern medical science, particularly, in treatment of infertility, certain cancers, menstrual and menopausal hormonal disorders as well as being commonly used for birth-control. The important issue is that many drugs *e.g.* birth-control pharmaceutical formulations are composed of estrogens and progestogens that show high physiological activity even at very low concentrations **[Crain 1998]**. They are excreted in urine mainly as water-soluble conjugates and then discharged into the environment *via* wastewater treatment plants. However, it has been reported that less active conjugated forms can be effectively deconjugated during, *e.g.* wastewater treatment and can generate the more potent parent compounds **[Ternes 1999]**. It is very important that both groups of steroids should be stable under typical environmental conditions and their concentration ranges from ng to µg levels per liter, depending on water type **[Shore 1993].** Therefore, the monitoring of steroid-like compounds in aquatic environments is of great importance and numerous studies have recently been conducted to develop analytical procedures suitable for

quantification of a wide range of steroids in water samples **[Isobe 2006]** [**Zarzycki[A] 2009**], **[Lisowski 2013]**.

Other important groups of compounds belonging to EDCs are PAHs derivatives and bisphenols. PAHs may be considered to be endocrine disrupters due to the fact that they structures can be present in several commonly consumed drugs like propranolol and its derivatives ***[S1]***. Bisphenols belong to a fairly homogenous group of low-molecular mass compounds, which with some exceptions (*e.g.* bisphenol S) are based on diphenylmethane skeleton **(Figure 1)**. This group of compounds, particularly bisphenol A, may mimic the action of natural steroids, mainly estrogens. It should be noted that bisphenols have been classified as "pseudo-persistent" chemicals **[Pivnenko 2015]** ***[S1]***. Bisphenols are commonly applied on an industrial scale as the chemical agents that are mixed with raw polymers resulting in soft plastic materials. As a consequence of the global plastic waste problem, various low-molecular mass plasticizers can be currently found in all water ecosystems on the Earth (for example: **[Tara Mediterranean expedition 2016]**.

Endocrine disruption is commonly considered to be a serious global issue and so far, there is no practical solution to this problem, particularly considering the common wastewater treatment technologies which are applied to the organic waste generated by large cities or industrial areas.

1.1.2. Common removal systems and technological wastewater treatment processes for micropollutant removal

Wastewater treatment can be classified as a technological process enabling the removal of pollutants and sediments from sewage. During this process dissolved chemical substances, colloids and suspensions may be also removed. Sewage treatment plants can remove a very wide range of organic substances. Importantly, while solid particles, carbonaceous substances, nutrients and pathogens are effectively eliminated from wastewater, the removal of micropollutants is usually inadequate. Therefore, it is necessary to improve technological processes for the efficient removal of potentially unsafe micropollutants from raw or purified wastewater.

Typical processes that are applied for wastewater treatment performed under large scale technological processing conditions are presented in **Figure 2**. Presently, common municipal treatment plants are not appropriately optimized for the removal of

low-molecular mass micropollutants and their metabolites through mechanical and biological processes **[Chang 2009], [Ternes[B] 2002], [Westerhoff 2005], [Shon 2006]**.

Conventional biological wastewater treatment plants use three-chamber biological reactors including denitrification, aerobic and anoxic chamber or sequencing bath reactor (SBR). During traditional biological treatment, the active sludge microorganisms may remove various contaminants, mainly by biochemical decomposition and/or the use of these chemicals as a nutrition source to build the sewage sludge biomass. SBR reactors were often proposed as drug residue removal tools. Currently, the SBR process for the removal of given micropollutants can be efficiently performed under laboratory conditions **[Łomotowski 1999]**. There is an increasing interest in the application of membrane bioreactors for micropollutant removal. This technology is considered to be the most effective in removing various contaminants flowing into treatment plants and a number of studies evaluating the effectiveness of membrane methods have recently been reported **[Tambosi 2010], [Kim 2005], [Barceló 2003]**. Typically, the membrane module is integrated with a device consisting of suitably coupled media streams of a classical bioreactor and a membrane separation centre. In water treatment technologies, membrane separation working in various high-pressure modes *e.g.*: microfiltration, ultrafiltration and processes involving electrical energy (for example electrodialysis) are commonly used **[Tambosi 2010], [Kim 2005], [Kimura 2004], [Nghiem 2002]**. Membrane reactors are characterized by low energy consumption and high effectiveness in the removal of bacteria. Moreover, it enables the required working area to be reduced by as much as 50% in comparison with biological reactors. The effectiveness of sewage treatment can be improved by using complementary methods, such as UV exposure with chlorination or ozonation. It has been documented that ozonation is an effective method for removal of drugs micropollution caused by diclofenac, carbamazepine and sulfamethoxazole as well as selected bisphenols **[Ternes 2003], [Snyder 2003], [Westerhoff 2005], [Pinkston 2004], [Maniero 2008]**. Other effective methods for the removal of toxic contaminants from sewage are photodegradation processes (photocatalytic oxidation) with the use of sunlight, UV radiation or photocatalysts (for example: metal oxides, like TiO_2, ZnO, SnO_2, and sulphates, *e.g.* ZnS, CdS). What is more, adsorption methods are commonly applied due to their simplicity and high effectiveness in drug related micropollutant removal **[Wang 2011], [Świderska-Dąbrowska 2018]**.

Most recently a number of new adsorbents involving nanocomposites and nanoparticles (mainly based on carbon materials like nanotubes, graphene or graphene oxide) have been invented **[Świderska-Dąbrowska 2018]**. They are frequently indicated as efficient media for the removal of micropollutants. The next option for micropollutants removal is the application of waste organic materials (including compounds extracted from orange bagasse, fungus biosorbent, or green algal biomasses) as effective, low-cost, and ecologically friendly sorbents. Moreover, various biomass driven technologies using macro organisms like duckweed are also regarded as efficient methods for micropollutants removal from wastewater **[Körner 1998], [Dalu 2003], [Oron 1994], [Bonomo 1997].**

1.1.3. Micropollutants encapsulation via inclusion complexes involving cyclodextrins

According to the definition provided by Degremont: "*Micropollutants are substances found in the aquatic environment at very low concentrations (ng/L to µg/L). In most cases, these are commonly known, but in order to detect them, it is necessary to use advanced analytical methods. Due to the increase in population density, industrialization and the frequency of drug use, more and more pollutants such as chemicals, pesticides, hormonal modulators or pharmaceutical wastewater go to ecosystems".* **[Degremont 2018]**

Recently, there is growing interest regarding the development of green technologies invented for the efficient removal of low-molecular mass compounds, referred as micropollutants (especially endocrine disrupters), which persist in agricultural products, water ecosystems and are generated during technological wastewater treatment processes. This interest is the consequence of an extensive research performed over the last decade and focusing on the determination of such micropollutants in environmental ecosystems and within living organisms as well as the studies considering the potential risk of long-term exposure to these molecules for both animal and human health **[Kowalkowski 2006]**, **[Zarzycki^{B} 2009], [Zarzycki^{B} 2017], [Ślączka 2017], [Piaskowski 2017]**. Selected natural and artificial endocrine disrupters are indicated as priority substances and this list is still in the process of being updated and extended ***[S1],*** **(Table 1)** and **(Table 2)**.

It should be emphasized that endocrine disruption is commonly considered to be a the serious global issue and so far, there is no practical solution to this problem, par-

ticularly if we are considering the common wastewater treatment technologies applied to the organic waste generated by large cities or industrial areas. Most recently, several studies summarized in the review papers, have strongly indicated that efficient elimination of a number of micropollutants, for example: heavy metals or organic compounds including benzene derivatives, polycyclic aromatic hydrocarbons and steroids, can be performed using host-guest complexation involving cyclodextrin based materials. This technology can be applied to sewage water technological processes, mainly through the solid/ polymeric adsorbents **[Amin 2014], [Crini 2005]**.

Cyclodextrins (CDs) belong to a broad group of low-molecular mass polysaccharides classified as macrocycles or donut-like compounds, due to their three-dimensional shape. At the beginning of the 1950s the inclusion properties of cyclodextrins were recognized and extensively investigated **[Cramer 1954]**. Cyclodextrins are water soluble and non-toxic. Due to the polar hydroxyl group locations (on the external surfaces of the donut) the internal cavity is relatively non-polar in comparison to different water non-soluble macrocycles, for example calixarenes.

Generally, the ability of macrocycles to form a host-guest (inclusion) complex with an external (guest) molecule is a function of two critical factors. The first key factor is steric and depends on the relative size/shape of the cyclodextrin cavity to the size/shape of the interacting guest molecule. If the guest molecule is not of a particular size and shape, it will not be possible for it to fit into the cyclodextrin cavity. The second key factor involves the thermodynamic interactions between components of the cyclodextrin-guest-solvent system. Successful complex formation requires the presence of a favorable net of electrostatic driving force that pulls the guest molecule into the cyclodextrin cavity and removes other guest molecules from this space, especially solvent molecules **[Lehn 1995].** The key physicochemical parameter limiting the number of analytical, medical and industrial applications is CDs solubility in water. It is well documented that α- and γ-cyclodextrin is one factor more soluble than β-cyclodextrin. Solubility of cyclodextrins is strongly affected by the presence of organic co-solvents (for example, decreasing with methanol or increasing it with several organic liquids at a given concentration range like ethanol, acetonitrile or solid additives including urea) as well as temperature **[Zarzycki 2006]**. The great interest in cyclodextrin applications, which has been observed over the last decades in analytical chemistry, medicine, pharmacy, cosmetology and food industry, particularly in comparison to other macrocyclic compounds,

is due to their several specific physicochemical properties **[Szejtli 1982], [Uekama 1998]**:

1. cyclodextrins can be produced in large amounts from natural and non-expensive materials like starch *via* simple green chemistry protocols,
2. host-guest complexes involving CDs can significantly modify the physicochemical properties of initial guest molecules *e.g.* increasing solubility and bioavailability that is the a key issue in the food and pharmaceutical industries,
3. stereoselective interaction with target substances (it should be noted that CDs are chiral molecules) can be conveniently controlled by simple factors including pH, temperature and the presence of low-molecular mass additives,
4. cyclodextrins are basically non-toxic if delivered per os in reasonable amounts and therefore, they can be consumed by the humans as food or cosmetic ingredients.

It should be highlighted that despite of long-term extensive research, the detailed mechanism of the host-guest supramolecular complex formation based on cyclodextrin guest molecules, particularly in multicomponent liquid phase environment as well as the properties of such complexes are still not exactly known **[Loftsson 1996], [Zarzycki^{A} 1996], [Zarzycki 2016], [Alsbaiee 2016], [Wang 2017], [Challa 2005], [Brewster 2007]**. Interestingly, the cyclodextrin based complexes have been recognized as temperature supersensitive objects **[Zarzycki^{A} 1998], [Zarzycki^{B} 1998]**. Temperature effects (including thermochromic properties) can be strongly disturbed by competitive interaction with low-molecular mass molecules like tetrahydrofuran (THF).

In the aquatic environment the addition of a small amount of THF may permanently block the cyclodextrin cavity for other host molecules and the CD-PP complex cannot be formed **[Zarzycki^{B} 1998]**. Competitive interaction with the cyclodextrin cavity is particularly visible for molecules containing long *n*-alkane chains. Based on the above mentioned phenomenon, a number of chromatographic protocols for the efficient multiple separation of steroid stereoisomers from complex biological materials have recently been established **[Berthod 1990], [Zarzycki 2001], [Liu 2005], [Zarzycki 2006], [Gebauer 1998], [Zarzycki ^{A} 2009], [Ohta 2017]**.

A literature search *via* the Web of Science databases indicates that there is still an increasing interest in cyclodextrin research focusing on their encapsulation properties. Despite the three major industrial application areas including: pharmaceutics, food and cosmetics, there is an extensive research concerning the removal of dissolved

EDCs chemicals as well as remaining low-molecular mass micropollutants from sewage waters, involving free cyclodextrins and a number of nanomaterials based on CDs **[Aoki 2007], [Furuta 2007], [Yamasaki 2008], [Banerjee 2009], [Bonenfant 2009], [Kim 2010], [Oishi 2010], [Shao 2010], [Chai 2012], [Badruddoza 2013], [Fan 2013], [Jurecska 2014], [Nagy 2014], [Sanchez 2014], [Wang 2014], [Han 2015], [Khaoulani 2015].** According to these research papers free cyclodextrins and polysaccharide - based materials are demonstrating outstanding removal capabilities for certain pollutants, particularly when compared to other commonly applied sorbents or commercial activated carbons **[Świderska-Dąbrowska 2018]**.

1.1.4. General protocols for micropollutants determination

Presently, there are two major trends in the data handling and quantification of multiple biocomponents from highly organic compounds loaded matrices, which are applied for both targeted and non-targeted investigations **[Zarzycki 2015]**.

The first approach is based on high-throughput analysis involving one, two or more dimensional separation or electroseparation systems (*e.g.* HPLC). Target analytes detection for such systems usually involves advanced and sensitive detectors (*e.g.* multiwavelength spectrophotometry, fluorimetry or mass spectrometry). These detectors enable the determination of UV-Vis transparent micropollutants and biomarkers that are commonly present in environmental samples like hopanoids **(Figure 3)**. Moreover, this approach allows for the efficient separation of any organic matrix and sensing of target molecules at even femtomole ranges. Additionally, the given detectors (like IR or MS) may be a source of additional data enabling chemical and spatial structure elucidation. Unfortunately, this approach is characterized by high analysis cost, complex hardware and requires multistep samples and pre-treatment protocols that are usually time consuming and may affect the analysis results.

The second approach is based on simple or even "primitive" separation systems or micro/nano-fluidic devices involving on *e.g.* bar adsorptive micro-extraction (BAμE), dried blood spot analysis (DBS), micro-planar chromatography (micro-TLC), paper-based analytical devices (μPADs) or micro-total analysis systems (μTAS) **[Zarzycki^{A} 2011], [Zarzycki^{B} 2011], [Suszyński 2015]**. It is noteworthy to say that in last 10 years the interest in these types of analysis is growing rapidly **[Piaskowski 2017]**.

Low-molecular mass endocrine disrupting compounds and related micropollutants can be efficiently analyzed by separation methods based on liquid mobile phases including: column, planar and electroseparation techniques **[Huang 2003], [Surowiec 2008], [Srivastava 2011], [Komissarchik 2014], [Andrade 2014], [Pool 2015], [Włodarczyk 2017]**. Examples of common protocols that are currently being used for selected micropollutants (drugs) determination in environmental samples are listed in **Table 1**. Similar protocols have been applied for the determination of endocrine disrupting compounds **[Migowska 2012]**.

Modern high throughput planar analytical techniques (HPTLC) are based on a wide range of polar and non-polar adsorbents. Contrary to column techniques these systems enable parallel samples separation of various micropollutants groups within one analytical run **(Figure 4)**. TLC plates can be covered by different stationary phases like monolithic layers, electrospun nanofibers or micro-fabricated in-plane anisotropic nanostructures formed as ultra-thin, conventional analytical or preparative layers **[Sherma 2003], [Bezuidenhout 2008], [Srivastava 2011], [Lisowski 2013]**. Unfortunately, commercially available layers can be strongly non-homogenous, which affect *e.g.* method robustness and repeatability **(Figure 5)**. In spite of its relatively low sensitivity, this is the main reason that column separation techniques dominate over the planar protocols invented for micropollutants determination in complex environmental samples. It is noteworthy to say that a number of researchers are seeking for new biomaterials that are non-toxic and can replace classical stationary phases based on silica, aluminium oxide or octadecylsilane, especially if such materials can separate enantiomers. They can be applied as chiral additives to mobile phases like cyclodextrins **[Zarzycki 2016]** or be composed of solid biopolymers like microcrystalline cellulose, starch or chitosan derivatives **[Lewandowska 2017]** and then used in the design of microfluidic or paper based devices.

2. MAIN AIMS OF PhD THESIS

The main goals of the literature search and experimental work presented in this PhD thesis are as follows:

1. Basic research focusing on the formation of supramolecular complexes (molecular encapsulation) between macrocyclic compounds (β-cyclodextrin and its more water-soluble derivative: 2-hydroxypropy-β-cyclodextrin) and selected host molecules, which may exist in wastewater as micropollutants and act as EDCs, including PAHs and bisphenols. Selected target host molecules, are considered as important xenobiotics that can be present in wastewater and surface water ecosystems as well as being generated during wastewater treatment processes. This part was performed to enable: (***i***) testing of given supramolecular systems for quantitative analysis of target components (particularly bisphenols) in complex organic matrices (***ii***) preliminary interaction studies for the selection of initial conditions and key factors for selective encapsulation and/or elimination of given xenobiotics from liquid phases. These studies have included experimental work involving complementary and orthogonal techniques such as temperature controlled UV-VIS spectroscopy and temperature-dependent separation, including high performance liquid chromatography (HPLC) and thermostated microplanar chromatography (micro-HPTLC).

2. Screening, quantification and classification of selected fractions of organic compounds, mainly focusing on bisphenols group that may be present in various products in daily use. Target compounds were determined using temperature-dependent inclusion chromatography involving cyclodextrin additives and an adapted solid-phase extraction SPE protocol designed to pre-purify and isolate number of low-molecular mass compounds with polarity starting from estetrol to progesterone. The materials of interest were selected due to their residues presence in surface water ecosystems and finally in raw wastewater including: rice bags, plastic bags, cloths, sanitary towels, fish baits and various plastic foils from food products. Treated sewage water released directly to the environment form a municipal treatment plant (Jamno, Koszalin) was also investigated.

3. Preliminary biological research was carried out using aquatic organisms containing chlorophyll, particularly, duckweed *(Lemna minor L)* that may work as an active biomass for the elimination of bisphenols micropollutants from water. This multivariate experiment was designed to check the potential encapsulation effect and removal efficiency of non-toxic macrocyclic oligosaccharide (β-cyclodextrin) acting as an encapsulation reagent to promote the removal of selected bisphenols from liquid phase both with and without the presence of duckweed biomass. It is hypothesized that the initial data set obtained from this preliminary experiment (and combined with supramolecular complex formation data calculated from chromatographic experiments), enable designing of further experiments focusing on the development of green chemistry technology, which may be used for the efficient removal of low-molecular mass micropollutants using classical technological wastewater treatment processes modified by biomass and macrocyclic additives.

3. EXPERIMENTAL PART

3.1. Reagents and solutions

As chemical and chromatographic standards following reagents were used:

Polycyclic aromatic hydrocarbons:

1-Acenaphthenol 99%; Aldrich-Chemie (Steinheim, Germany),

Acenaphthene; POCh Gliwice (Gliwice Polska),

Acenafthylene 99%; Aldrich-Chemie (Steinheim, Germany),

Naphtalene 99%; Aldrich-Chemie (Steinheim, Germany),

2.6-DMN 99%; Aldrich-Chemie (Steinheim, Germany),

2.3-DMN 97%; Aldrich-Chemie (Steinheim, Germany),

1.8-DMN 95%; Aldrich-Chemie (Steinheim, Germany),

1.5-DMN 98%; Aldrich-Chemie (Steinheim, Germany),

Bisphenols:

Bisphenol A; Sigma-Aldrich (St. Louis MO, USA),

Bisphenol B; 2.2-Bis(4-hydroxyphenyl)butane; ChemCruz (Dallas USA),

Bisphenol BP; Sigma-Aldrich (St. Louis MO USA),

Bisphenol Z; Sigma-Aldrich (St. Louis MO USA),

Bisphenol; Sigma-Aldrich (St. Louis MO USA),

Bisphenol AP; Sigma-Aldrich (St. Louis MO USA),

Bisphenol C; Sigma-Aldrich (St. Louis MO USA),

Bisphenol E; Sigma-Aldrich (St. Louis MO USA),

Bisphenol F; Sigma-Aldrich (St. Louis MO USA),

Bisphenol FL; Sigma-Aldrich (St. Louis MO USA),

Bisphenol S; Sigma-Aldrich (St. Louis MO USA),

Remaining chemicals:

β-Cyclodextrin; Merk (Darmstadt, Germany),

2-Hydroxypropyl-β-cyclodextrin; Sigma-Aldrich (Steinheim, Germany),

7,8-Dimethoxyflavone; Sigma-Aldrich (Steinheim, Germany),

Sodium nitrate; POCh Gliwice (Gliwice Polska),

Glucose anhydrous; Chempur (Piekary Śląskie Polska),

3.2. Organic solvents

Following organic liquids were used in the experiments conducted:
Acetonitrile 99%; LiChrosolv Merck (Darmstadt, Germany),
Ethanol 99.8% anhydrous; EUROCHEM BGD (Tarnów, Poland),
Methanol 99,8%; LiChrosolv Merck, (Darmstadt, Germany),

Binary chromatographic mobile phases were prepared using freshly distilled water.

3.3. Temperature controlled UV-Vis spectrophotometry.

All details of experiment preformed using temperature controlled UV-Vis spectrophotometry are listed in supplementary material ***[S2]***. Briefly, UV-Vis absorption spectra were recorded using Hewlett Packard HP-8453 one beam spectrophotometer and all measurements were carried out using standard 1-cm-thick quartz cell placed in home-made anti-frosting thermostatic module **(Figure 6)**.

3.4. Temperature controlled micro-thin-layer chromatography (micro-TLC).

Separation of target compounds was performed using thermostated horizontal chamber **[Zarzycki^{A} 2008]**, involving analytical protocols described in supplementary material ***[S2]***. Acquisition system for spots developed on the micro-TLC plates was invented by P.Z. and equipped with ring of 12 LED lamps (JDR, SMDHLCW-250; 3.5 W; 6400 K; 250 lm, Sanico Electronics, Warszawa, Poland) and two linear UV 365/254 nm light sources: VL-6.LC obtained from Vilber Lourmat (Cedex, France).

3.5. Temperature dependent inclusion chromatography (HPLC).

Column chromatography separation was conducted using experimental setup described in supplementary material ***[S2]***, **(Figure 7)**. Due to solubility limitations, stock solutions of naphthalene's and bisphenols (1 mg/mL) were prepared in methanol and ethanol, respectively. For both types of analytes HPLC separation was carried out using isocratic system and the mobile phase flow of 1 mL/min. The hold up time (t_o) of column chromatographic system was monitored each day using sodium nitrate marker (10 µg/mL) dissolved in the mobile phase without cyclodextrins additive (acetonitrile/water, 35%, v/v).

3.6. Solid phase extraction (SPE).

Solid phase extraction (SPE) was performed using SPE Supelclean TM LC-18 tubes, (5 mL, 0.5 g columns obtained from Supelco, Bellefonte, PA, USA) and a SPE vacuum chamber (Supelco, Bellefonte, PA, USA) connected to a N86 vacuum pump. KN 18 KNF (Nueberger Laboport, Freiburg, Germany).

For recovery studies sample of 1000 mL of distilled water was spiked with 1 µg mass of internal standard and 0.1 µg mass of each bisphenol investigated (11 target components). Particularly, 100 µL (35%, v/v, acetonitrile/water) of stock solution containing 1 µg/mL of bisphenols mixture and 10 µg/mL internal standard was added to 1000 mL volume of the sample. Volume of 1000 µL of stock solution was prepared by mixing of 10 µL x 11 (= 110 µL) of each bisphenol (at concentration of 100 µg/mL in 35%, v/v, acetonitrile/water), 10 µL of internal standard at concentration of 1 mg/mL in ethanol and 880 µL of solvent (35%, v/v, acetonitrile/water). Then SPE procedure was applied. Final sample for HPLC determination was reconstituted in 100 µL of acetonitrile/water (35%, v/v). The sequence graph for this protocol including SPE steps is presented in **Figure 8** and **Figure 9**, **Figure 10**.

For screening studies (chromatographic profiles detected by DAD-UV-Vis detector concerning daily used products and wastewater samples) following protocol was applied: to 250 mL of tap water 2 g of solid material was added. Solid materials listed in **Table 3** were investigated. Samples were boiled for 15 min. in 100^{o}C, cooled to room temperature and spiked with 0.25 µg of internal standard (IS volume of 25 µL at concentration of 10 µg/mL in 35%, v/v, acetonitrile/water). In case of wastewater 250 mL sample was mixed with IS as above. Wastewater chromatographic profiles were collected for raw material and after heating of the sample in 100^{o}C as described above. Then SPE procedure was applied. Final sample for HPLC determination was reconstituted in 100 µL of acetonitrile/water (35%, v/v). The sequence graph for this protocol including SPE steps is presented in **Figure 9-10** and **Figure 8**.

SPE procedure was based on the analytical protocol invented previously and designed for purification/concentration of wide range of polar compounds from liquid samples according to data presented in literature **[Bielecka-Dasziewicz 2013], [Zarzycki 2006], [Zarzycki^{A} 2009], [Zarzycki^{B} 2009], [Zarzycki^{C} 2009]**. Briefly, the SPE columns were conditioned using 5 x 1 mL of 100% methanol and 5 x 1 mL methanol/water (1%,

v/v). Samples (250 mL) were passed through the SPE columns and then purified with a cleaning mixture (5 x 1 mL methanol/water, 30%, v/ v). Target compounds were eluted with four portions of 0.5 mL of 100% methanol and obtained liquid was evaporated at room temperature in a Savant SPD121P vacuum centrifuge (Thermo Electron Corporation, Milford, MA, USA), which was connected to a cold trap (Refigerated Vapor Traps RVT 4104, Asheville, NC, USA) and the Thermo Savant VLP80 oil vacuum pump, model RV3 (Thermosavant Instruments Inc., Holbrook, NY, USA). The dry residue was dissolved in 100 µL of mobile phase without the addition of cyclodextrins (acetonitrile/ water, 35%, v/v) **(Figure 8)**.

3.7. Daily products, packaging and treated wastewater samples acquisition

Daily used products:

Rice bags (1-Canos, 2- Sanko, 3- Kupiec);
Plastic bags (1-3- Sarantis);
Cloths (1-3- Sarantis);
Sanitary towels (1- 2- Procter&Gamble, 3- TZMO S.A);
Fish baits (1- Caperlan, 2- Robinson, 3- Troker), were purchased in general stores in Koszalin (Poland).

Environmental samples (700 mL of treated wastewater, approximately) were collected (five times: 2018_04_16-18, 2018_04_25-26) from chamber of the secondary settling tank placed in the JAMNO SEWAGE TREATMENT PLANT, located close to Koszalin area (N 54^{o} 14.196' E 16^{o} 9.528'). Wastewater samples were immediately processed by SPE isolation, prepurification and concentration protocol.

3.8. Biological experiment

3.8.1. Duckweed source

Duckweed samples were collected 11 October 2012 by PZ from surface water ecosystem that is part of Dzierżęcinka River passing through Koszalin (N 54^{o} 11.579' E016^{o} 11.021'; **(Figure 11A)**. Until experiment time performed in 2018, duckweed organisms were breeding in small aquarium (volume 28L; temperature 20-26^{o}C; photoperiod: 14h light interval in a 24h period using 25 W incandescent light bulb) and regularly

refilled with tap water **(Figure 11B, C)**. Water container consisted natural wood block and was cohabitated with 2-5 fish - *Ancistrus dolichopterus*, which were feed with common fish food. In September 2015, due to accidental electric energy shutdown for 11 days, 99% of duckweed plants were lost. However, duckweed population was reconstructed from 2-3 plant organisms that survived.

3.8.2. Growth dynamics of duckweed water plant organisms under given experimental setup

This part involved home-made open-air Dewar chambers (2x5 units) invented and manufactured by PKZ **(Figure 12A)**. Chambers were temperature controlled using an external circulation thermostat Huber CC®-K6 to keep the temperature 20^{o}C with accuracy ± 0.2^{o}C during the whole experiment. Chambers were illuminated with LED fluorescent lamps (LED Tube-SWS061W, diameter 0.26mm, length 0.6 m, TempColor 2800-3000K) according to **Figure 12B** and with photoperiod set as 12 h/d. Nine chambers were filled with 200 mL of tap water and ~0.05 g duckweed biomass was added **(Figure 13)**. The chambers were divided into three groups, depending on the liquid medium contents:

A: plain tap water,

B: tap water and 1 mM β-cyclodextrin,

C: tap water and 7 mM glucose.

Due to liquid medium evaporation an appropriate volume of distilled water was added to keep the total volume in the chamber at level of 200 mL. During the experiment time (48 days) water surface was photographed to observe any changes in the amount of biomass in the chambers 9 time points; **(Figure 14)**. Within 22 day of cultivation 7 explants were taken from each chamber to examine the root length **(Figure 15)**. After measurement, the plants were transferred back to the appropriate chambers.

3.8.3. Degradation study of selected bisphenols from water phase using β-cyclodextrin and/or in the presence of duckweed water plant (Lemna minor L.)

Degradation studies of bisphenols (A, B, S) were performed under similar equipment setup as described above **Figure 13**. In the same way, each chamber was filled with 200 mL of tap water. However, in this case 8 chambers were used and filled as follow:

Chamber No 1: Tap water and 200 µL of ethanol.

Chamber No 2: Tap water and 200 µL of bisphenols mixture in ethanol.

Chamber No 3: Tap water and 200 µL of bisphenols mixture in ethanol and β-cyclodextrin (final concentration in cultivation media 1 mM).

Chamber No 4: Tap water and 200 µL of bisphenols mixture in ethanol and glucose (final concentration in cultivation media 7 mM).

Chamber No 5: Tap water and 200 µL of ethanol and 0.05 g duckweed biomass.

Chamber No 6: Tap water and 200 µL of bisphenols mixture in ethanol and 0.05 g duckweed biomass.

Chamber No 7: Tap water and 200 µL of bisphenols mixture in ethanol and β-cyclodextrin (final concentration in cultivation media 1 mM) and 0.05 g duckweed biomass.

Chamber No 8: Tap water and 200 µL of bisphenols mixture in ethanol and glucose (final concentration in cultivation media 7 mM) and 0.05 g duckweed biomass **(Table 3)**.

Final concentrations of bisphenols in water media were 1 mg/L that is equivalent of 0.0044 mM for bisphenol A 0.0041 mM for bisphenol B 0.0040 mM for bisphenol S. Overall experiment setup was summarized in **Table 3**.

From each cultivation media volumes of 100 µL were taken for quantitative HPLC analysis. A loss of cultivation media was observed daily and appropriately refilled with distilled water to maintain a constant volume of 200 mL (the contents of the chambers were mixed with a glass rod after supplementing and before sampling). Additionally, on the first and last day of the cultivation, leafs photos on the cultivation media surface were taken and the length of the roots were measured to observe any changes in the amount of biomass in the culture **(Figure 16)**. Due to large number of samples for analysis, HPLC quantification was performed on raw samples (without SPE step) using column described in **chapter 3.5** and mobile phase composed of 10 mM β-CD and 35% (v/v) acetonitrile/water. All separations for bisphenols determination were conducted at 40^{o}C enabling baseline separation of target components **(Figure 42)**. Quantification of bisphenols was performed by analyzing of the peaks heights recorded at the analytical wavelength 280 nm and using external standards method.

3.9. Data acquisition and analysis

Quantitative retention data (HPTLC spots position) were extracted from unprocessed digital images using ImageJ software (ver.1.48 Wayne Rasband, National Institutes of Health, USA; http://rsb.info.nih.gov/ij). For micro-chromatograms Images presented in this work, a global manual balance filter was applied to increase the contrast for spots visual evaluation.

Quantitative data obtained from UV-Vis spectra of PAHs and PAHs/β-CD complexes as well as bisphenols degradation experiments were treated as multidimensional vectors without special identification of single peaks and such data were inspected with a principal component multivariate statistical procedure using XLSTATPro=3DPlot (version 2008.2.01) provided by Addinsoft (Paris, France).

4. RESULTS AND DISCUSSION

4.1. ENCAPSULATION STUDIES OF SELECTED PAHs BASED ON micro-TLC, UV-Vis and HPLC DATA

Main goal of this experimental part of PhD thesis concerns adjustment of phenomenological models describing liquid chromatography retention and solubility behavior of low-molecular mass guest molecules, controlled by supramolecular interactions with selected macrocycles. Initial results, which were co-authored by PhD dissertation author, were published in *Analytical and Bioanalytical Chemistry* **[Ohta 2017]**. In this work unexpected differences between planar and column liquid chromatographic behavior of 1-acenaphthenol/β-cyclodextrin complexes at subambient temperatures were described and explained. This paper is provided as supplementary material ***[S2]*** and attached to the printed form of this dissertation.

The reported experimental work **[Ohta 2017]** focused on host-guest supramolecular complex creation between β-cyclodextrin and a racemic mixture of 1-acenaphthenol. The starting point was the observation of strong a retention of 1-acenaphthenol at subambient temperatures and under planar chromatographic conditions, where β-cyclodextrin was added to the mobile phase **(Figure 17).** The experiments described involved a liquid phase composed of plain 35% acetonitrile in water (v/v) or modified with β-CD and were conducted at different temperatures ranging from 0 to 90^{o}C. The behavior of supramolecular complexes was investigated using several analytical protocols based on: (***i***) classical non-forced flow planar chromatography (RP-18 TLC plates and micro-TLC RP-18W HPTLC plates), (***ii***) column chromatography (HPLC with C-18 and C-30 analytical columns), (***iii***) UV-Vis spectrophotometry and (***iv***) optical microscopy.

It has been documented that under various planar chromatographic conditions like: stationary plates types, chamber shape and volume, development mode and saturation, non-typical retention (extremely high) of 1-acenaphthenol at subambient temperatures can be observed. According to present knowledge, the reported results were counter to currently existing retention models explaining column chromatographic retention of host-guest complexes. Typically, where strong interaction of analytes with macrocyclic mobile phases additives is possible, the retention of target compounds is shortened at subambient temperatures. This is valid for the systems where macrocyclic additives are not strongly retarded by stationary phase and therefore, supramolecular inter-

actions may predominantly occur in the mobile phase **[Seidel 1993], [Vazquez 1992], [Bielejewska 1999]**, **[Morin 1998], [Sadlej-Sosnowska 1996]**, **[Lepri 1990]**, **[Lamparczyk 1994]**. Such conditions are fulfilled if *e.g.* 35% of acetonitrile/water binary mixture is applied as a mobile phase **[Zarzycki 1995]**, **[Zarzycki 1997]**, **[Zarzycki 2001]**. In the case of a C18 column filled with this eluent, β-cyclodextrin is virtually not retarded by *n*-alkane chains attached to the stationary phase surface and this macrocyclic additive may migrate close to the retention of the dead volume marker. The consequence of this is a low retention of supramolecular complexes involving β-cyclodextrin.

To explain the TLC phenomenon of a strong retention of supramolecular complexes at subambient temperatures several experiments were conducted:
(i) acenaphthenol chromatography under different instrumental conditions **(Figure 17)**,
(ii) cyclodextrin retention measured in two modes: as an analyte or mobile phase additive **(Figure 18)**,
(iii) plate development time under different mobile phases and temperature settings **(Figure 18), (Figure 19)**,
(iv) various columns including C-18 and C-30 **(Figure 20)**,
(v) UV-Vis spectrophotometry at different temperatures **(Figure 21)** and
(vi) microscopic inspection of precipitated crystals of acenaphthenol/β-CD complex **(Figure 22)**.

Analysis of the data collected has revealed that most probable reasons for the TLC retention behavior of 1-acenaphthenol under β-cyclodextrin additive conditions can be associated with:
(i) solubility changes of the created host-guest complex,
(ii) kinetics of solid complex precipitation and
(iii) differences with analysis time between planar and column chromatography.

To study this phenomenon more closely, in this dissertation several additional naphthalene derivatives as the guest molecules were also investigated **(Figure 23)**. From this PAHs set acenaphthylene, 1,8-DMN, 2,3-DMN and 2,6-DMN were selected for the micro-TLC experiment, due to the detection ability of such compounds under fluorescence conditions. Results presented in **Figure 19** confirm that the retention behavior of acenaphthylene and 1,8-DMN at subambient temperatures is similar to the

previously investigated 1-acenaphthenol. There are no differences in the retention of 2,3-DMN and 2,6-DMN for both mobile phases (with and without cyclodextrin) and the whole range of temperatures investigated. This strongly suggests that the high TLC retention of 1-acenaphthenol, acenaphthylene and 1,8-DMN is due to a favorable fit to the macrocycle host molecule present in the mobile phase. As it was documented in ***[S2]***, the precipitation phenomenon may cause strong retention due to the relatively long run time of TLC separation. Appropriate UV-Vis data concerning 1-acenaphthenol precipitation are presented in **Figure 21, Figure 22**, whilst **Figure 24** contains an additional data set for the selected PAH (acenaphthylene) at different temperatures. Similar UV-Vis spectral data were generated for 8 target compounds (naphthalene and its derivatives), whose chemical structures are presented in **Figure 23**.

Based on the above mentioned data the initial matrix composed of 26880 elements, namely 128 objects (PAHs molecules under different temperatures 0-70^{o}C and solvents with or without a cyclodextrin additive) and 210 variables (absorbance values measured for individual wavelengths from 190-400 nm) was generated. This enabled multivariate computations allowing objects grouping and comparison. The resulting PCA graphs are presented in **Figure 25**. From such data it is clear to see that significant differences in UV-Vis spectra concern similarly structured PAHs: 1,8-DMN, acenaphthene and acenaphthylene in the presence of a cyclodextrin additive. It should be noted that under given experimental conditions the spectrophotometer is detecting solvent turbidity caused by supramolecular complex precipitation. It should be noted that this phenomenon cannot be observed for 1-acenaphthenol because the analytical protocol was designed to eliminate precipitation for this molecule, according to the data presented in **Figure 21**. Such experiments may help to select potential host molecules that should be eliminated from the liquid phase using interaction with a given macrocycle. Based on presented PCA graph, naphthalene can be also considered as the a guest molecule that can be eliminated from the liquid phase using a cyclodextrin additive at subambient temperature.

The described precipitation phenomenon may have a massive impact on analytes quantification involving macrocycles as the mobile phase additives. Therefore, previously reported data generated by Włodarczyk **[Włodarczyk 2009]** concerning a number of low-molecular compounds (mainly steroids and non steroidal endocrine disrupting chemicals) using HPLC methodology based on binary mobile phases with and

without β-cyclodextrin and its hydroxypropyl derivatives were re-examined. It has been found that the precipitation problem may concern the mobile phases modified with native β-CD and selected analytes listed in **Figure 26**. Considering this finding the HPLC experiment was conducted for naphthalene and its derivatives involving mobile phases with and without β-CD additive. The calculated trajectories of the peak areas in temperature domain (bottom graph on **Figure 27** support the concept of supramolecular complexes precipitation at subambient temperatures for given guest molecules (1-acenaphthenol, 1,8-DMN, acenaphthylene, acenaphthen and naphthalene). As was proven previously, these compounds may strongly interact with cyclodextrin and therefore, can precipitate at subambient temperatures in both static (solutions) and dynamic (chromatographic mobile phase) conditions.

4.1.1. Detailed conclusions to part 4.1.

The observed phenomenon of the strong retention of supramolecular complexes on solid thin layers, may have a number of practical applications, especially for selective, high throughput separation involving microchromatographic and/or microfluidic devices, fractionation and extraction protocols (using *e.g.* bar extraction systems) as well as designing of purification systems for sewage water and drinking water using cyclodextrins as active molecules.

1-Acenaphthenol enantiomers and selected naphthalene derivatives can be efficiently separated at ambient and subambient temperatures using reversed phase HPLC systems and involving a mobile phase modified with β-cyclodextrin additive (10 mM) and various C-18 and C-30 columns. Significant differences between planar and column chromatographic behavior of 1-acenaphthenol and selected PAHs at ambient/subambient temperatures using a mobile phase modified with β-cyclodextrin has been demonstrated based on various TLC and HPLC conditions.

It was demonstrated that solubility changes in the supramolecular complexes studied and the kinetics of solid complex precipitation as well as differences in total analysis time between TLC and HPLC separation, may trigger strong retention of 1-acenaphthenol and PAHs in planar chromatographic systems. In particular cases (a long retention time of β-CD/host molecule complex), quantification of low-molecular analytes using a HPLC mobile phase modified with native β-cyclodextrin may be affected by the precipitation phenomenon of the supramolecular complex which is created.

This may occur at subambient temperatures close to 0°C. This disadvantage can be eliminated using *e.g.* more soluble hydroxypropyl-β-cyclodextrin instead of native β-CD additive.

The data presented has revealed that the solubility properties of supramolecular complexes with native β-cyclodextrin may be critical for the modeling of chromatographic retention driven by host-guest interaction. PCA graphs based on spectroscopic experiments involving target molecules and macrocyclic compounds may be used to predict strong host-guest interactions. Moreover, supramolecular complex precipitation combined with plate or bar solid phase extraction can be applied as a very selective method for the fractionation or separation of low-molecular mass components involving micro-chromatography or microfluidic devices.

The solubility decrease phenomenon of host-guest complexes with native β-cyclodextrin investigated may be utilized to design efficient water purification systems, which can be highly selective for given low-molecular mass micropollutants including their optical isomers.

4.2. OPTIMIZATION OF BISPHENOLS SEPARATION AND SELECTED VALIDATION ISSUES OF THE QUANTIFICATION PROTOCOL

This part of the research reports a new analytical protocol enabling the rapid separation of eleven bisphenols using temperature-dependent inclusion chromatography (HPLC) involving mobile phases modified with natural and biodegradable biomaterials: cyclodextrins. The separation process was performed on a typical octadecylsilane (low carbon load C18) analytical column **[Zarzycki 2002].** In particular, the retention of supramolecular host-guest complexes occurring between native β-cyclodextrin (β-CD) or its highly soluble in water (and water/organic liquids) hydroxypropyl derivative (2-HP-β-CD) and target compounds, namely: bisphenol A, B, BP, Z, AF, AP, C, E, F, FL and S, was analysed **(Figure 1)**. It has been documented that temperature sensitive inclusion complexes created within the chromatography mobile phase enables multiple separation of target molecules in a fast and optimal manner. Optimization results concerning total retention time, peaks distribution on chromatograms and peaks resolution were compared to chromatographic behavior of analytes under plain binary mobile phase (acetonitrile/water 35% v/v) conditions. Similar to previously reported research focusing on polycyclic aromatic hydrocarbons and steroid hormones mixtures, results of present study have revealed strong interaction of cyclodextrins with analytes, particularly in the subambient temperature region **[Zarzycki 2008^{B}]**, **[Zarzycki 2016],** [**Zarzycki^{B} 2009**], **[Zarzycki^{A} 1998], [Zarzycki 2001], [Zarzycki 2006], [Włodarczyk 2009].** The raw retention data set obtained under subambient, room and elevated temperatures conditions (10, 20, 30, 40 and 50^{o}C) is presented within **Table 4**. As with steroids molecules, it has been found that the relationship between the logarithmic form of the chromatographic retention factor (***k***) and reversed temperature (1/T [K]) is in most cases non-linear (with the exception of bisphenol S). **Table 5** consists of calculated values of quadratic regression coefficients (a,b,c) and determination coefficient (r^2) for the equation in the form of ***equation 1***:

$$\ln k = a(1000/T)^2 + b(1000/T) + c \qquad (\textbf{eq. 1})$$

Considering the determination coefficient (r^2) values presented in **Table 5** a quadratic model can be appropriate for determining the given analyte retention within temperatures investigated. These data were necessary to calculate optimization pa-

rameters for multiple separations of bisphenols and an internal standard mixture, particularly: total analysis time ($t_{max,min}$), resolution ($R_{s,min}$) and peaks distribution along the time axis (***r***; relative resolution product). The last optimization parameter was calculated according to ***equation 2***:

$$r = \Pi R_{s\,i+1}/[\Sigma R_{s\,i+1})/(n - 1)]^{n-1} \qquad (\textit{eq. 2})$$

Approximated elution times of analytes, within temperatures ranging from 0 to 60°C (with step 1°C) together with the calculated optimization parameters profiles are visualized in **Figure 28.** With reference to total analysis time and considering the whole set of target analytes, the an elevated temperature region for the efficient separation of bisphenols may be preferred. Examples of isocratic separation performed at 40°C and using different mobile phase additives are presented in **Figure 29.** As can be seen, baseline separation of selected bisphenols can be obtained and the retention time reduced using cyclodextrin additives. However, for efficient separation of the given bisphenols mixtures *e.g.* containing bisphenol Z (No 11), a subambient temperature region should be selected, if cyclodextrin modified phases are applied. In such case, total analysis time can be significantly reduced in comparison with plain acetonitrile: water mobile phase. It should be highlighted that using the isocratic systems studied, bisphenol AP (No 7) and bisphenol BP (No 8) cannot be separated, regardless of the mobile phase additive and temperature **(Figure 28), (Figure 29)**. For such components of interests a different concentration of cyclodextrins, macrocyclic additive type, acetonitrile % or gradient elution system should be tested and applied.

To illustrate and compare the efficiency of bisphenols interaction with macrocyclic additives the ratio k_{0mMCD}/k_{10mMCD} for each temperature point was calculated **(Table 6)**. As it was observed for different classes of low-molecular mass compounds, a strong interaction with macrocyclic additives at low temperatures is more significant **[Zarzycki^{A}1998]**, **[Zarzycki 2001]**. A decrease in the retention time of analytes at a subambient temperature is particularly visible for bisphenol **B (5)** and **Z (11)** in the case of native cyclodextrin as well as for **A (4)**, **B (5)**, and **Z (11)** in case of a hydroxypropyl derivative. Such results suggest preferable interactions of cyclodextrins with bisphenols containing *n*-alkanes chains or saturated rings (cyclohexane). This observation could be useful for

designing an selective chromatographic system for bisphenols analysis as well as the removal of such molecules from the liquid phase based on host-guest interaction.

Interestingly, the interaction intensity of bisphenols with the macrocycles investigated is similar for both: native β-CD and the hydroxypropyl derivative. In the case of low-molecular mass compounds, which strongly interact with β-CD, for example: steroids (17β-estradiol, testosterone, 20-α-hydroxyprogesterone, diethylstilbestrol) and PAHs (1,8-dimethylnaphthalene, acenaphthenol and acenaphthylene), the observed interaction with hydroxypropyl derivative was less significant **[Zarzycki^{A} 2009], [Zarzycki^{B} 2008].** This can be applied for the selective analysis and/or removal of bisphenols using hydroxypropyl β-CD complexation systems.

Detailed validation of the quantification protocol (including detection limits, selectivity, intra/interday precision, method robustness and more) for various analytes including PAHs, steroids and bisphenol A using an internal standard substance (7,8-dimethoxyflavone) and temperature-dependent inclusion chromatography were reported previously **[Zarzycki 2006], [Zarzycki^{B} 2009]**. In this work similar SPE extraction, separation and detection protocols were applied, therefore, in the case of the bisphenols group investigated only recovery studies were conducted. This is because the individual breakthrough curves for these compounds were not investigated and therefore, a previously optimized SPE protocol (for analytes polarities ranging from estetrol to progesterone) may have a significant impact on bisphenols determination. As can be seen from the recovery data presented in **Table 7** the recovery rate is acceptable for the majority of target analytes with the exception of bisphenols S, A and AF. In the case of bisphenol S relatively low recovery was observed. This may affect the sensitivity of the quantification protocol for this molecule. However, appropriate optimization of the elution mixture (for SPE step) should improve the low recovery rate of this compound. High recovery of bisphenol A is associated with high background contents of this substance in distilled water from our laboratory. Therefore, in such cases the excess of bisphenol A can only be determined above the 100 µg/L level. High recovery of bisphenol AF can be associated with low chromatographic resolution and co-elution of matrix interfering peaks.

4.2.1. Detailed conclusions to part 4.2.

High recovery of bisphenols clearly indicates that the previously optimized SPE protocol can be used to determine these compounds from liquid samples. Particularly, composi-

tions and volumes of cleaning and eluting solvents can be applied for bisphenols extraction, purification and pre-concentration.

Chromatographic data revealed that both β-CD and its hydroxypropyl derivative strongly interact with selected bisphenols. This is contrary to the steroids and PAHs molecules investigated previously, where a strong interaction with β-cyclodextrin was observed.

The proposed SPE extraction and chromatographic determination are simple, non-expensive and are based on biodegradable materials, , therefore, they can be considered a green chemistry method for the efficient fractionation, extraction and separation of bisphenols from complex environmental and food related samples.

4.3. REAL SAMPLES ANALYSIS

4.3.1. Daily products, packaging and treated wastewater

There are a number of publications dealing with the quantification of bisphenol A and related endocrine disrupting micropollutants in various environmental matrices including water, soil and sediments **(Table 11)**. The problem of such low-molecular mass compounds is currently extensively investigated in terms of microplastic presence in water and in the tissues of living organisms as well as in relation to the potential endocrine modulation risk **[Fendall 2009], [Andrady 2011], [Cole 2011], [Cauwenberghe 2013], [Ivar do Sul 2014], [Barboza 2015], [Eerkes-Medrano 2015], [Xanthos 2017]**. This is a consequence of a global environmental pollution with: (***i***) plastic originated macro objects (various plastic bags, containers, cosmetic sticks) that are slowly ground and disintegrated, mainly under marine conditions and (***ii***) the common modification of daily used products with plastic micro beads (*e.g.* present in cosmetics) **[Fendall 2009]**, [**Napper 2015], [Cheung 2017]**. However, interpretation of quantitative data reported in literature may be difficult, due to complex analytical matrices and a lack of widely acceptable standardized analytical protocols enabling quantification of multiple target compounds. Some of them are based on sensitive sensors **[Yin 2010], [Tan 2016]**, **[Zhang 2014], [Liu 2014]**, **[Fan 2012], [Zhou 2012]** but this technology is still problematic due to the relatively low selectivity of such systems, especially in the case of target components with similar chemical structures. The main advantages of such an approach are the low cost of determination and a rapid quantification procedure. More time consuming and expensive but robust and widely accepted quantification protocols usually involve classical and miniaturized separation techniques (capillary electrophoresis, gas chromatography, liquid column/planar chromatography **[Guart 2014], [Cacho 2013]**, **[Zhu 2010]**, **[Nerın 2002]**, **[Regueiro 2015]**, **[Yang 2014]**. It should be noted that even if very efficient separation systems (*e.g.* multidimensional elution) and selective detectors are applied (based on fluorimetry, mass spectrometry or electrochemical detection), sample pretreatment is still needed (typically using SPE or SPME), which may strongly affect the quantification results **[Zarzycki 2015], [Zarzycki ^{A}2017]**.

This part of the study focus on the screening of low-molecular mass compounds that can be emitted from various daily products or which are present in treated wastewater. Chromatographic profiles of SPE extracts were recorded by UV-Vis DAD detector. Additionally, profiles of distilled and tap water samples obtained from our laboratory

were analyzed. The extraction and separation protocol was optimized for the selective analysis of a wide range of matrix compounds (polarity from estetrol to progesterone) **[Bielecka-Daszkiewicz 2013] [Zarzycki^{C} 2009] [Zarzycki 2006]**. Additionally, the HPLC separation step involved selective interaction of target compounds with β-cyclodextrin in the mobile phase **[Zarzycki 2006].** As was proven in chapter **1.1.4**, cleaning and elution solvents, which were selected and previously optimized for the quantification of various steroids, may also effectively clean and concentrate target bisphenols. Therefore, recorded HPLC profiles of SPE extracts should reflect the contents of known and unknown low-molecular mass compounds, which may work as endocrine disrupters, including bisphenols and steroids.

Selection of materials of interest was based on the observation that raw (non-treated) sewage water may be composed of various solid objects identified as *e.g.* plastic bags, cloths, sanitary towels, wet wipes and similar **(Figure 30H)**. Moreover, some food products are prepared by the boiling of grain portions in plastic bags (*e.g.* rice, buckwheat or wheat products), therefore, plastic decomposition products, which may be generated at elevated temperatures, can be finally present in raw sewage water. For this research, number of materials were investigated as potential sources of bisphenols fractions in sewage water. They are listed in **Table 8** and in **Figure 30**. Plastic fishing bait was also investigated due to the potential problem of plasticizers emission from such products. This issue may be a problem in the lakes with strong anthropogenic pressure from the angling community.

The samples were processed with a 15 min boiling step **(Figure 31)** in accordance with common food products preparation instruction (rice grains in plastic bags). In the case of the remaining samples the boiling step was performed to simulate a long term extraction process in the aquatic environment, similarly to *e.g.* food products stability tests that are conducted at elevated temperature **[Gertz 2000], [Van Elteren 1997]**. In the case of tap water and sewage water, two protocols were applied (boiled and non boiled samples) to monitor the the effect of temperature on bisphenol A contents and to detect overall changes in chromatographic profiles during sample heating. All samples were processed using an SPE protocol **(Figure 32)** and analyzed by HPLC DAD-UV-Vis separation system.

The results of this investigation are presented in the form of the diode array chromatograms presented in **Figure 33**. As can be seen, there are significant differ-

ences between all samples which underwent chromatography. These analyses clearly indicate that the products investigated can decompose to a number of low-molecular mass chemicals. Chromatographic profiles related to the analytical wavelength 280 nm (characteristic for bisphenols and phenolic compounds *e.g.* estrogenic steroids), are presented in **Figure 34**. These clearly indicate the massive differences in bisphenol A level that can be present in the extracts, based on quantification methodology involving internal standard addition. It has been found that the bisphenol A levels in these samples may change by 4 factors: from 0.1 to 107 (BA/IS ratio), which correspond to concentrations of this micropollutant from 5 to 4466 µg/L **(Table 9)**. Unfortunately, the chromatogram complexity and detection type disable accurate identification/quantification of the remaining bisphenols. Therefore, in the future studies this problem should be solved by using a more efficient analytical column (25 cm long instead of the 10 cm that was used for the present study) and the application of a selective MS detection system.

Data presented on the chromatograms **(Figure 34)** are visualized as the values corresponding to all peaks areas integrated for the given sample type **(Figure 35)**. According to this data there are significant differences in the total organic matrix emitted from the samples investigated. Heating of the sewage water does not change the overall contents of the SPE extracts, indicating that temperature manipulation cannot be really used to decrease of the level of low-molecular mass compounds level in treated sewage water. Interestingly, the level of bisphenol A was increased after the boiling process.

Quantitative data **(Table 9)** has revealed possible high level of bisphenol A that may be emitted from rice bags, in comparison with to tap water samples, even if the overall area of chromatographic profiles for these samples were similar **(Figure 35)**. Generally, all of the materials investigated can be a source of bisphenol A and related micropollutants, particularly wet wipes, plastic bags and fish baits. Within each material type a high variability in the level of total organic matrix is observed **(Figure 36)**. There is no correlation between the bisphenol A level and the total organic matrix eluted from SPE tubes and detected by UV-Vis detector for all samples investigated **(Figure 37A)**. Nevertheless, such correlation can be significant for selected materials **(Figure 37B, C, D)**. This observation may be applied to the design of low resolution microfluidic systems (*e.g.* paper based microfluidic devices) enabling fast screening for the presence of such

compounds in polymers related samples. Simply, as the first screening step, the SPE extracts should be analyzed using low-resolution microfluidic devices. All samples characterized by high contents of organic matrix should be then quantified by more specific and sensitive HPLC or GC protocols.

It should be noted that the extracted mass of bisphenol A from fish bait material **(Table 9)**, may cause a real pollution problem for small water ecosystems. For example, a typical lake with high anthropogenic pressure from the angling community *e.g.* Lake Morskie Oko N 54.079093, E 16.472463; **(Figure 38)** with a water volume of $4x10^5$ m^3 (lake diameter 212 and depth 23 m) can be compromised by high number of fish baits, which were lost on underwater hooks. This situation is realistic due to frequent reports from divers who saw a number of fish baits on *e.g.* underwater tree residues in this lake. For our estimations, the following assumptions were made: the possible number of plastic containing flexible fish baits that can be lost on underwater hooks during *e.g.* 10 years ≈ 1000 and this corresponds to the total mass of 10 g of bisphenol, which may be emitted from such number of fish baits (considering that average mass of each fish bait = 5 g). Based on these assumptions a pollution level close to 25 ng/L may be expected in this lake. It should be mentioned that even if the flexible fish baits analyzed are made of silicone related materials, for storage purposes they are lubricated with unknown oils and packed in various plastic containers. This allows for the uncontrolled diffusion of plasticizers (like bisphenol A) to fish baits and then to the water ecosystem.

4.3.1.1. Detailed conclusions to part 4.3.1.

Described extraction and quantification protocols are capable for fast screening of bisphenols and related low-molecular mass micropollutants fraction from various complex materials. Quantitative data has revealed the problem of bisphenol A release to the environment, and also in the case of sewage water produced by wastewater treatment processes. It has been proven that: (***i***) some of the food products may emit high level of low-molecular mass compounds during the food cooking process and (***ii***) common fish baits may cause real environmental pollution of freshwater ecosystems.

4.3.2. Removal study of selected bisphenols from water phase using β-cyclodextrin and/or in the presence of duckweed water plant (*Lemna minor L.*)

4.3.2.1 Problem overview

Bisphenols may be fairly easily eluted from plastics to food products and the environment and then, act as endocrine disrupters (Endocrine Disrupting Compounds; EDCs). Therefore, a variety of methodologies have been invented to remove of these and similar EDC compounds from various environmental matrices (wastewater, sediments soils and agricultural products). In spite of new wastewater technologies focusing on micropollutants elimination, bisphenols can still be detected in various environmental samples. It is noteworthy that, they may be active at concentrations in water below ng/L level. This is because that they are characterized by low polarity resulting with effective accumulation by organisms consisting of fat (non-polar) composed tissues. For that reason, bisphenols are very difficult to remove from the environment and/or living organisms and consequently they may work as toxic chemicals. For example, there is some evidence are that a high level of bisphenol A can be associated with diabetes and related diseases in the humans. **[Rochester 2013] [Rezg 2014]**.

The experimental study described in this part of the doctoral dissertation is primarily focused on the systematic research dealing with the degradation/biodegradation of selected bisphenols (A, B and S) that can be present in liquid phases of food or environmental samples (*e.g.* vegetables/fruit juices, milk, drinking water or treated wastewater) Following the search through literature it is hypothesized that elimination of such molecules can be possible involving supramolecular interactions with non-toxic oligosaccharides - cyclodextrins **[Nagy 2014]**, **[Taka 2017], [Bhattarai 2014]**, **[Wang 2017].** In experiments reported in this PhD dissertation, the expected effect of host-guest inclusion on the biodegradation rate of target EDC molecules is investigated in the presence of aquatic plant life, particularly *Lemna minor L.*, under different cultivating conditions. The experimental setup was organized in order to enable collection of the initial data set for multivariate analysis and to allow for the design of further experiments concerning application of macrocycles as acting molecules for EDCs removal from water phase.

For the experiments conducted, the duckweed organism was selected due to the fact that such water plant organisms are common worldwide and may grow rapidly in various surface water conditions **(Figure 39)**. Duckweed biomass can be relatively easily collected from the water surface and is quickly reproduced.. Moreover, this organism

is also used for water purification purposes in technological water plant processes **[Adhikari 2015], [Zhao 2014]**, **[Mohedano 2012].**

4.3.2.2. Growth dynamics of duckweed water plant organisms under the given experimental setup

The biological experiment was conducted in temperature controlled chambers **(Figure 13)**, under open air and fixed lighting conditions **(chapter 3.8.2)**. In the first instance the duckweed biomass growth rate in time domain was investigated. Due to the simplicity of the experiment tap water was used as the base liquid. The growing biomass of duckweed was monitored during a 48 day period. Duckweed organisms were cultivated in separate chambers that were filled with pure tap water and also with two additives, namely: β-cyclodextrin (at a concentration of 1 mM) or glucose (7 mM). The glucose additive was considered to test the nutritional effect of potential degradation products of β-cyclodextrin. The concentration of glucose was selected on the basis that each β-cyclodextrin molecule is composed of 7 glucose units in the macrocyclic ring. Examples of duckweed leaves for these cultivation media are presented in **Figure 14**. Rate of dieback of the duckweed cultures investigated was estimated on the basis of the average number of green leaflets. As can be seen from the quantitative data presented in **Figure 40** duckweed biomass was progressively developed during first 10-12 breeding days and then a decay phase was observed. Moreover, a difference in biomass quantity was detected between those cultivated in plain tap water and those in mixtures modified with β-cyclodextrin as well as glucose. To investigate this phenomenon more closely simple morphological measurements of duckweed roots were performed. According to the photos presented in **Figure 15** there is a difference in the root length for the cultivation media investigated. Statistically significant shortest roots were observed for β-cyclodextrin and glucose additives in comparison with the plain tap water **(Figure 41)**, however, no significant differences were observed between duckweed roots cultivated in β-cyclodextrin and glucose modified tap water **(Table 10)**.

The shortest observed for β-CD and glucose modified media may suggest a nutritional effect of these additives (or the increase of nutrition availability from the liquid phase in the case of cyclodextrin presence). Similar morphological changes were observed for different experimental setups involving duckweed organisms **[Lasfar 2007]**,

[Xu 2011], **[Yin 2015].** However, in the plain tap water more duckweed organisms were proliferated in the given time period.

4.3.2.3. Results and discussion of the behavior of selected bisphenols under different liquid phase compositions and duckweed presence.

This experiment aims to explore the degradation effect of selected bisphenols in liquid phase, namely tap water under different experimental conditions. The selection of compounds of interest was based on the following criteria:

I) relatively high water solubility to obtain working solutions (with a target component level of at least 1 mg/L) due to further determination using a simple as possible direct injection HPLC protocol with quantification involving a UV detector **(Table11)**,

II) given retention properties allowing one run baseline isocratic separation of target components and sample matrix peaks **(Figure 29)**, **(Figure 28)**,

III) relatively strong interaction with β-cyclodextrin molecules allowing effective creation of host-guest complexes at the selected temperature of the biological experiment (20^{o}C) **(Table 6)**,

IV) environmental presence as micropollutants and potential endocrine disruptors at relative high concentration in real samples [**Song 2014], [Rochester 2015], [Yu 2015], [Rodriguez-Mozaz 2004],**

According to the results of previous experiments concerning host-guest interactions under HPLC conditions involving native cyclodextrin modified mobile phases (Chapter 3.6.) as target compounds, bisphenols A, B, E, F, S, and Z were considered initially. At a temperature of 20^{o}C they are characterized by relatively high $\boldsymbol{k}_{0mMCD}/\boldsymbol{k}_{10mMCD}$ ratios (3.86, 4.03, 2.80, 2.08, 1.45 and 7.73 respectively), in comparison to the remaining bisphenols which were investigated. This ratio is directly related to the number of moles of the target analyte in the mobile phase modified with the macrocyclic additive divided by the number of target analyte moles present in unmodified mobile phase. Such a simple and easy to calculate parameter corresponds to more general parameters: association or dissociation constants. For practical application ***k*** ratio can be useful for fast estimation of the stability of supramolecular complexes observed under given chromatographic conditions **[Zarzycki^{B} 1996]**. It is expected that in the case of a pure water environment the strongest interactions between bisphenols and β-CD can be

observed in comparison to acetonitrile:water (35:65; v/v) binary mobile phase, considering the fact that competitive interaction between macrocycle cavities and acetonitrile molecules from the chromatographic mobile phase can be expected **[Ikeda 1975] [Connors 1987]**, **[Matsui 1979], [Zarzycki 1999]**,**[Zarzycki^{B} 1998]**. Considering solubility data in water **(Table 11)** and separation efficiency as well as the analysis time of target bisphenols in an isocratic HPLC system **(Figure 29)**, three bisphenols, namely A, B and S were selected for further degradation experiments.

A general view of the cultivation chambers containing duckweed organisms is presented in **Figure 16**. Initial concentrations of the target compounds for the degradation experiment were set at 1 mg/L. This is a relatively high level but such concentrations have also been reported in real environmental samples **(Table 11)**. It should be noted that the planned experiment required direct injection of the reaction mixture samples into our HPLC system for simple, fast and non-expensive quantification of the target components over the given time of the degradation experiment. As can be seen from the chromatographic profile of the plain sample (tap water) presented in chromatogram **A** on **Figure 42A**, apart from bisphenol A, no interfering peaks were recorded. Based on UV spectra recorded by DAD-UV-Vis detector, the background level of bisphenol A in the tap water used for this experiment was detected at level of 300±100 µg/L. This corresponds to the level of BA that may be expected and can be detected in surface water **(Table 11)**. According to chromatograms **B** and **C** all peaks of target bisphenols were separated from the remaining matrix peaks. In the case of bisphenol A, the sum of the background level and bisphenol additive (1 mg/L) can be detected **(Figure 42 B, C)**.

This part of the research was designed as a multivariate experiment, according to data presented in experiment part **4.3.2**. For each individual cultivation media, selected bisphenols mixtures (A, B and S) were added. As the objects, bisphenols levels from individual cultivation media were considered, whilst as variables degradation time points were investigated. A matrix containing raw quantitative data for bisphenols from all cultivation media against a time axis is presented in **Table 5**. This data was also calculated as a percentage of the initial level of the target compound **(Table 6)** indicating a decrease in bisphenols in the cultivation media during the duration of the experiment. Examples of typical chromatographic patterns recorded for cultivation media after 2 and 257 hours are presented in **Figures 43** and **44**. In comparison with the blank profile

(without any additives) the mixture with bisphenol additives after 2 h, no additional peaks were recorded at the end of the experiment, indicating a lack of production of bisphenols. This strongly suggests that the decrease in bisphenols concentration may be caused by simple evaporation, adsorption or precipitation in the case of interaction with native β-cyclodextrin.

Generally, there was a systematic decrease in bisphenols levels in all cultivation mixtures investigated **(Figure 45)** and at the end of this experiment the level of the target compounds decreased to approximately 30% of the initial concentration **[Table 12]**. To determine possible latent information from the raw data set and simultaneous comparison of target components behavior in different cultivation media, principal component computations were performed. Firstly, the matrix composed of 18 objects characterized by 9 variables was analyzed **(Table 13)**. For this matrix the following sequence of eigenvalues was calculated: 8.485, 0.252, 0.132 and the remaining values were below 0.07. Considering Kaiser criterion (only factors with eigenvalues > 1 should be retained) the first factor should be considered and this explains over 94% of the total variability. Such results strongly support of our earlier hypothesis based on chromatographic patterns inspection that one simple phenomenon may be responsible for bisphenols behavior under the experimental conditions investigated. As presented in **Figure 46** separate clusters for all bisphenols types can be distinguished within 2D space (consisting of F1 and F2 factors, which accounted for 94.3 and 2.8% of variability respectively). Considering the most important F1 axis values, clear separation between bisphenol S data and the remaining bisphenols is visible. Moreover, within each individual bisphenol data, cyclodextrin and cyclodextrin/duckweed modified samples (labeled as white and green dots, respectively) can be distinguished, suggesting different behavior of these samples in comparison with the remaining cultivation media. This is confirmed by re-computation of raw data sets for cultivation media concerning each individual bisphenol. In such cases data matrices composed of 6 objects characterized by 9 variables were considered. As can be seen from the 2D graphs presented in **Figures 47**,**48 and 49** the same clustering with respect to the F1 axis and cyclodextrin contents can be observed for each bisphenol investigated.

4.3.2.4. Detailed conclusions to part 4.3.2.

[1] Duckweed organisms can be cultivated in the tap water modified with macrocyclic compounds in a liquid phase at a concentration of 1 mM and fixed laboratory conditions (given media volume, chamber shape, water temperature and lighting intensity/time period).

[2] The biological experiment involving duckweed should be performed for at least 10-12 days where a progressive development of biomass was observed.

[3] Significant decrease in bisphenols A, B and S levels was recorded under experimental conditions regardless of the cultivation media investigated - this strongly suggests that evaporation effects can be dominant.

[4] Recorded concentration profiles are similar for all additives tested.

[5] The multivariate experiment involving all cultivation media and time points clearly suggests differences in bisphenols behavior in the presence of β-cyclodextrin as well as β-cyclodextrin and duckweed additives. This effect, after proper optimization may be used for water treatment involving macrocyclic additives and duckweed organisms.

[6] When considering the results obtained further experiments should include:

a) A testing of each component of interest separately (not as a target component mixture).

b) Optimization of experimental conditions to maximize inclusion effects particularly, when performing degradation experiments at subambient temperatures (*e.g.* 10 or 15^{o}C), changing macrocyclic modifier concentration and type (e.g. different native cyclodextrins and their more soluble derivatives).

c) Analysis of the cultivation media to identify potential degradation products using different detection techniques *e.g.* mass spectrometry.

d) Monitoring of cyclodextrin levels and its potential degradation products for the duration of the experiment.

d) Experiment pattern re-organization to identify the main factors affecting the decrease in bisphenols in the cultivation media (evaporation, adsorption, degradation).

5. MAIN CONCLUSIONS

The research presented has revealed the high potential of host-guest complexation based on cyclodextrin molecules for analytical and further technological wastewater treatment applications. The addition of given macrocycles, namely native β-cyclodextrin and its hydroxypropyl derivative, to the liquid phase significantly changes the retention behavior of the target (guest) molecules including polycyclic aromatic hydrocarbons (naphthalene, its methyl derivatives and acenaphthenol optical isomers) as well as a battery of selected bisphenols (A, B, C, E, F, S, Z, AF, AP, BP, FL) in the liquid phase, both under static (solutions) and dynamic (chromatographic separation) conditions. It has been documented that this phenomenon is more visible at subambient temperatures (temperatures ranging from 5 to 20^{o}C), similar to different classes of low-molecular mass compounds investigated previously (*e.g.* steroid hormones acting as endocrine modulators). However, experimental data revealed that supramolecular interactions at elevated temperatures (25 - 50^{o}C) are also possible, for selected host molecules (bisphenols). This phenomenon can be applied for highly selective extraction of the given micropollutants from the liquid phase.

It has been found that chromatographic retention data obtained from planar chromatography may be used as a guide for target components and host molecules selection to enable the design of selective extraction systems for the removal of PAHs residues various liquid phases. On the other hand, the column chromatographic experiment focusing on the separation efficiency of selected bisphenols in the presence of macrocyclic additives, clearly indicated that such modifiers can significantly improve analysis time and selectivity of the isocratic system at the given temperature for simultaneous determination of various bisphenols mixtures. An optimized chromatographic protocol based on octadecylsilane column and acetonitrile/water binary mobile phase can be applied for fast and non-expensive quantification of target compounds involving green chemistry protocols. Quantification protocol invented, due to its simplicity, may be applied for highly selective monitoring of micropollutants during technological wastewater treatment processes.

It has been demonstrated that a whole range of low-molecular mass compounds, which may be detected using UV-Vis detector, can easily be emitted from various in daily use products. This issue must be seriously taken into account in the case of the presence of micropollutants in treated wastewater, water ecosystems and plastic waste

utilization *via* technological wastewater treatment processes, especially in terms of microplastic originated pollutants acting as endocrine disrupters. Preliminary multivariate biological experiments involving duckweed biomass and native β-cyclodextrin additive clearly indicated that β-CD or combined β-CD/duckweed system has an effect on bisphenols elimination from water. This process needs to be optimized but the results presented have revealed that such green chemistry technology, if successful, may be an interesting alternative for the selective removal of the micropollutants investigated from wastewater using classical adsorbents (e.g. carbons and carbon-related nanomaterials), particularly in terms of the worldwide problem with microplastic pollutants in the environment and food products.

The experimental data presented in this doctoral dissertation can be treated as an initial platform and starting point for designing of the further experiments, which may improve the effectiveness of low-molecular mass micropollutants removal during technological processes of wastewater treatment, involving biomass and/or supramolecular encapsulation driven by the presence of macrocyclic oligosaccharides in the liquid phase.

6. TABLES

TABLE 1. Concentrations and determination methods of active micropollutants in environmental samples (modified and extended table 2 from ***[S1]***)

Group	Active sub-stance	Sample	Collection site	Method of determination			Concentration detected	Source
				Preparation	Chromatographic technique	Detector		
Non-steroidal anti-inflammatory drugs	Diclofenac	Surface water	Germany	SPE	GC	MS MS/MS	0.05 µg/L	**[Ternes 2001]**
		Surface water	USA	SPE		MS	10 µg/L	**[Ollers 2001]**
		Surface water	Switzerland	LLE		MS	12 ng/L	**[Buser 1998]**
		Drinking water	Germany	SPE		MS	0.4-0.9 µg/L	**[Ternes 2001]**
		Sewage	Canada	SPE	HPLC	ESI-MS	10-20 ng/L	**[Miao 2002]**
	Naproxen	Surface water	Germany	LLE SPE	HPLC	CE-MS MS	0.5 µg/L	**[Ahrer 2001]**
		Surface water	Germany	SPE		MS MS/MS	0.39 µg/L	**[Ternes 2001]**
		Surface water	USA	SPE	GC	MS	10 µg/L	**[Hogenboom 1998]**
		Sewage	Canada	SPE	HPLC	ESI-MS	5-20 ng/L	**[Miao 2002]**

Continuation of Table **1**

	Ibuprofen	Surface water	Switzerland	SPE	HPLC	MS	0.1-1.0 µg/L	**[Buser 1998]**
		Sewage	Canada	SPE	HPLC	ESI-MS	5-20 ng/L	**[Miao 2002]**
		Surface water	Germany	LLE SPE	HPLC	CE-MS MS	0.6 µg/L	**[Ahrer 2001]**
		Sea water	North Sea	LLE	GC	MS	0.6 ng/L	**[Weigel 2002]**
Steroid hormones	Estrone	Surface water	USA	SPE	GC	MS	0,01 µg/L	**[Hogenboom 1998]**
		Sludge	Germany	LLE SPE	HPLC GC	MS	0.02 µg/L	**[Ternes[A] 2002]**
	17β- estradiol	Sludge	Germany	LLE SPE	LLE SPE	MS	0.02 µg/L	**[Zarzycki[B] 2009]**
		Surface water	Poland	SPE	HPLC	DAD UV	0,51 ng/L	**[Zarzycki[B] 2009]**

Continuation of Table **1**

	17α- etyny-loestradiol	Surface water	Poland	SPE	HPLC	UV DAD	0.47 ng/L	**[Zarzycki[B] 2009]**
		Sludge	Germany	LLE SPE	LLE SPE	MS	0.09 µg/L	**[Ternes[A] 2002]**
EDC	Bisphenol A	Surface water	Germany	SDE	GC	MS/MS	0.0005 to 0.41 mg/L	**[Fromme 2002]**
		Surface water	Germany/ Czech Re-public		GC/MSD	MS-EI+	4 and 66 ng/L	**[Stachel 2003]**
		Ground-water	Spain	SPE	LC–APCI	MS	0.006 ug/L	**[Rodriguez-Mozaz 2004]**
Antibacterial drugs	Sulphonamides	Surface water	USA	SPE	HPLC	MS	0.07-15 µg/L	**[Lindsey 2001]**

Continuation of Table **1**

	Trimethoprim	Sea water	-	LLE	HPLC	APCI-MS	2.5 µg/L	**[Sorensen 2002]**
				SPE				
	Sulfadiazines	Sea water	-				2.5 µg/L	**[Sorensen 2002]**
Drugs regulating lipid metabolism	Clofibric acid	Sea water	North Sea	LLE	GC	MS	0.013 µg/L	**[Weigel 2002]**
		Surface water	Germany	SPE		FID	0.049 µg/L	**[Ternes 2001]**

DAD – Diode-array detector,
SPE- Solid phase extraction,
LLE – Liquid–liquid extraction,
GC – Gas chromatography,
HPLC – High-performance liquid chromatography,
MS – Mass spectrometry,
FID – Flame ionization detector,
ESI - MS – Electrospray ionization mass spectrometry,
CE-MS – Capillary electrophoresis–mass spectrometry,
APCI - MS – Atmospheric pressure chemical ionization mass spectrometer,
LC–APCI-MS-Liquid chromatography–atmospheric pressure chemical ionization-mass spectrometry

TABLE 2. List of water policy priority substances with suggested amendments (Journal of Law of the European Union of 24.12 2008 **[EU 2013]** (according to data listed in table 1 from ***[S1]***)

Water policy priority substances	Substances that can be potentially considered as priority or hazardous priority substances	Suggested to be addend to the list of priority substances (since 31.01.2012)
1. Alachlorine	1. AMPA	A. Plant preservatives:
2. Anthracene	2. Bentazone	1. Aclonifen
3. Atrazine	3. Bisphenol-A	2. Bifenox
4. Benzene	4. Dicofol	3. Cypermethrin
5. bromium diphenylether	5. EDTA	4. Dicofol
6.Cadmium and its compounds	6. Free cyanide	5. Heptachlor
7. C10-13chloralcanes	7. Glyphosate	6. Quinoxyfen
8. Chlorfenwinfos	8. Mecoprop (MCPP)	
9. Chlorpiryfos (ethyl chlorpiryfos)	9.Musk xylene	B. Biocidal substances:
10. 1,2-dichloroetan	10. Perflurooctanesulfonic acid	1. Cibutrin
11. Dichloromethane	11. Quinoxyfen	2. Dichlorovos
12. DEHP	12. Dioxins	3. Terbutryn
13. Diuron		C. Industrial chemical compounds:
14. Endosulfan		1. PFOS
15. Fluoranten		2. HBCDD
16. Hexachlorbenzene		
17. Hexachlorbutadiene		D. Combustion by-products:
18. Hexachlorcycloheaane		1. Dioxins and digoxin derivates
19. Isoproturon		
20. Lead and its compounds		E. Substances of pharmaceutical industry:
21. Mercury and its compounds		1. 17 alpha-ethynylestradiol (EE2)
22. Naphthalene		2. 17 beta-estradiol (E2)
23. Nickel and its compounds		3. diclofenac
24. Nonylphenol		
25. Octylphenol		
26. Pentachlorbenzene		
27. Pentachlorophenol		
28. Simazine		
29. Tributyltin compounds		
30. Trichlorbenzenes		
31.Trichloromethane (chloroform)		
32. Trifluralin		

TABLE 3. Chamber numbering and contents for multivariate experiment focusing on bisphenols degradation.

Chamber number	Analyte
1	**Tap water** (200 mL) and **ethanol** (200µL)
2	**Tap water** (200 mL) and bisphenols **mixture** (200 µL of solution at concentration 1 mg/mL in ethanol).
3	**Tap water** (200 mL) and **bisphenols mixture** (200 µL of solution at concentration 1mg/mL in ethanol) and **β-cyclodextrin** (at concentration 1mM).
4	**Tap water** (200 mL) and **bisphenols mixture** (200 µL of solution at concentration 1 mg/mL in ethanol) and **glucose** (at concentration 7mM).
5	**Tap water** (200 mL) and **ethanol** (200µL) and **duckweed** (0.05g).
6	**Tap water** (200 mL) and **bisphenols mixture** (200 µL of solution at concentration 1 mg/mL in ethanol) and **duckweed** (0.05g).
7	**Tap water** (200 mL) and **bisphenols mixture** (200 µL of solution at concentration 1 mg/mL in ethanol) and **β-cyclodextrin** (at concentration 1mM) and **duckweed** (0.05g).
8	**Tap water** (200 mL) and **bisphenols mixture** (200 µL of solution at concentration 1 mg/mL in ethanol) and **glucose** (at concentration 7mM) and **duckweed** (0.05g).

TABLE 4 Values of retention coefficients (***k***) of analytes chromatographed on a 10 cm long LC-18 column at various temperatures and using mobile acetonitrile/water (35%, v/v) unmodified (A) and modified phases β-cyclodextrin (B) and its hydroxypropyl derivative (C) at a concentration of 10 mM. The substance numbers correspond to the order of the analytes given in the **Figure 1**.

A (unmodifed mobile phase)

k values

Analyte	Separation temperature [°C]				
	10	**20**	**30**	**40**	**50**
Bisphenol S (1)	2.863	2.162	1.959	1.629	1.394
Bisphenol F (2)	6.383	4.889	4.420	3.305	3.105
Bisphenol E (3)	9.483	7.428	6.487	5.165	4.592
Bisphenol A (4)	13.837	10.665	9.398	7.365	6.523
7,8-Dimethoxyflavone (12)	22.674	18.213	17.051	14.287	13.077
Bisphenol B (5)	26.150	19.277	16.722	12.756	11.187
Bisphenol C (6)	40.741	29.965	26.902	20.321	17.829
Bisphenol AP (7)	48.169	33.228	29.417	22.246	18.394
Bisphenol BP (8)	50.195	34.221	29.174	21.318	18.509
Bisphenol Z (11)	53.030	37.737	32.982	24.294	21.462
Bisphenol AF (9)	52.820	38.002	32.990	24.858	20.700
Bisphenol FL (10)	100.303	67.296	57.400	41.380	34.518

B (β-cyclodextrin in mobile phase)

k values

Analyte	Separation temperature [°C]				
	10	**20**	**30**	**40**	**50**
Bisphenol S	1.770	1.585	1.412	1.295	1.188
Bisphenol F	2.595	2.474	2.313	2.166	2.028
Bisphenol E	2.749	2.736	2.679	2.617	2.518
Bisphenol A	3.048	3.041	2.980	2.854	2.722
7,8-Dimethoxyflavone	16.462	15.147	13.772	12.419	11.084
Bisphenol B	4.687	4.976	5.195	5.237	5.170
Bisphenol C	18.422	17.453	16.363	14.748	13.050
Bisphenol AP	24.576	22.071	18.898	16.030	13.434
Bisphenol BP	24.504	21.709	18.851	16.048	13.433
Bisphenol Z	4.715	5.161	5.540	5.825	5.966
Bisphenol AF	28.970	25.442	21.908	18.471	15.443
Bisphenol FL	58.406	49.536	40.997	33.466	26.676

C (2HP-β-cyclodextrin in mobile phase)

k values

Analyte	Separation temperature [°C]				
	10	**20**	**30**	**40**	**50**
Bisphenol S	1.656	1.456	1.305	1.157	1.086
Bisphenol F	2.289	2.129	2.010	1.908	1.793
Bisphenol E	2.302	2.293	2.273	2.214	2.223
Bisphenol A	2.485	2.605	2.685	2.752	2.746
7,8-Dimethoxyflavone	14.581	13.315	12.066	10.968	9.841
Bisphenol B	4.208	4.413	4.526	4.634	4.511
Bisphenol C	14.638	14.328	13.557	12.680	11.253
Bisphenol AP	16.392	15.127	13.562	11.920	10.716
Bisphenol BP	16.507	15.161	13.663	11.913	10.583
Bisphenol Z	4.293	4.640	4.941	5.112	5.271
Bisphenol AF	21.881	19.333	16.793	14.742	12.395
Bisphenol FL	46.732	39.875	33.112	27.068	22.372

TABLE 5. Values of non-linear regression coefficients and determination coefficient (r^2) for the equation in the form $\ln k = ax^2 + bx + c$ (where x = 1000/T) for substances chromatographed on a 10 cm LC-18 column and mobile acetonitrile/water phases (35%, v/v) without a macrocyclic modifier and with the addition of β-cyclodextrin and hydroxypropyl-β-cyclodextrin, calculated on the basis of the data presented in **Table 4**.

Analyte	Unmodified mobile phase				10mM β-cyklodextrin				10mM 2 HP-β-cyklodekstrin			
	a	***b***	***c***	r^2	***a***	***b***	***c***	r^2	***a***	***b***	***c***	r^2
Bisphenol S	0.58	- 2.23	1.85	0.986	0.18	- 0.25	- 0.73	0.999	0.40	- 1.69	1.44	0.997
Bisphenol F	0.77	- 3.45	4.38	0.974	-0.39	3.17	- 5.35	0.999	-0.0006	0.55	- 1.11	0.998
Bisphenol E	0.46	- 1.39	1.42	0.993	-0.47	3.34	- 4.88	0.998	-0.057	0.47	- 0.12	0.863
Bisphenol A	0.44	- 1.25	1.45	0.990	-0.59	3.64	- 4.5	0.994	-0.55	3.39	- 4.24	0.994
Bisphenol B	0.73	- 2.94	4.46	0.990	-1.00	6.43	- 8.63	0.995	-0.84	5.35	- 7.07	0.962
Bisphenol C	0.53	- 1.69	2.96	0.983	-1.28	9.28	- 13.8	0.999	-1.41	9.91	- 14.78	0.996
Bisphenol AP	0.65	- 2.23	3.52	0.984	-1.32	10.1	- 16.14	0.999	-0.755	5.99	- 8.95	0.998
Bisphenol BP	1.31	- 6.42	10.2	0.988	-1.21	9.40	- 14.9	1	-0.92	7.15	- 10.93	0.998
Bisphenol Z	0.95	- 4.26	7.1	0.985	-0.75	4.42	- 4.72	0.999	-0.59	3.50	- 3.45	0.999
Bisphenol AF	0.31	0.05	- 0.01	0.990	-1.15	9.08	- 14.3	1	-0.90	7.28	- 11.35	0.999
Bisphenol FL	0.92	- 3.7	6.16	0.988	-1.36	10.8	- 17.15	1	-1.00	8.36	- 13.15	0.999

TABLE 6. Retention factor ratios (k_{0mMCD}/k_{10mMCD}) reflecting host-guest interaction intensity calculated from data presented in **Table 4** for β-cyclodextrin (**A**) and 2-hydroxypropyl-β-cyclodextrin (**B**); Target components highlighted in red were selected for degradation experiment with duckweed under different conditions *(Chapter 4.3.2.3).*

Analyte	Separation temperature °C				
	10	**20**	**30**	**40**	**50**
A: k_{0mMCD}/k_{10mMCD} ratio values for β- cyclodextrin					
Bisphenol A	5.02	3.86	3.07	2.51	2.11
Bisphenol AF	1.78	1.57	1.45	1.37	1.33
Bisphenol AP	1.89	1.64	1.49	1.40	1.36
Bisphenol B	5.44	4.03	3.13	2.53	2.11
Bisphenol BP	1.96	1.68	1.50	1.39	1.33
Bisphenol C	2.16	1.80	1.58	1.43	1.34
Bisphenol E	3.40	2.80	2.36	2.04	1.79
Bisphenol F	2.41	2.08	1.83	1.64	1.48
Bisphenol FL	1.65	1.46	1.34	1.28	1.26
Bisphenol S	1.57	1.45	1.35	1.26	1.18
Bisphenol Z	10.89	7.73	5.72	4.39	3.48

Continuation of Table **6**

B: k_{0mMCD}/k_{10mMCD} ratio values for hydroxypropyl β-cyclodextrin

Bisphenol A	5.47	4.24	3.38	2.78	2.33
Bisphenol AF	2.36	2.07	1.87	1.74	1.65
Bisphenol AP	2.82	2.39	2.09	1.87	1.71
Bisphenol B	6.07	4.56	3.56	2.89	2.41
Bisphenol BP	2.90	2.42	2.08	1.85	1.69
Bisphenol C	2.72	2.20	1.88	1.68	1.55
Bisphenol E	4.04	3.34	2.80	2.38	2.04
Bisphenol F	2.74	2.39	2.11	1.87	1.67
Bisphenol FL	2.06	1.82	1.66	1.57	1.51
Bisphenol S	1.67	1.58	1.48	1.38	1.29
Bisphenol Z	11.93	8.60	6.43	4.97	3.95

TABLE 7. Recovery values of bisphenols and internal standard (***n*** = 5; samples A-E) at concentration corresponding to 100 ng/L and 1 µg/L (for each bisphenols and IS, respectively) of water sample for the SPE procedure tested.

Analyte	Recovery (%)					AVG	STD	CV%
	A	B	C	D	E			
BPS	25.24	31.04	37.69	26.48	24.10	**28.91**	**5.57**	19.28
BPF	91.47	96.80	97.96	99.51	90.35	**95.22**	**4.07**	4.27
BPE	98.15	96.03	97.85	97.71	96.60	**97.27**	**0.91**	0.93
BPA	208.33	194.10	194.11	237.39	234.28	**213.64**	**21.10**	9.88
BPB	90.42	96.18	98.05	97.02	99.06	**96.14**	**3.38**	3.52
BPZ	91.64	113.98	95.83	102.45	101.80	**101.14**	**8.44**	8.35
BPC	88.76	93.02	78.26	95.42	109.65	**93.02**	**11.38**	12.24
BPAP+BPBP	71.54	71.74	99.50	75.23	70.43	**77.69**	**12.33**	15.87
BPAF	257.14	120.00	90.91	213.33	114.29	**159.13**	**72.01**	45.25
BPFL	87.80	94.29	92.11	97.22	93.33	**92.95**	**3.44**	3.70
7,8-DMF	84.13	99.25	99.38	98.95	90.03	**94.35**	**6.96**	7.37

TABLE 8. List of samples and materials analyzed by SPE/HPLC/DAD-UV-Vis protocol.

Lp	Samples and materials
1	Tap water boiled (250 mL)
2	Rice bags (2 g)
3	Plastic bags (2 g)
4	Cloth (2 g)
5	Fish baits (2 g)
6	Sanitary towels (2 g)
7	Wet wipes (2 g)
8	Boiled purified sewage (250 mL)
9	Raw purified sewage (250 mL)
10	Distilled water (250 mL)
11	Raw tap water (250 mL)

TABLE 9. Quantitative data (values of peak heights and bisphenol A/internal standard ratio) for all samples investigated.

SAMPLE TYPE: BOILED TAP WATER (1)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	865.0	4053.0	0.21
(**B**) (*n*=2)	1307.5	2749.5	0.47
(**C**) (*n*=2)	1039.0	4118.5	0.25
AVG	1070.5	3640.3	**0.31** ***{12.9}***
STD	222.9	772.2	
CV%	20.8	21.2	

SAMPLE TYPE: RICE BAGS (2)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	1604.5	4225.0	0.38
(**B**) (*n*=2)	1761.0	4190.5	0.42
(**C**) (*n*=2)	4657.5	5290.0	0.88
AVG	2674.3	4568.5	**0.56** ***{23.3}***
STD	1719.3	625.1	
CV%	64.3	13.7	

SAMPLE TYPE: PLASTIC BAGS (3)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	257.0	1627.0	0.16
(**B**) (*n*=2)	155957.0	7043.0	22.14
(**C**) (*n*=2)	3730.5	3068.5	1.22
AVG	53314.8	3912.8	**13.63** ***{567,5}***
STD	88907.7	2805.0	
CV%	166.8	71.7	

SAMPLE TYPE: CLOTH (4)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	54927.5	4747.0	11.57
(**B**) (*n*=2)	4265.5	7043.0	0.61
(**C**) (*n*=2)	3730.5	3068.5	1.22
AVG	20974.5	4952.8	**4.23** ***{176.8}***
STD	29405.4	1995.2	
CV%	140.2	40.3	

SAMPLE TYPE: FISH BAITS(5)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	5953.5	2362.0	2.52
(**B**) (*n*=2)	248460.5	4492.5	55.31
(**C**) (*n*=2)	1003649.5	4882.0	205.58
AVG	419354.5	3912.2	**107.19** ***{4466.2}***
STD	520339.2	1356.5	
CV%	124.1	34.7	

SAMPLE TYPE: SANITARY TOWELS (6)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	7370.0	522.5	14.11
(**B**) (*n*=2)	705.5	6736.5	0.10
(**C**) (*n*=2)	9342.0	4496.5	2.08
AVG	5805.8	3918.5	**1.48** ***{61.7}***
STD	4525.7	3147.1	
CV%	78.0	80.3	

SAMPLE TYPE: WET WIPES (7)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	13330.5	4124.0	3.23
(**B**) (*n*=2)	11834.5	2527.5	4.68
(**C**) (*n*=2)	23285.5	3303.5	7.05
AVG	16150.2	3318.3	**4.87** ***{203}***
STD	6224.5	798.4	
CV%	38.5	24.1	

SAMPLE TYPE: BOILED PURIFIED SEWAGE (8)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	61888.5	4598.0	13.46
(**B**) (*n*=2)	362477.0	3326.5	108.97
(**C**) (*n*=2)	50848.0	3326.5	15.29
AVG	158404.5	3750.3	**42.24** ***{1760.8}***
STD	176818.2	734.1	
CV%	111.6	19.6	

SAMPLE TYPE: RAW PURIFIED SEWAGE (9)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	35839.0	2907.5	12.33
(**B**) (*n*=2)	37057.0	4032.0	9.19
(**C**) (*n*=2)	30623.0	3700.0	8.28
AVG	34506.3	3546.5	**9.73** ***{405.4}***
STD	3417.8	577.8	
CV%	9.9	16.3	

SAMPLE TYPE: DISTILLED WATER (10)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	3233.0	24947.0	0.13
(**B**) (*n*=2)	3640.0	27988.0	0.13
(**C**) (*n*=2)	3325.0	26221.0	0.13
AVG	3399.3	26385.3	**0.13** ***{5.41}***
STD	213.4	1527.1	
CV%	9.9	16.3	

SAMPLE TYPE: RAW TAP WATER (11)

SAMPLE SOURCE	BPA (peak heights; a.u.)	IS (peak heights; a.u.)	BPA/IS ratio *{concentration µg/L}*
(**A**) (*n*=2)	1896.0	4193.0	0.45
(**B**) (*n*=2)	1695.0	3974.0	0.43
(**C**) (*n*=2)	1400.0	4257.0	0.33
AVG	1663.7	4141.3	**0.40** ***{16.7}***
STD	249.5	148.4	
CV%	15.0	3.6	

Table 10. Result of t-test for data presented on Figure 41 concerning average root length of the duckweed organisms depending on the medium used.

COMPARED SAMPLES	TEST T			
tap water β-cyclodextrin	p p1	0.05 0.002893	p>p1	**H0- there're difference between samples** H1- there're no difference between samples
	There is no reason to reject H0			
β-cyclodextrin glucose	p p1	0.05 0.27365	p<p1	H0- there're difference between samples **H1- there're no difference between samples**
	There are reason for rejecting H0			
tap water glucose	p p1	0.05 0.000851	p>p1	**H0- there're difference between samples** H1- there're no difference between samples
	There is no reason to reject H0			

TABLE 11. Solubility and concentration of selected bisphenols in environmental samples.

Name	**Systematic name**	**Solubility** (water or another solvent, via literature)	**Concentration in various environmental samples** (via literature)
Bisphenol **A** (BPA)	2,2-Bis(4-hydroxyphenyl) propane	A) **300mg/L** at 25 ◦C [**European Union Risk Assessment Report 2012**]. B) **120mg/L** at 25 ◦C **[Dorn 1987].** C) **120 mg/L** at 25 ◦C **[Meti rep. 2018].** D) Water solubility range: **5.44e^{-04}** to **1.31e^{-03} mol/L** (**124-299mg/L**) **[EPA A 2018].**	1) **0.0005 to 0.41 mg/L** (surface water), **0.018 to 0.702 mg/L** (sewage effluents), **0.01 to 0.19 mg/kg** (sediments), **0.004 to 1.363 mg/kg** (sewage sludge) **[Fromme 2002].** 2) **4 and 66 ng/L** (surface water)**[Stachel 2003].** 3) **0.295 ug/L** (surface water), **0.007, 0.006 ug/L** (grounwater).**[Rodriguez-Mozaz 2004]** 4) **42-417 ng/L** (surface water) **[Mőder 2007].** 5) **34.95 g/L(± 6.52)** and **35.2g/l (±8.81) g/L** (sewage effluents) **[Ko 2007].** 6) **54–1950 ng/L** (surface water) **[Yamazaki 2015].** 7) **4.69 ng/g dw** (sewage sludge) **[Song 2014].** 10) **6.5–4700 ng/g d.w** (sewage sludge) **[Yu 2015].**
Bisphenol **AP** (BPAP)	1,1-Bis(4-hydroxyphenyl)-1-phenyl-ethane	E) Water solubility range: **1.29e^{-05}** to **5.66e^{-04} mol/L (3,7-164 mg/L) [EPA AP 2018].**	9) **nd – 252 ng/g d.w** (sediments) **[Liao 2012].** 10) **<1.79 ng/g d.w** (sewage sludge) **[Yu 2015].**
Bisphenol **AF** (BPAF)	2,2-Bis(4-hydroxyphenyl)hexafluoropropane	F) **Negligible [Halocarbon 2012].** G) Water solubility range: **4.78e^{-06}** to **8.26e^{-03} mol/L** (**1,6-1277 mg/L**) **[EPA AF 2018].**	8) **<LOD to 1.53 × 10^{4} ng/L** (surface water), **0.520 – 2.00 × 10^{3} ng/g d.w.** (sediments), **<LOD to 331 ng/g d.w**. (soils), **7.82 – 739 ng/g d.w.** (indor dust) **[Song 2012].** 9) **nd – 4.23 ng/g dw.** (sediments) **[Liao 2012].** 7) **0.42–45.1 ng/g d.w.** (sewage sludge) **[Song 2014].** 10) **<1.79–72.2 ng/g d.w.** (sewage sludge) **[Yu 2015].**

Continuation of Table **11**

Bisphenol **B** (BPB)	2,2-Bis(4-hydroxyphenyl)butane	H) Approximate solubility per 100 g: water **<0.1 g**. Approximate solubility per 100 g: acetone **266 g**; benzene **2.3 g**; carbon tetrachloride **<0.1 g**; ether **133 g**; methanol **166 g**; V.M.P. naphtha **<0.1 g [O'Neil 2006].** I) Water solubility range: **1.21e^{-04}** to **1.05e^{-03} mol/L (29-254mg/L) [EPA B 2018].**	9) **10.6 ng/g d.w**. (sediments) **[Liao 2012].** 10) **<1.79–5.60 ng/g d.w.** (sewage sludge) **[Yu 2015].**
Bisphenol **BP** (BPBP)	Bis-(4-hydroxyphenyl) diphenylmethane	J) Water solubility range: **1.65e^{-06}** to **2.10e^{-04} mol/L (0,58-74 mg/L) [EPA BP 2018].**	
Bisphenol **C** (BPC)	2,2-Bis(3-methyl-4-hydroxyphenyl) propane	K) Water solubility range**: 2.91e^{-05}** to **5.79e^{-04} mol/L (7,4-148,4 mg/L) [EPA C 2018].**	
Bisphenol **F** (BPF)	Bis(4-hydroxyphenyl) methane	M) Water solubility: **360 mg/L [Fromme 2002].** N) Ethanol, ether, chloroform, alkali; slightly soluble in DMSO; insoluble in carbon disulfide **[Toxnet 2018].** O) Water solubility range: **1.42e^{-03}** to **3.52e^{-02} mol/L (248-7048 mg/L) [EPA F 2018].**	1) **0.0001 to 0.180 mg/L** (surface water), **0.022 to 0.123 mg/L** (sewage water), **1,2-7,3 ug/kg** (sediments), **4.2 -181 mg/kg** (sewage sludge) **[Fromme 2002].** 6) **2850 ng/L** (surface water) **[Yamazaki 2015].** 7) **3.84 ng/g** (sewage sludge) **[Song 2014].** 9) <**LOQ to 9650 ng/g d.w.** (sediments) **[Liao 2012].** 10) <**1.79–242 ng/g d.w.** (sewage sludge) **[Yu 2015].**
Bisphenol **E** (BPE)	1,1-Bis(4-hydroxyphenyl) ethane	L) Water solubility range: **9.68e^{-04} to 4.90e^{-03} mol/L** (**270-1049 mg/L**) **[EPA E 2018].**	7) **0.06–167 ng/g d.w.** (sewage sludge) **[Song 2014].**

Continuation of Table **11**

Bisphenol **S** (BPS)	Bis(4-hydroxyphenyl) sulfone	P) Decreased according to the following order: acetone > acetonitrile > ethyl acetate >1-butanol > (methanol, ethanol, n-propanol, 2-methyl-1-propanol) > isopropyl alcohol. **[Yong 2016].** R) Water solubility range: **2.73e^{-03}** to **2.83e^{-02} mol/L** (**945,8-9805,1 mg/L**) **[EPA S 2018].**	7) **3.02 ng/g** (sewage sludge) **[Song 2014].** 9) **<LOQ to 1970 ng/g d.w.** (sediments) **[Liao 2012].** 10) <**1.79–1480 ng/g d.w.** (sewage sludge) **[Yu 2015].** 11) **0.28-67 ng/L** (surface water), **0.61-46 ng/L** (surface water), **0.22-52 ng/L** (surface water) **[Jin H 2016].**
Bisphenol **Z** (BPZ)	1,1-Bis(4-hydroxyphenyl)-cyclohexane	S) Water solubility range: **1.41e^{-05}** to **1.72e^{-04}** mol/L (3,7- 46,1 mg/L) **[EPA Z 2018].**	9) **63.3 ng/g d.w.** (sediments) **[Liao 2012].** 10) **<1.79–66.7 ng/g d.w.** (sewage sludge) **[Yu 2015].**
Bisphenol **FL** (BPFL)	4,4'-(9-fluorenylidene) diphenol	T) Water solubility range:**3.36e^{-08}** to **1.41e^{-05} mol/L (0,01-4,9 mg/L) [EPA FL 2018].**	

LOD - limit of detection

d.w - dried weight

LOQ - limit of quantification

TABLE 12. Bisphenols (A, B, S) degradation matrix for all cultivation media and times investigated (time unit: hour). Target components contents was measured as the % of initial peak heights measured at analytical wavelengths 280 nm (arbitrary units).

% of initial peak heights

		TIME 0	TIME 24	TIME 48	TIME 72	TIME 101	TIME 137	TIME 185	TIME 209	TIME 257
		1	2	3	4	5	6	7	8	9
TAP WATER BPS	**1**	100	67.95	62.32	63.25	42.8	49.43	53.87	43.62	35.31
TAP WATER BPA	**2**	100	58.92	59.7	55.7	59.92	62.27	46.91	46.3	41.29
TAP WATER BPB	**3**	100	69.03	23.96	18.94	15.8	45.26	76.69	17.16	0.77
TAP WATER + DUCKWEED BPS	**4**	100	67.95	66.5	38.28	38.17	36.85	42.89	33.45	27.8
TAP WATER + DUCKWEED BPA	**5**	100	68.12	66.16	42.64	55.65	52.88	43.75	40.49	37.53
TAP WATER + DUCKWEED BPB	**6**	100	30.85	30.07	14.69	15.78	59.2	68.87	18.52	14.28
TAP WATER + CD BPS	**7**	100	55.74	60.05	42.69	28.44	29.69	37.87	30.48	26.3
TAP WATER + CD BPA	**8**	100	59.93	63.92	48.55	45.43	46.67	39.67	37.65	35.51
TAP WATER + CD BPB	**9**	100	35.39	38.04	24.77	18.79	12.01	58.56	19.98	18.1
TAP WATER + CD + DUCKWEED BPS	**10**	100	70.06	70.41	62.75	44.48	44.54	47.59	39.55	40.49
TAP WATER + CD + DUCKWEED BPA	**11**	100	75.97	75.35	69.55	59.92	62.8	51.58	49.59	49.04
TAP WATER + CD + DUCKWEED BPB	**12**	100	45.98	43.44	34.58	24.01	66.23	78.54	25.65	22.95

Continuation of Table **12**

								% of initial peak heights		
TAP WATER + GLUCOSE BPS	**13**	100	62.37	72.12	49.12	44.07	40.25	49.15	39.63	36.08
TAP WATER + GLUCOSE BPA	**14**	100	59.26	66.82	50.26	56.34	56.66	45.25	45.61	41.05
TAP WATER + GLUCOSE BPB	**15**	100	25.03	25.55	19.26	18.93	0	71.81	12.72	12.27
TAP WATER + GLUCOSE + DUCKWEED BPS	**16**	100	57.67	52.23	32.66	34.57	29.14	37.36	30.18	30.77
TAP WATER + GLUCOSE + DUCKWEED BPA	**17**	100	25.33	14.43	13.27	14.35	12.04	10.38	9.92	8.81
TAP WATER + GLUCOSE + DUCKWEED BPB	**18**	100	36.99	28.72	16.58	20.7	0	48.4	12.72	10.81

TABLE 13. Bisphenols (A, B, S) degradation matrix for all cultivation media and times investigated(time unit: hour). Target components contents was measured as the peak heights measured at analytical wavelengths 280 nm (arbitrary units).

peak heights

		TIME 0	TIME 24	TIME 48	TIME 72	TIME 101	TIME 137	TIME 185	TIME 209	TIME 257
		1	2	3	4	5	6	7	8	9
TAP WATER BPS	**1**	3555.5	2416	2216	2249	1522	1757.5	1915.5	1551	1255.5
TAP WATER BPA	**2**	1149	677	686	640	688.5	715.5	539	532	474.5
TAP WATER BPB	**3**	1293.5	893	310	245	204.5	585.5	992	222	10
TAP WATER + DUCKWEED BPS	**4**	5200	3533.5	3458	1991	1985	1916.5	2230.5	1739.5	1446
TAP WATER + DUCKWEED BPA	**5**	1352	921	894.5	576.5	752.5	715	591.5	547.5	507.5
TAP WATER + DUCKWEED BPB	**6**	1333.5	411.5	401	196	210.5	789.5	918.5	247	190.5
TAP WATER + CD BPS	**7**	5725	3191.5	3438	2444.5	1628.5	1715.5	2168.5	1745.5	1506
TAP WATER + CD BPA	**8**	1779.5	1066.5	1137.5	864	808.5	834	706	668.5	632
TAP WATER + CD BPB	**9**	1963.5	695	747	486.5	369	236	1150	392.5	355.5
TAP WATER + CD + DUCKWEED BPS	**10**	4350	3048	3063	2730	1935	1937.5	2070.5	1720.5	1761.5
TAP WATER + CD + DUCKWEED BPA	**11**	1355	1029.5	1021	942.5	812	851	699	672	664.5
TAP WATER + CD + DUCKWEED BPB	**12**	1461.5	672	635	505.5	351	968	1148	375	335.5

Continuation of Table **13**

										peak heights
TAP WATER + GLUCOSE BPS	**13**	4150	2588.5	2993	2038.5	1829	1670.5	2040	1633.5	1497.5
TAP WATER + GLUCOSE BPA	**14**	1249.5	740.5	835	628	704	708	565.5	570	513
TAP WATER + GLUCOSE BPB	**15**	1352	338.5	345.5	260.5	256	0	971	172	166
TAP WATER + GLUCOSE + DUCKWEED BPS	**16**	5200	2999	2716	1698.5	1798	1515.5	1943	1569.5	1600.5
TAP WATER + GLUCOSE + DUCKWEED BPA	**17**	1317.5	907.5	750.5	690.5	746.5	626.5	540	516	458.5
TAP WATER + GLUCOSE + DUCKWEED BPB	**18**	1178.5	436	338.5	195.5	244	0	570.5	150	127.5

7. FIGURES

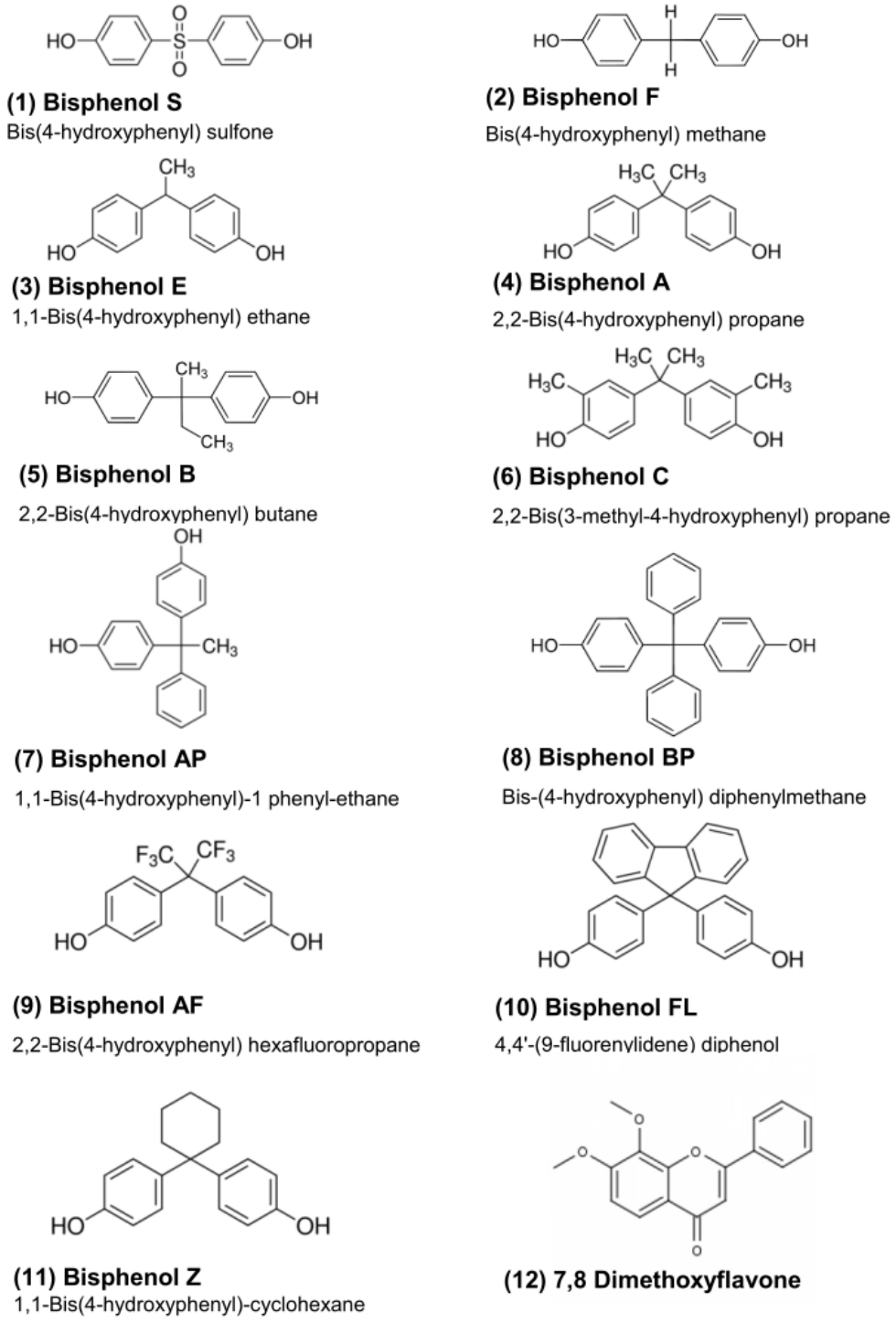


FIGURE 1. Chemical structures of bisphenols and internal standard substance (7,8-dimethoxyflavone) investigated.

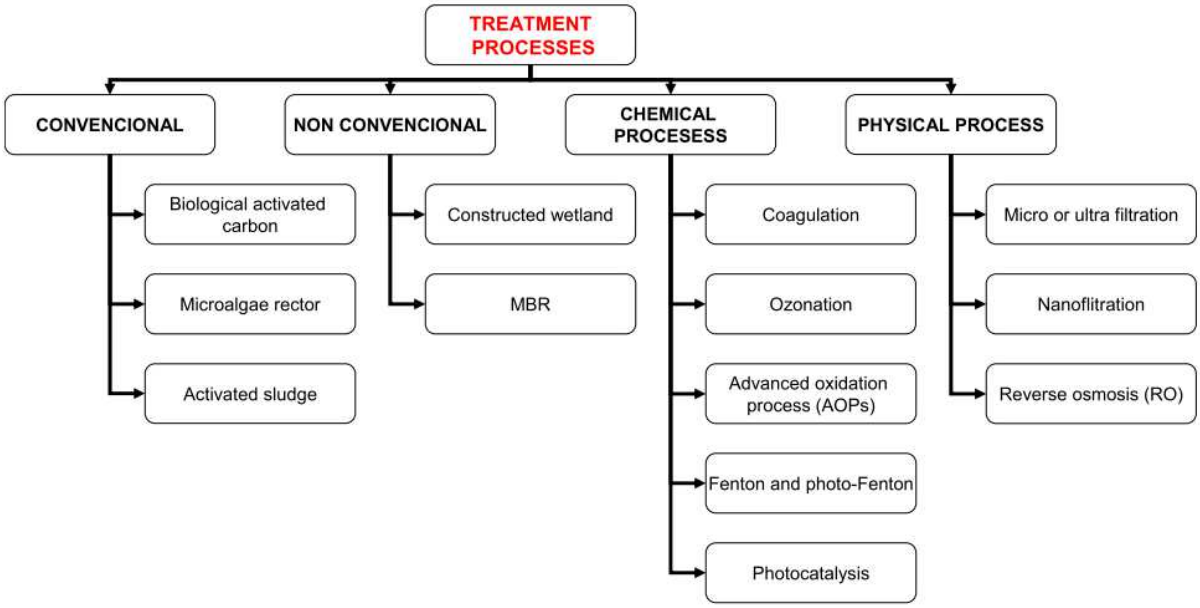


FIGURE 2. General classification of wastewater treatment performed under large scale technological processes conditions.

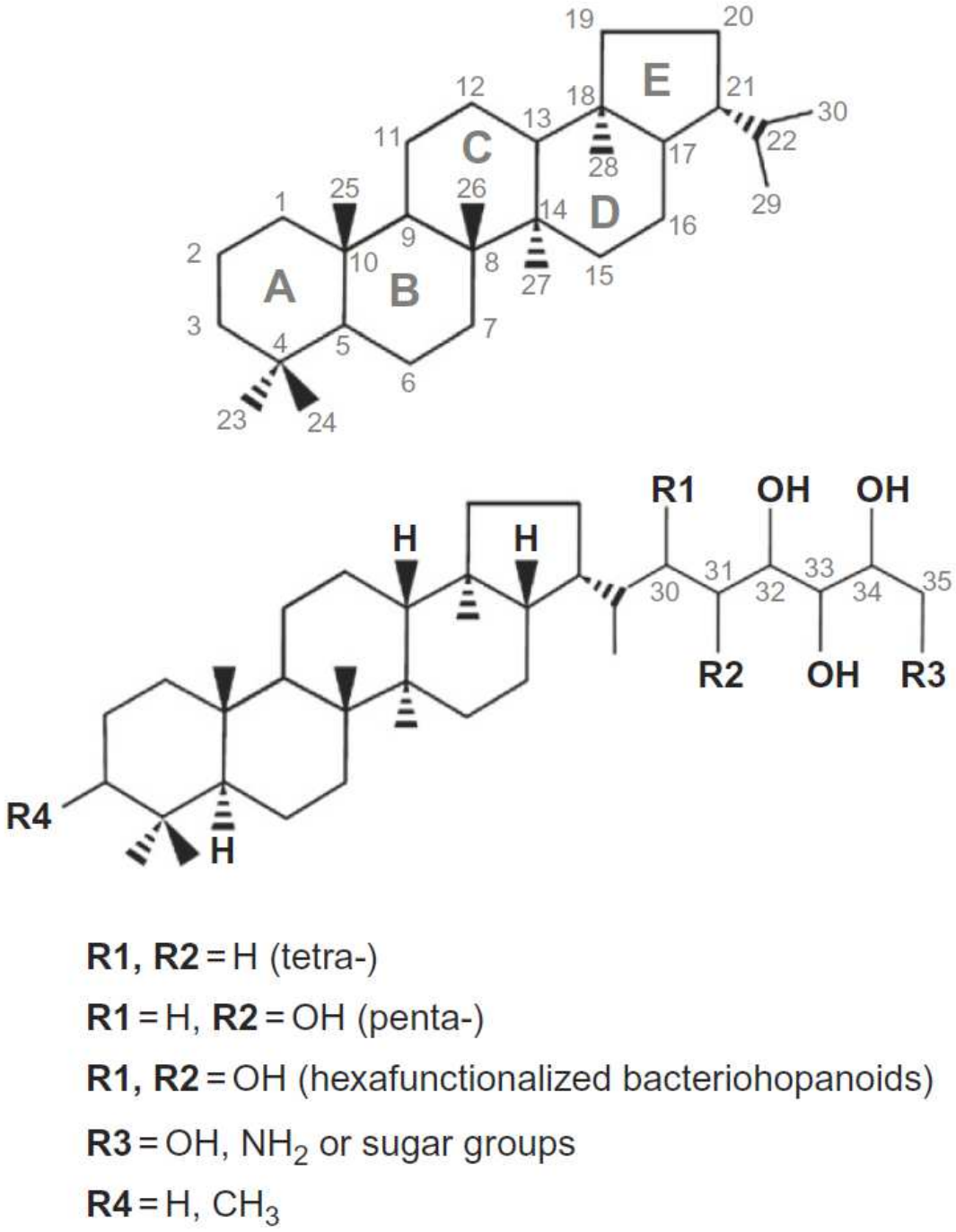


FIGURE 3. Typical carbon atoms numbering and chemical structures of hopane skeleton (top) as well as bacteriohopanoids (bacteriohopanepolyols; BHPs) molecules (bottom). **[Zarzycki[A] 2017]** Copyright © 2017 Elsevier, reprinted with permission.

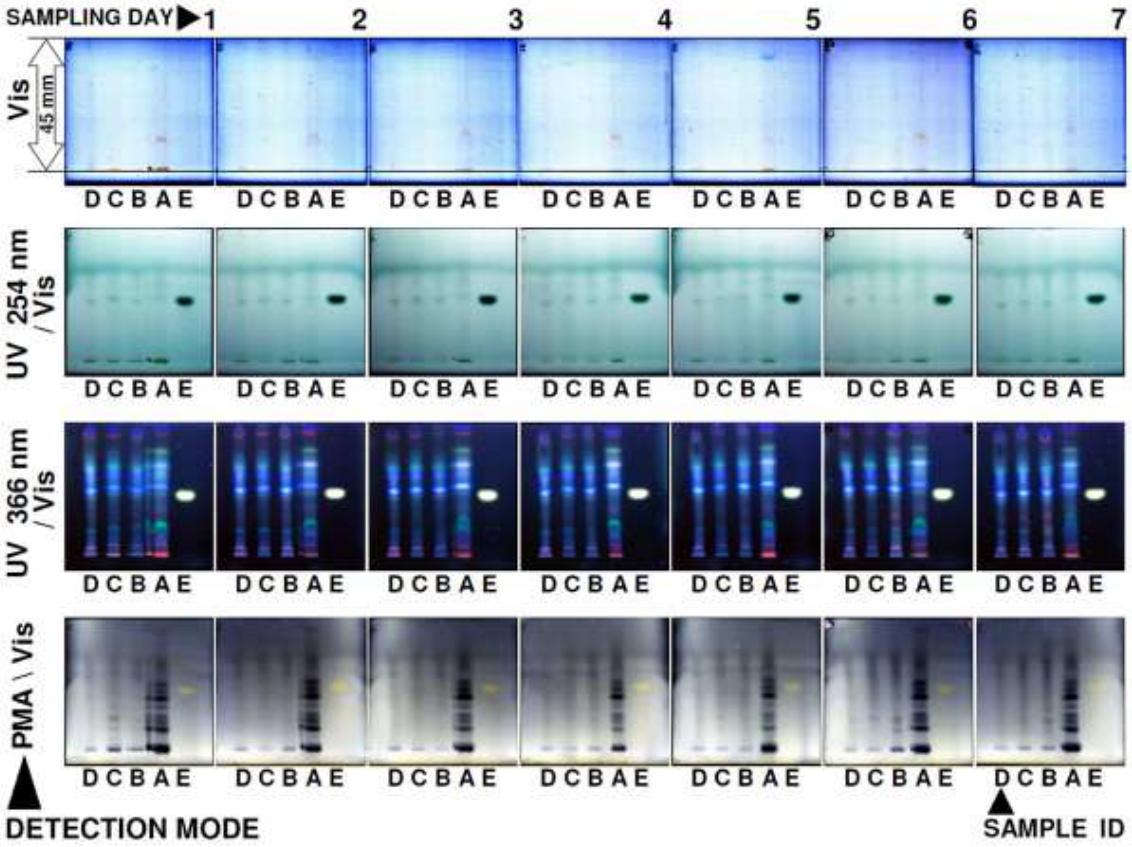


FIGURE 4. Array of micro-TLC plates with separated SPE extracts of liquid samples collected from the JSTP. Sample lanes were visualized using multiple detection modes: (top to bottom) visible light, fluorescence quenching, fluorescence, and PMA derivatization. Samples: A, untreated wastewater; B, denitrification chamber; C, nitrification chamber; D, treated wastewater; and E, the retention marker substance 7,8-DMF (1 µg/spot). **[Ślączka 2017]** Copyright JAOAC © 2017, reprinted with permission.

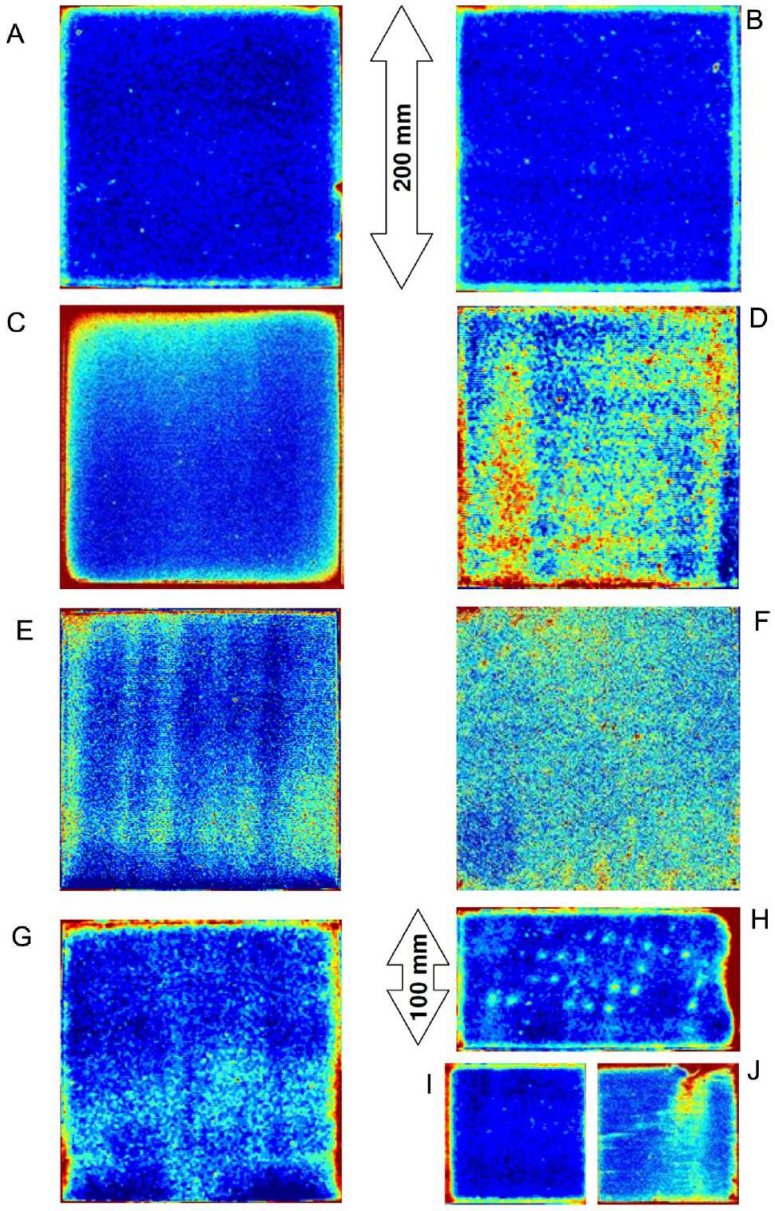


FIGURE 5. Stationary phases patterns on different TLC plates using thermovision detection and signal processing protocol (3D filtration). Color changes from blue to red correspond to increase of the adsorbent layer thickness. Plates ID: (A) TLC silica gel 60; (B) TLC silica gel 60WF 254 S; (C) TLC silica gel 60 F 254; (D) TLC aluminum oxide 60 F 254 Type E; (E) TLC cellulose; (F) chromatography paper, cellulose Whatman 1CHR; (G) TLC; polyamide 11F 254 ; (H) HPTLC RP-18W; (I) silica gel 60 RP-18WF 254 S; and (J) silica gel 60 RP-18F 254 S. **[Suszyński 2014]** Copyright Elsevier © 2014, reprinted with permission.

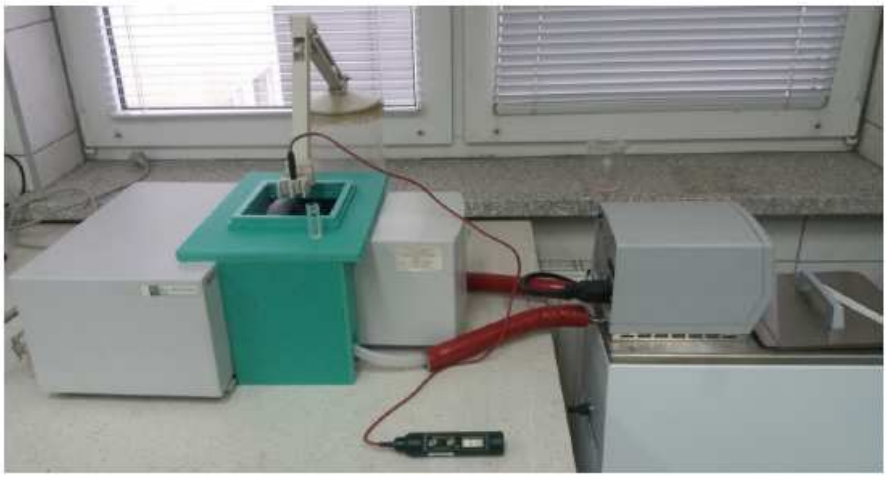


FIGURE 6. Spectrophotometer hardware setup for temperature controlled experiment with home-made thermostatic module.

FIGURE 7. Temperature controlled inclusion chromatography: hardware setup for HPLC-DAD system. Yellow arrow indicate insulated water jacket containing HPLC column equilibrated with cyclodextrin modified mobile phase.

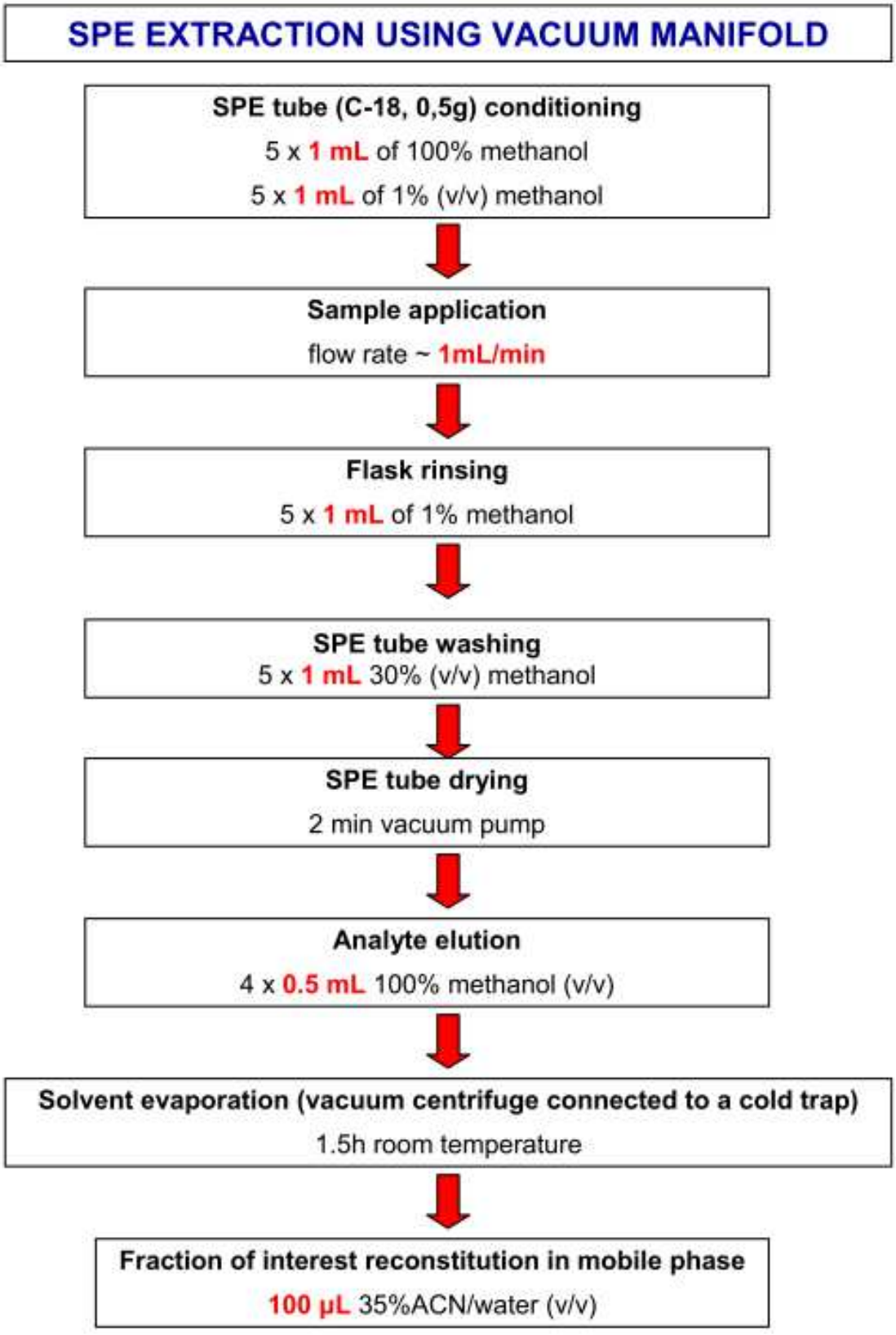


FIGURE 8. General scheme of solid-phase extraction procedure.

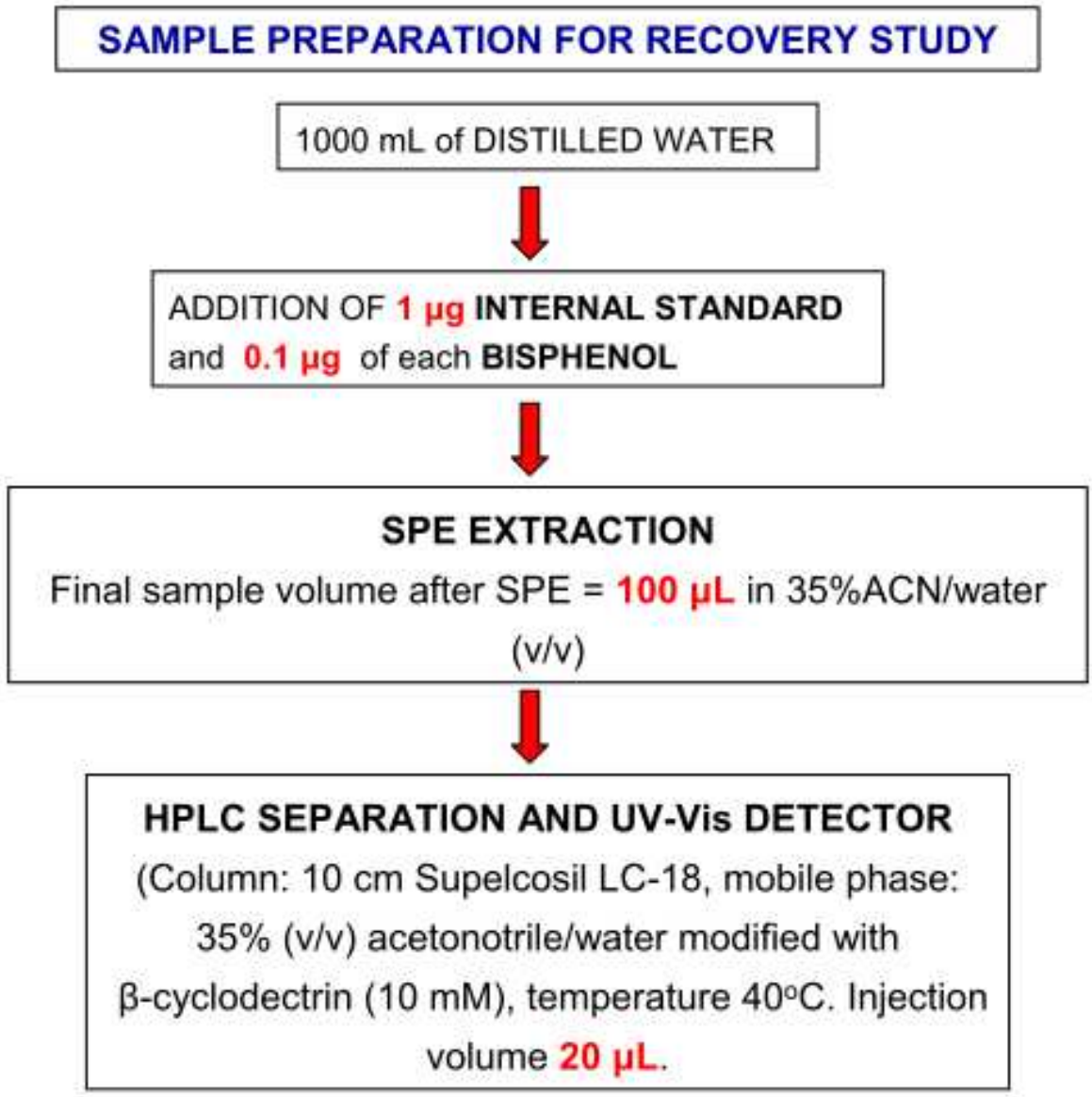


FIGURE 9. General scheme for recovery study of bisphenols

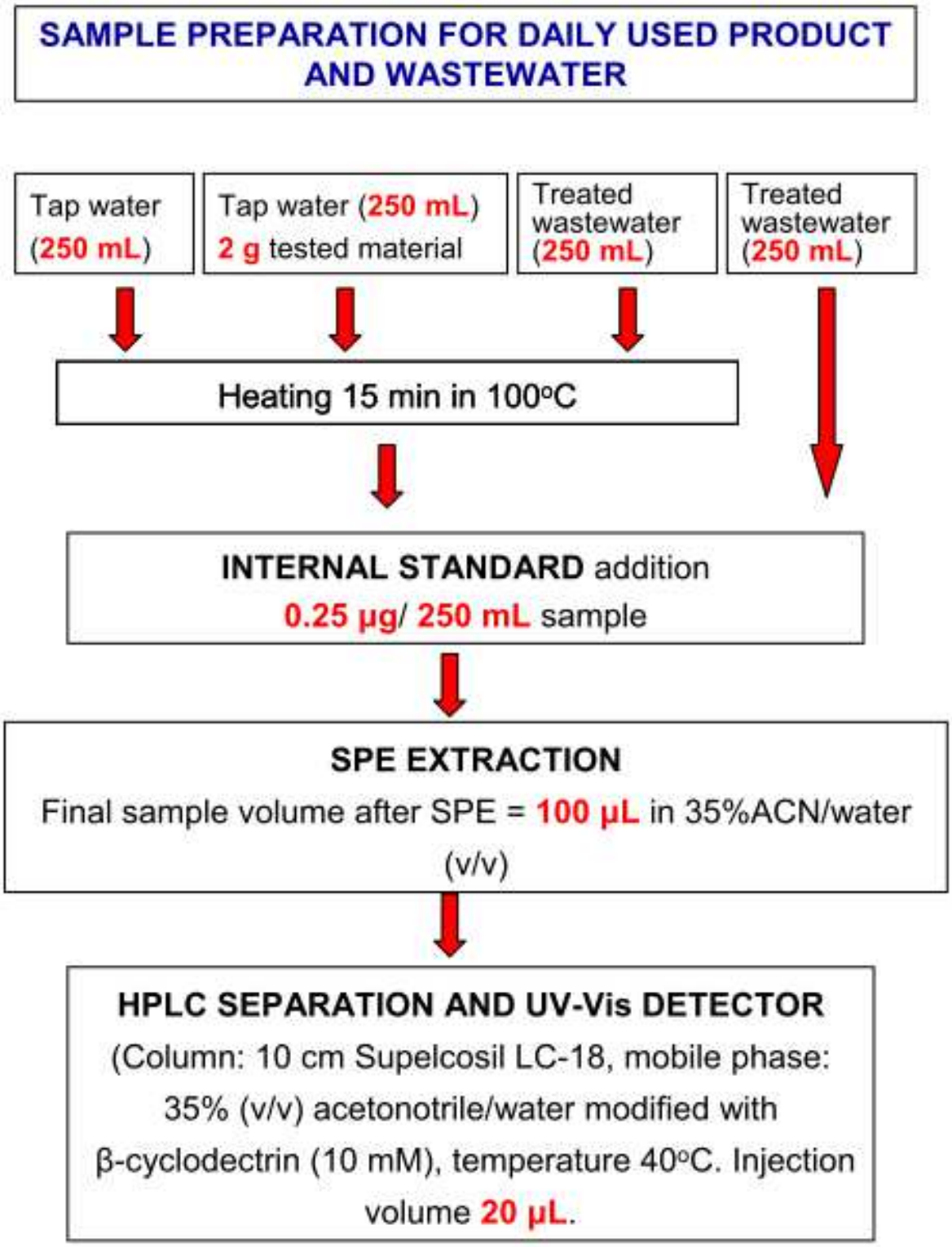
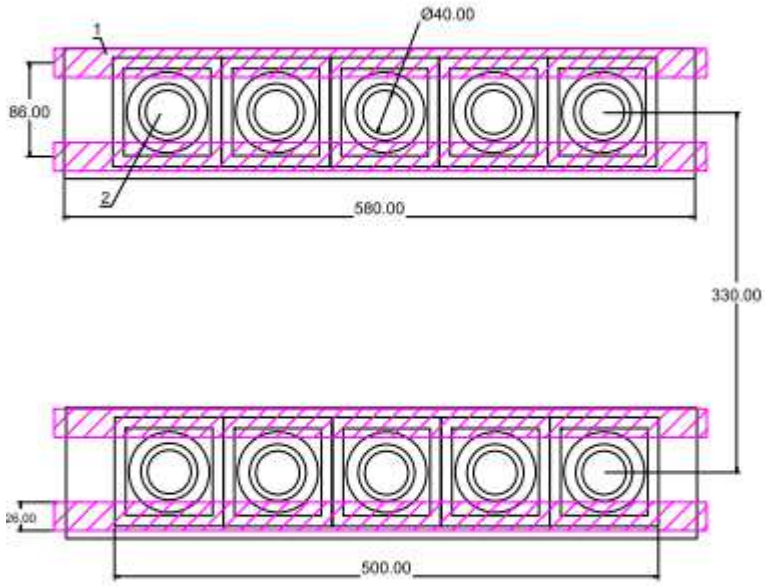


FIGURE 10. General scheme for real samples preparation protocol allowing quantitative analysis of daily use and environmental samples**.**

FIGURE 11. Duckweed sampling location spot (**A**; N 54° 11.579' E 016° 11.021') and water container for duckweed biomass breeding (**B**, **C**) (All photography copyrights by Paweł. K. Zarzycki © 2012 with permission).

A



B

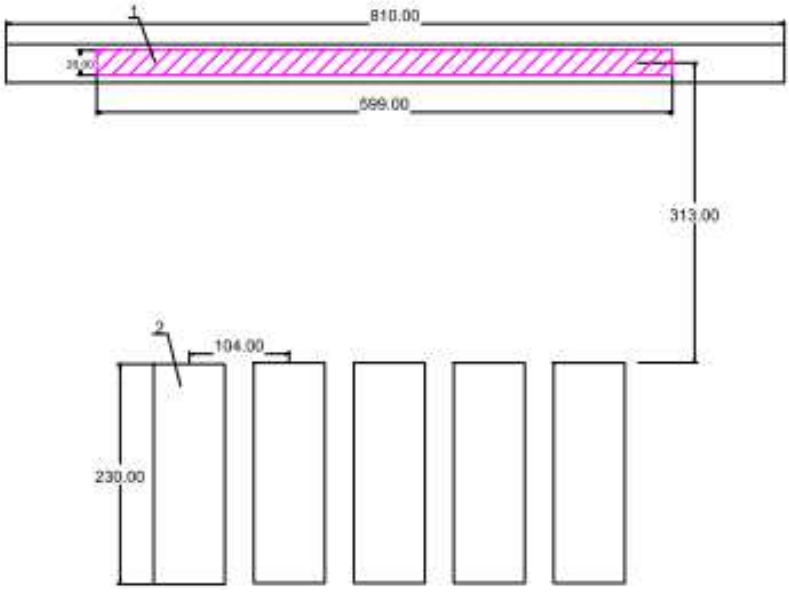


FIGURE 12. General scheme of temperature controlled cultivation chambers (A - top view; B - side view). 1 LED light tubes, 2 Dewar chamber.

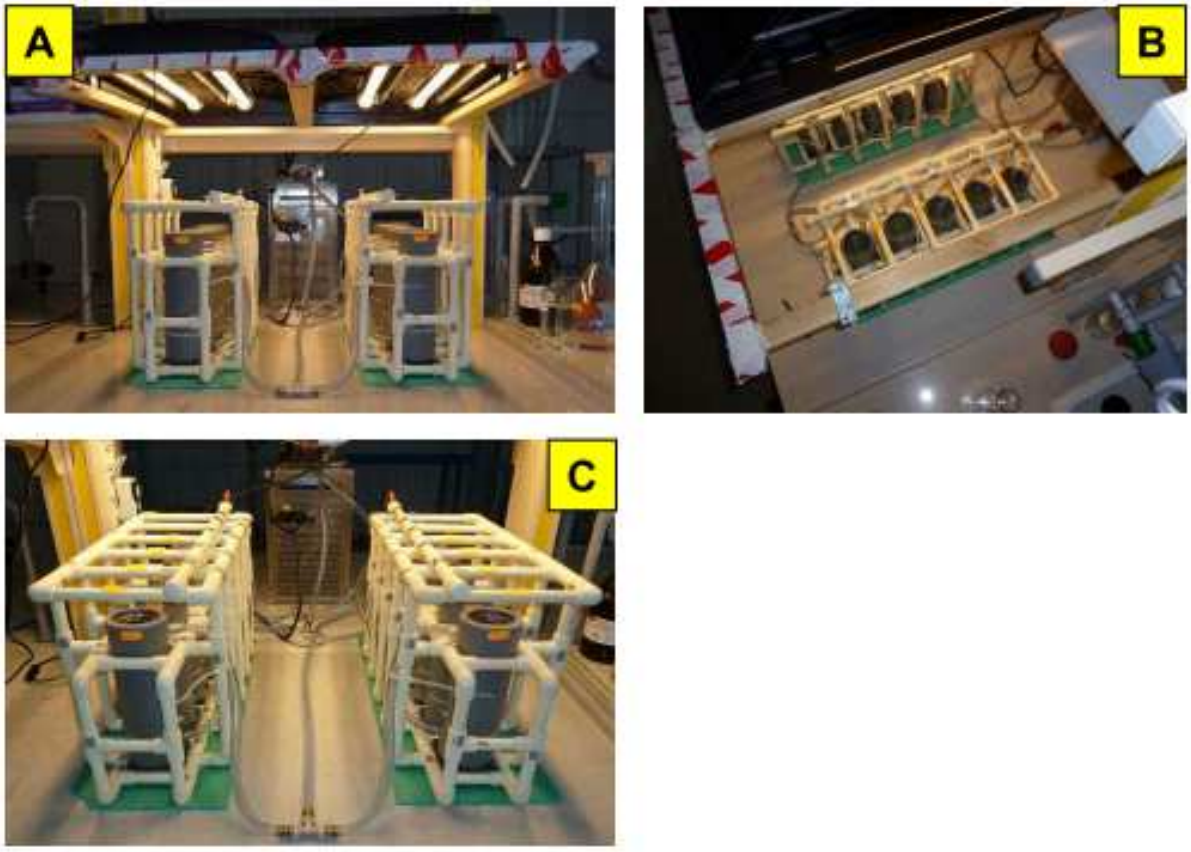


FIGURE 13. Temperature controlled chambers and LED lamps spatial arrangement for duckweed and bisphenols degradation experiments.

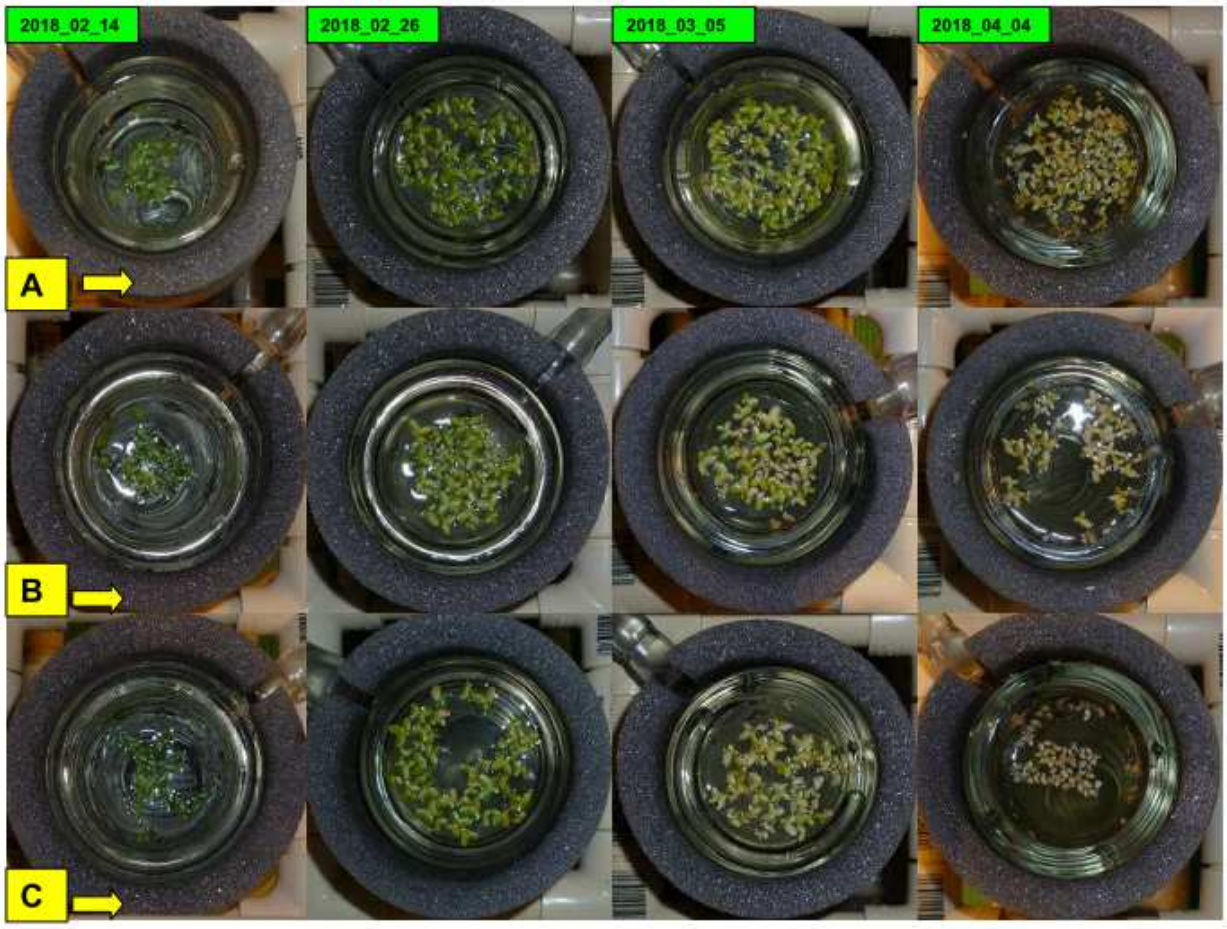


FIGURE 14. Rate of dieback of duckweed cultures depending of type of medium used. **A** tap water , **B** tap water and 1 mM β-CD, **C** tap water and 7 mM glucose.

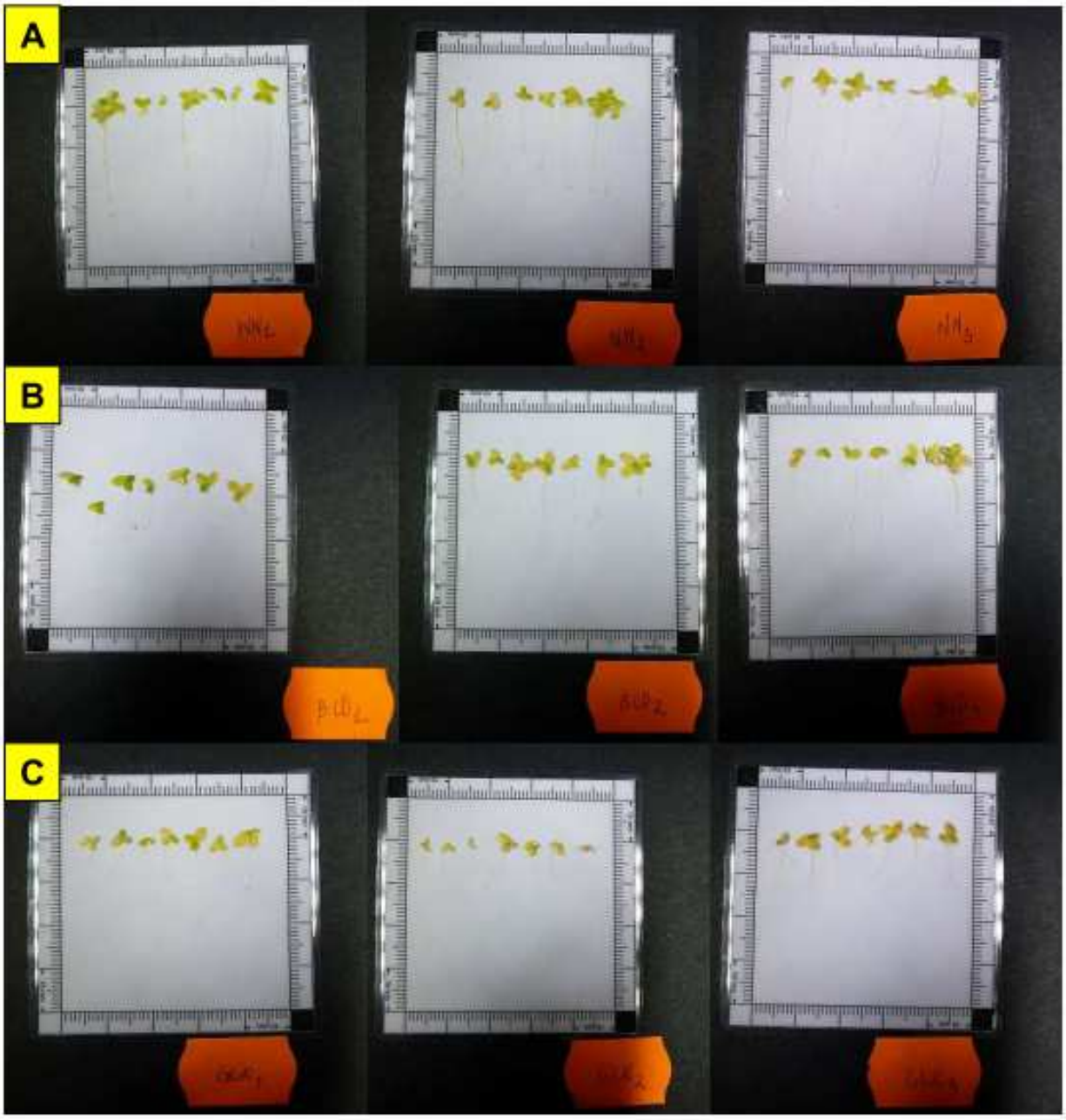
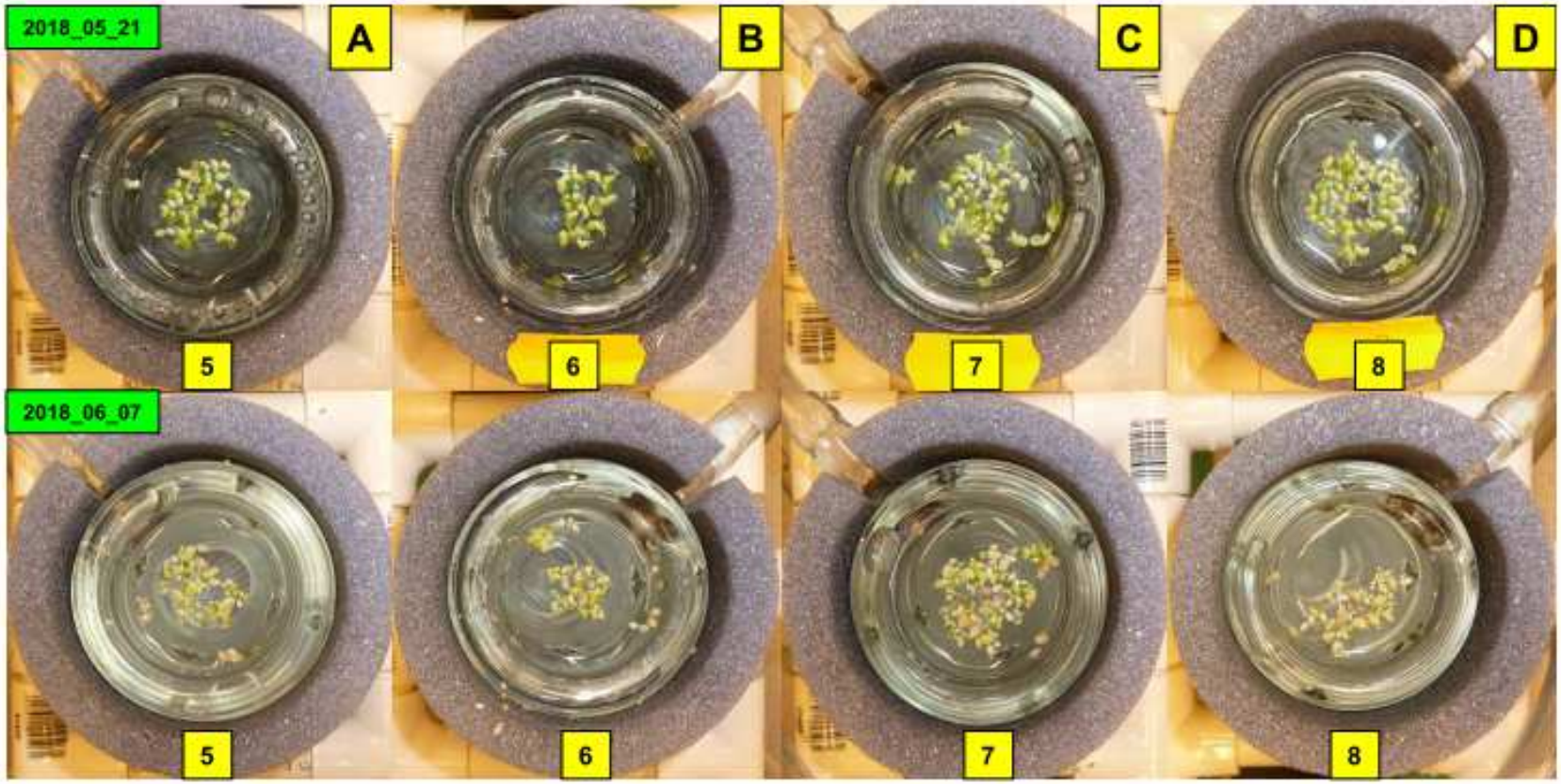


FIGURE 15. Differences in the length of duckweed roots depending on the used medium measured after 22 days of cultivation. Sample labels: **A** tap water, **B** tap water and β-CD (1 mM), **C** tap water and glucose (7 mM).



FIGIRE 16. General view of Dewar chambers containing duckweed cultures at the beginning of degradation experiment (top) and after 257 hours of experiment (bottom). **A**- tap water and ethanol (200uL), **B**- tap water and bisphenols (200 uL at concentration 1 mg/L), **C**- tap water and bisphenols (200 uL at concentration 1 mg/L) and β- cyclodextrin (1mM), **D**- tap water bisphenols (200 uL at concentration 1 mg/L) and glucose (7 mM).

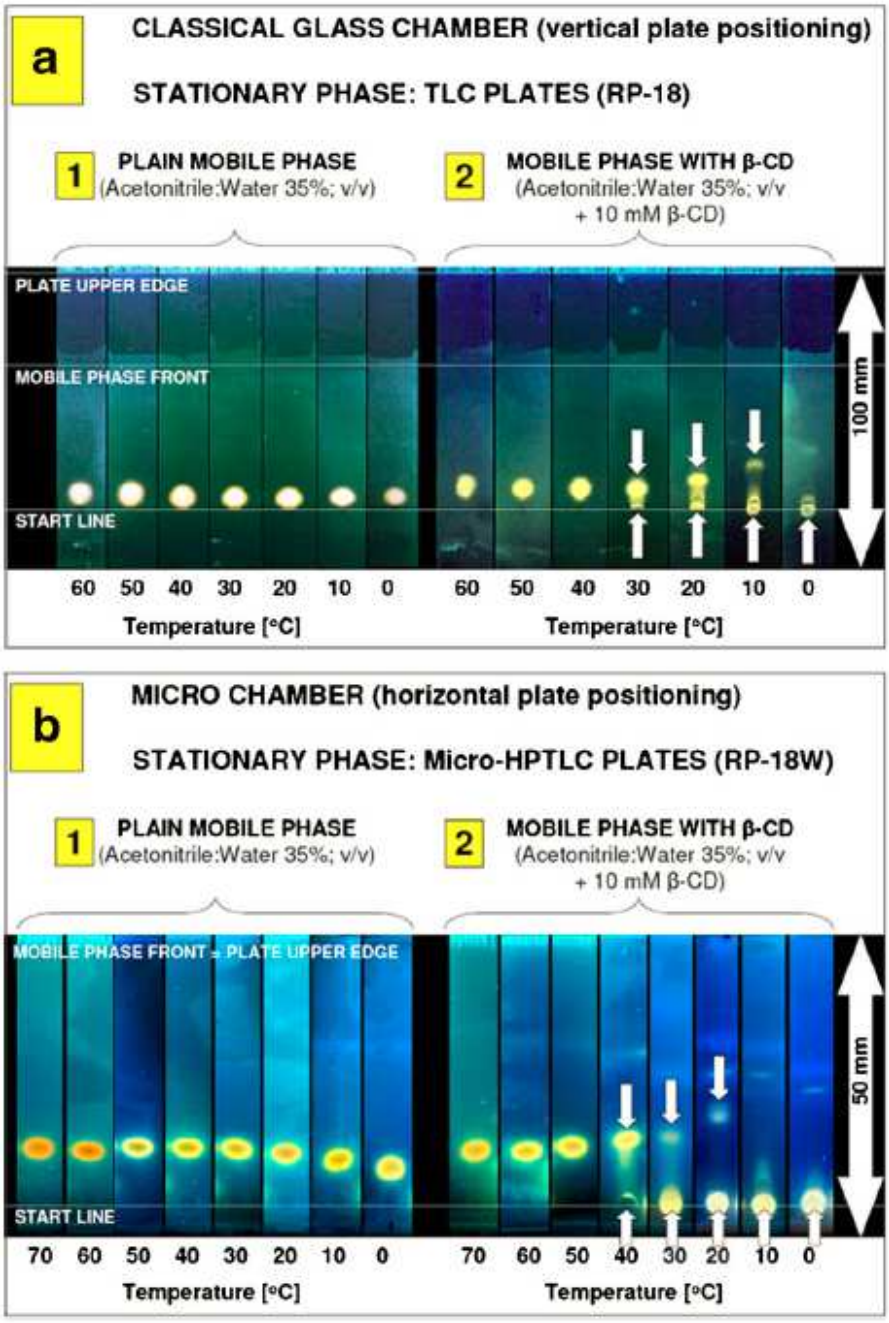


FIGURE 17. Chromatographic analysis of racemic mixture of 1-acenaphthenol performed under thermostatted conditions at different temperatures on RP-18 F254S classical TLC plates (a; vertical development) and RP-18 WF254S HPTLC microplates (b; horizontal development) using simple binary acetonitrile: water mobile phase (1) and modified with β-cyclodextrin at concentration of 10 mM (2). Small arrows indicate the main spots separated. Detection mode: fluorescence (366 nm/Vis). **[Ohta 2017]** Copyright Springer © 2017, reprinted with permission.

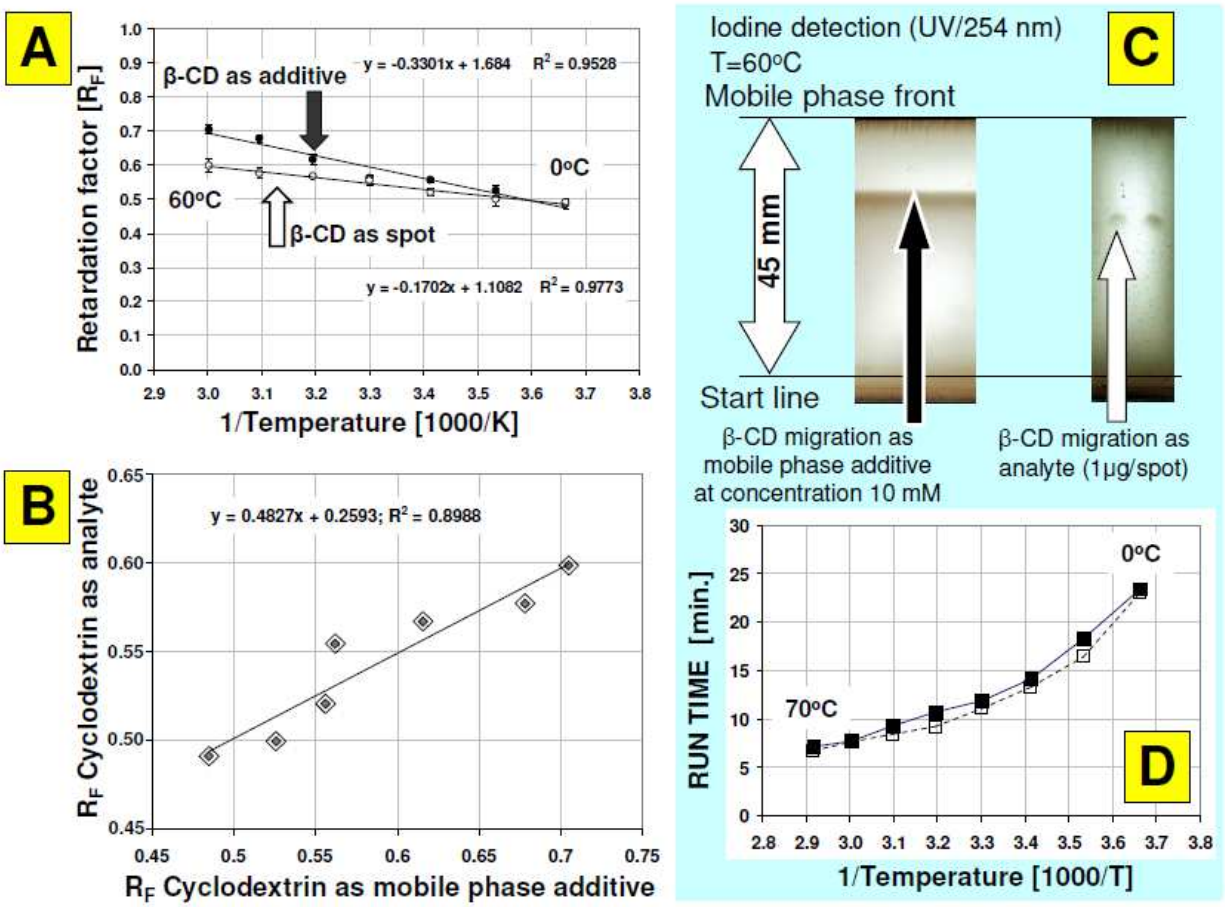


FIGURE 18. Results of chromatographic analysis (planar chromatography) of β-cyclodextrin eluted as analyte applied to the start line in form of spot (**β-CD spot position**) or as mobile phase additive at concentration of 10 mM (**β-CD front position**) on HPTLC RP-18 WF254S plates at different temperatures using 35% (v/v) acetonitrile in water mobile phase. Presented graphs correspond to: retention data (**A**), correlation between two retention modes (**B**), examples of microchromatograms (**C**), and run time for mobile phase migration at distance of 45 mm (**D**) measured for plain mobile phase (**empty squares**) and eluent modified with 10 mM β-CD (**black squares**). **[Ohta 2017]** Copyright Springer © 2017, reprinted with permission.

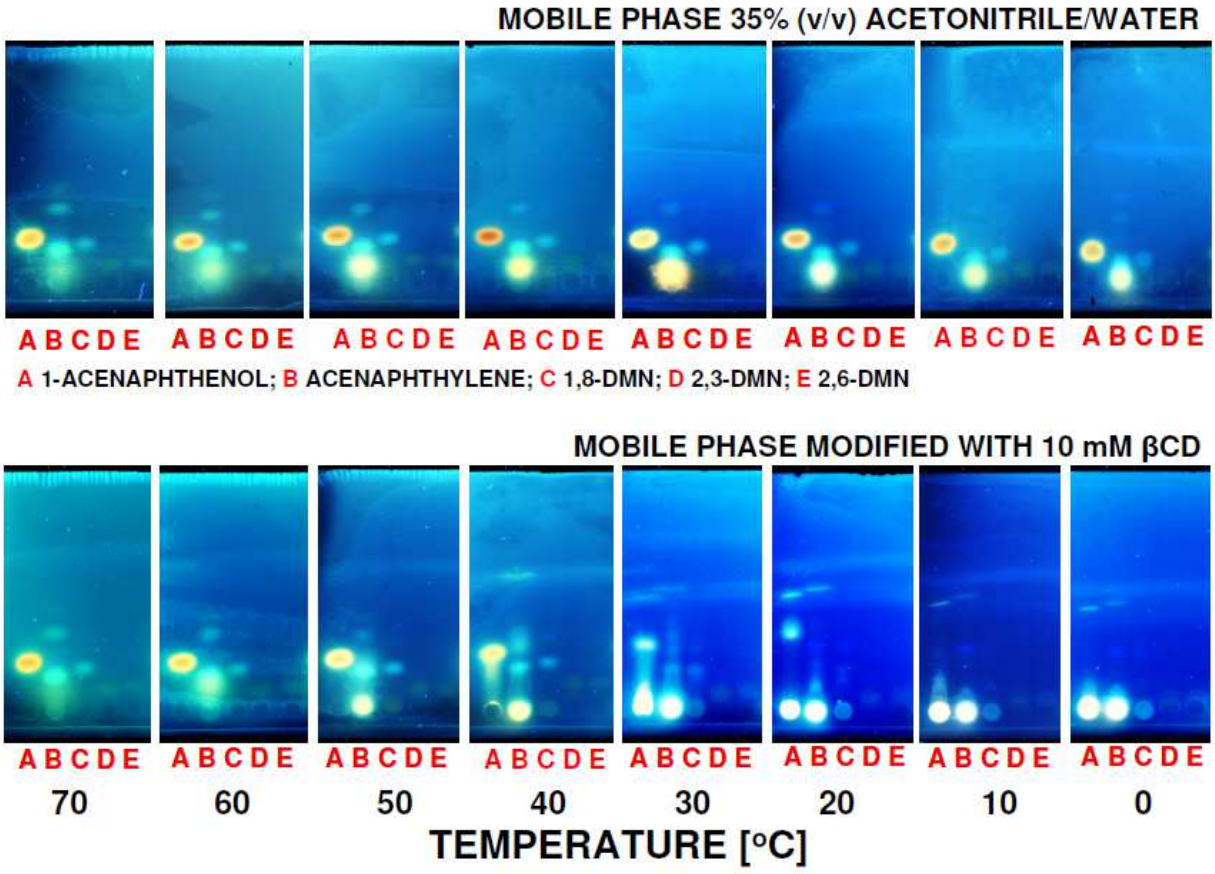


FIGURE 19. Planar chromatographic behavior of selected PAHs at different temperatures using mobile phases with and without β-cyclodextrin additive. Lane labels: 1-acenaphthenol (**A**); acenaphthylene (**B**); 1,8-DMN (**C**); 2,3-DMN (**D**); 2,6-DMN (**E**).

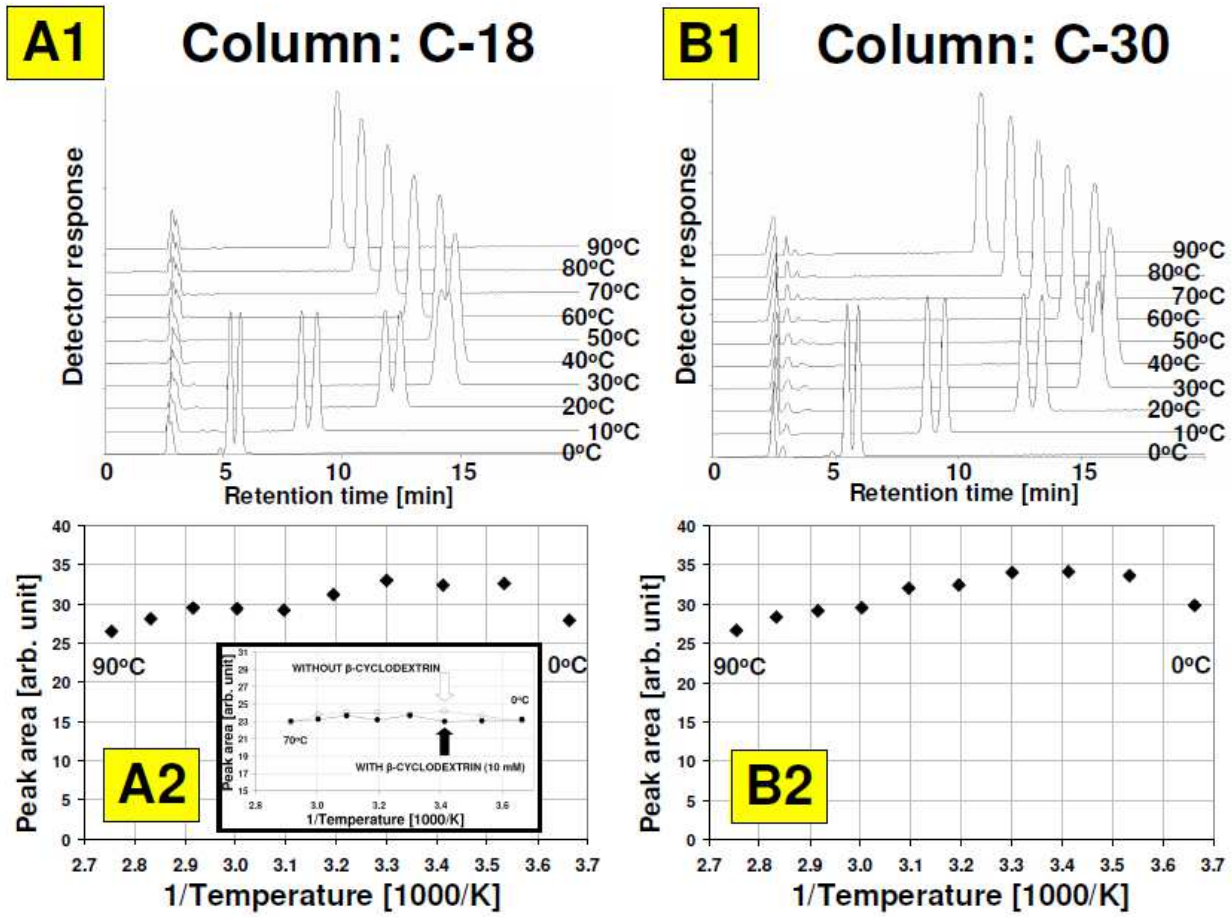


FIGURE 20. Column chromatographic (HPLC) separation of acenaphthenol enantiomers involving β-CD mobile phase (acetonitrile:water; 35:65, v/v) additive using C-18 (**A1**) and C-30 (**B1**) ***[S2]*** stationary phases (both 15 cm long columns; mobile phase flow 0.5 mL/min) at different temperatures. Bottom graphs reveal peak integration results (**A2**, **B2**; where peak areas for separated enantiomers were summarized). Graph inserted within plot A2 is related to acenaphthenol peak area data obtained on Supelcosil LC-18 column (10 cm, flow 1 mL/min) without and with β-cyclodextrin additive (labeled as empty circles and black dots, respectively). **[Ohta 2017]** Copyright Springer © 2017, reprinted with permission.

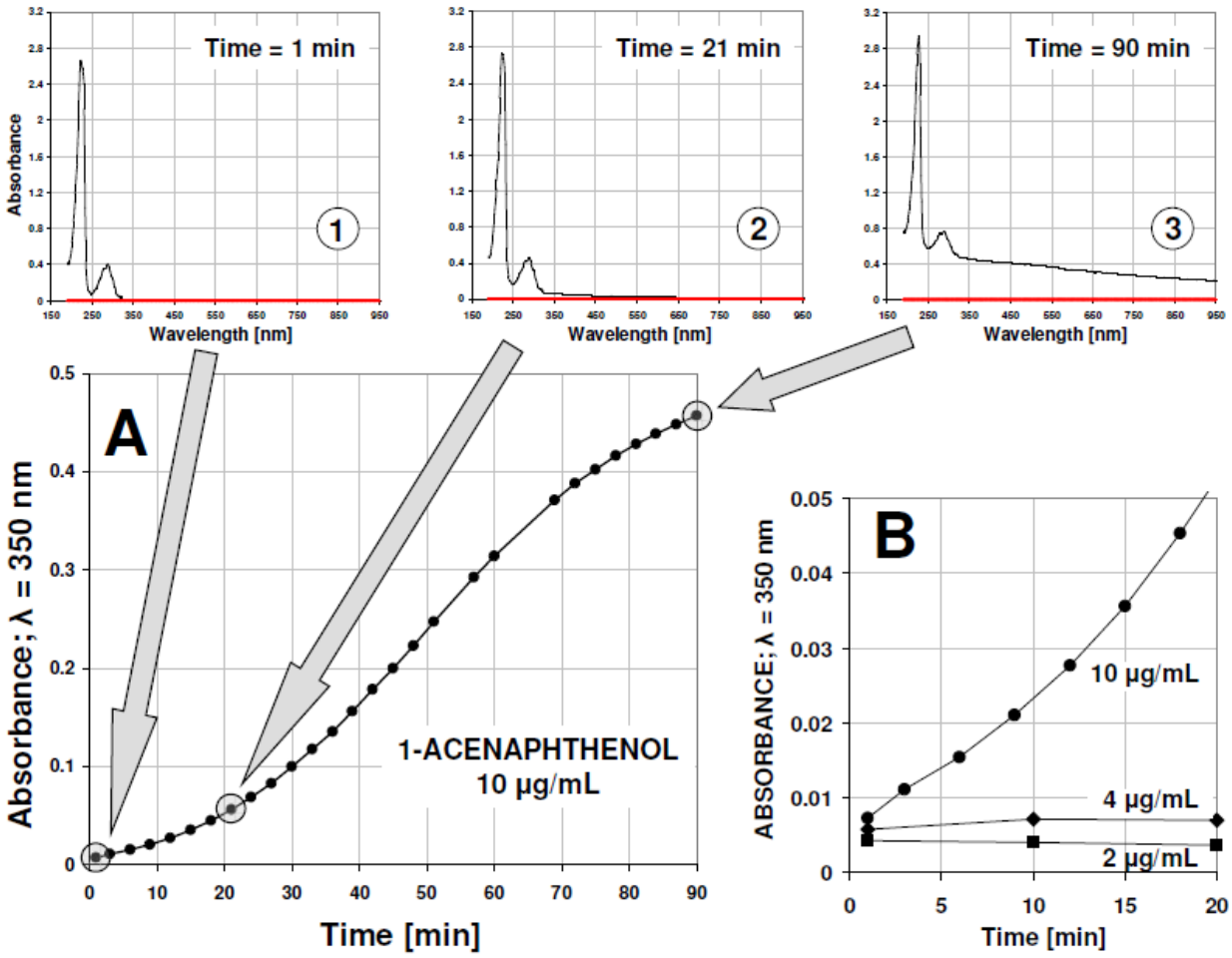


FIGURE 21. UV-Vis detection of crystallization phenomenon observed for 1-acenaphthenol and β-cyclodextrin complex in acetonitrile:water (35:65, v/v) liquid phase (measurement temperature: 20.0 ± 0.1 °C). a Background increase monitored at 350 nm for 1-acenaphthenol at concentration of 10 µg/mL and 10 mM β-CD (UV-Vis spectra presented at top were recorded for given crystallization times: 1, 21, and 90 min.). b Comparison of solid complex creation for different 1-acenaphthenol concentrations 2, 4, and 10 µg/ mL using β-cyclodextrin at concentration of 10 mM. **[Ohta 2017]** Copyright Springer © 2017, reprinted with permission.

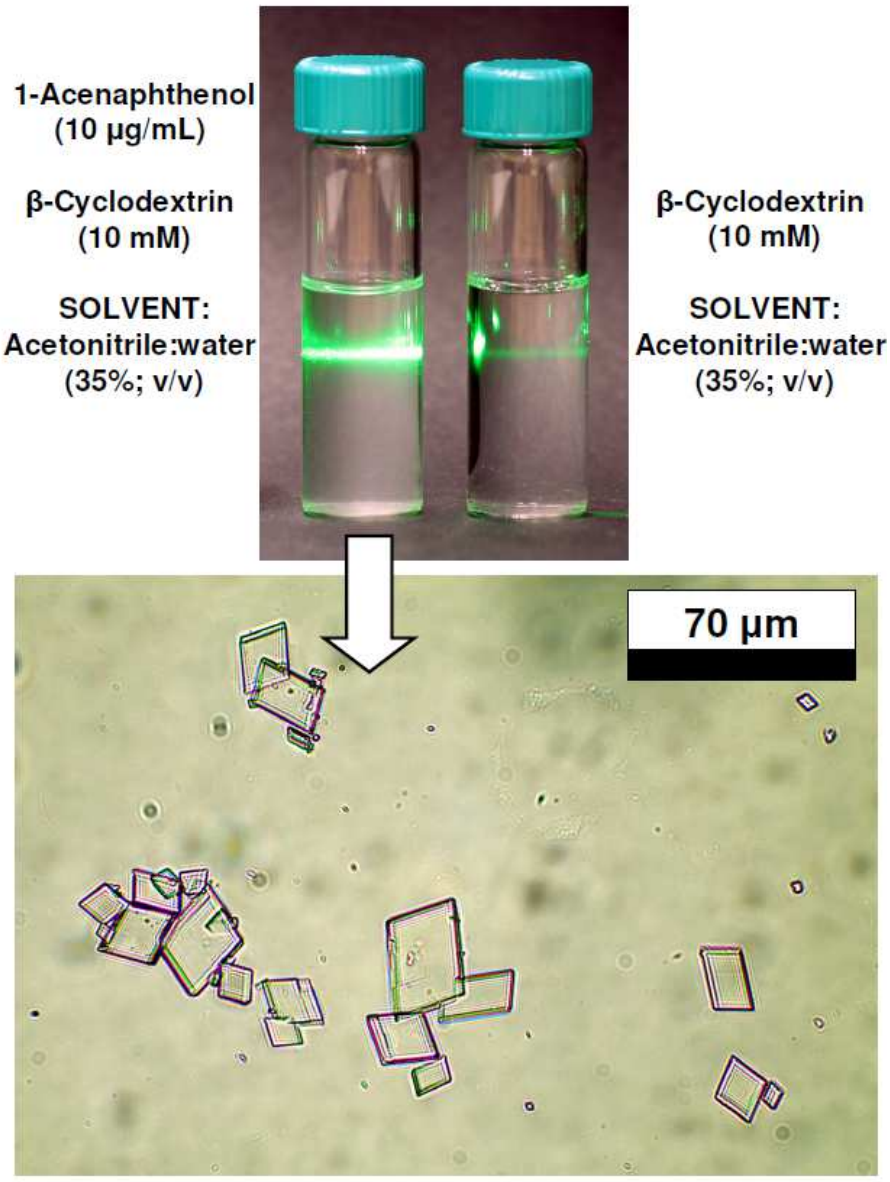


FIGURE 22. Visible light scattering (green laser beam; 532 nm; <10 mW) observed for solid particles of supramolecular complex generated from 1-acenaphthenol (10 µg/mL) and β-cyclodextrin (10 mM) mixture in acetonitrile:water (35:65, v/v), liquid phase, after 3 days at room temperature (22 ± 1 °C) conditions (top) and optical microscope view of precipitated crystals (bottom). **[Ohta 2017]** Copyright Springer © 2017, reprinted with permission.

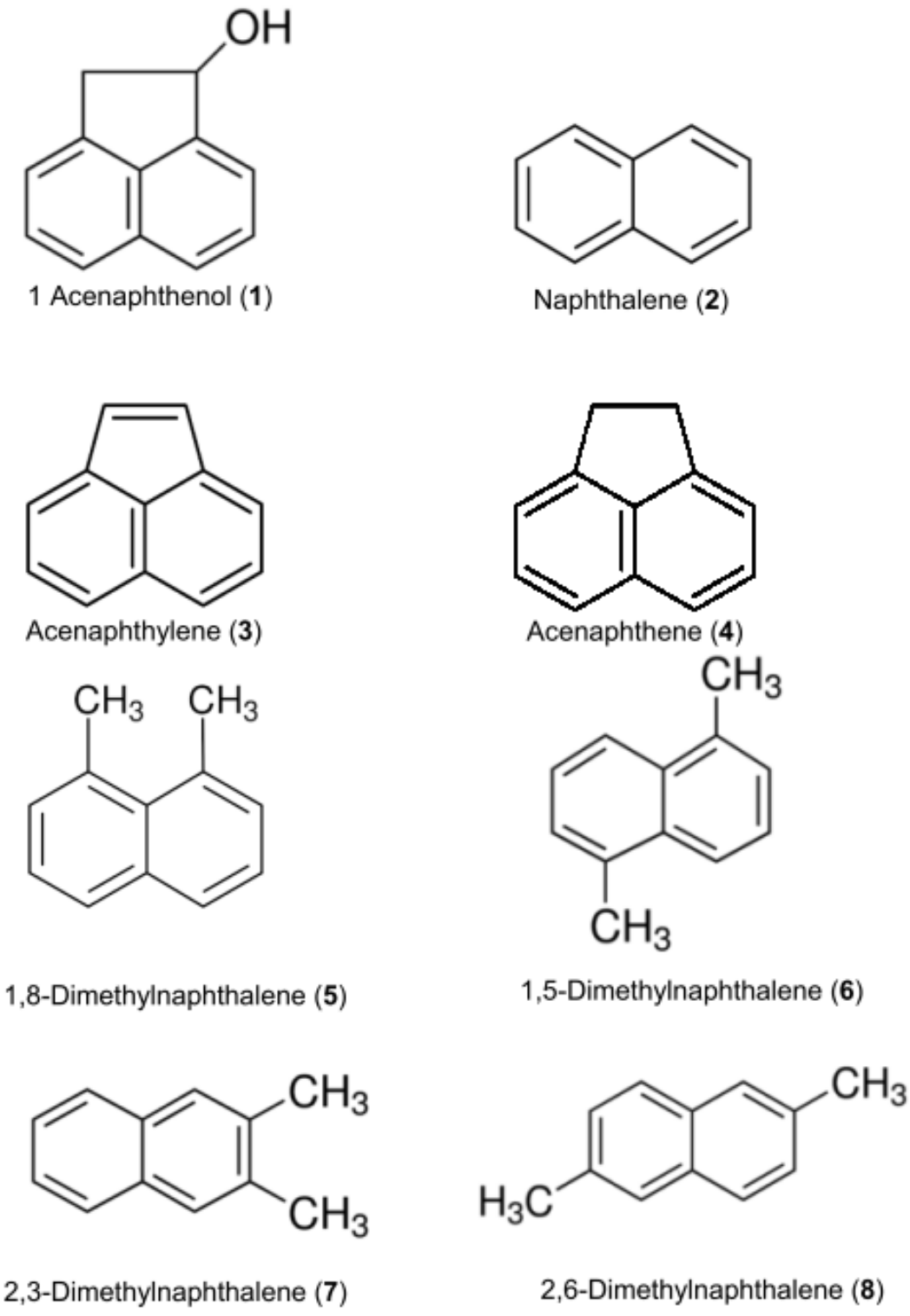


FIGURE 23. Chemical structures of 1-acenaphthenol, naphthalene and its derivatives.

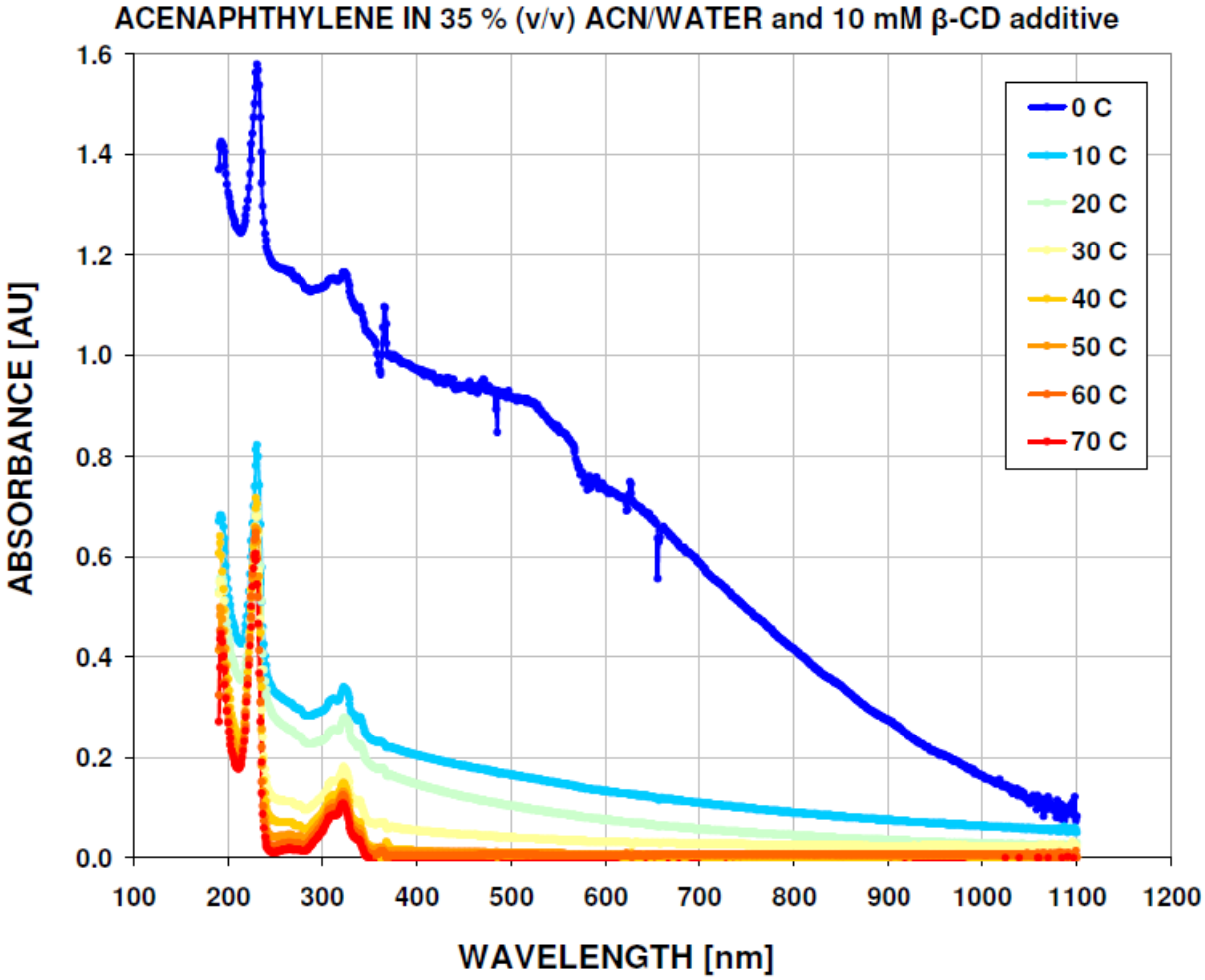


FIGURE 24. Changes in UV-Vis spectra of acenaphthylene at different temperatures. Spectra acquisition was performed 15 minutes after reagents mixing (2 µg/mL acenaphthylene, 10 µL methanol, 5 mL 35% acetonitrile

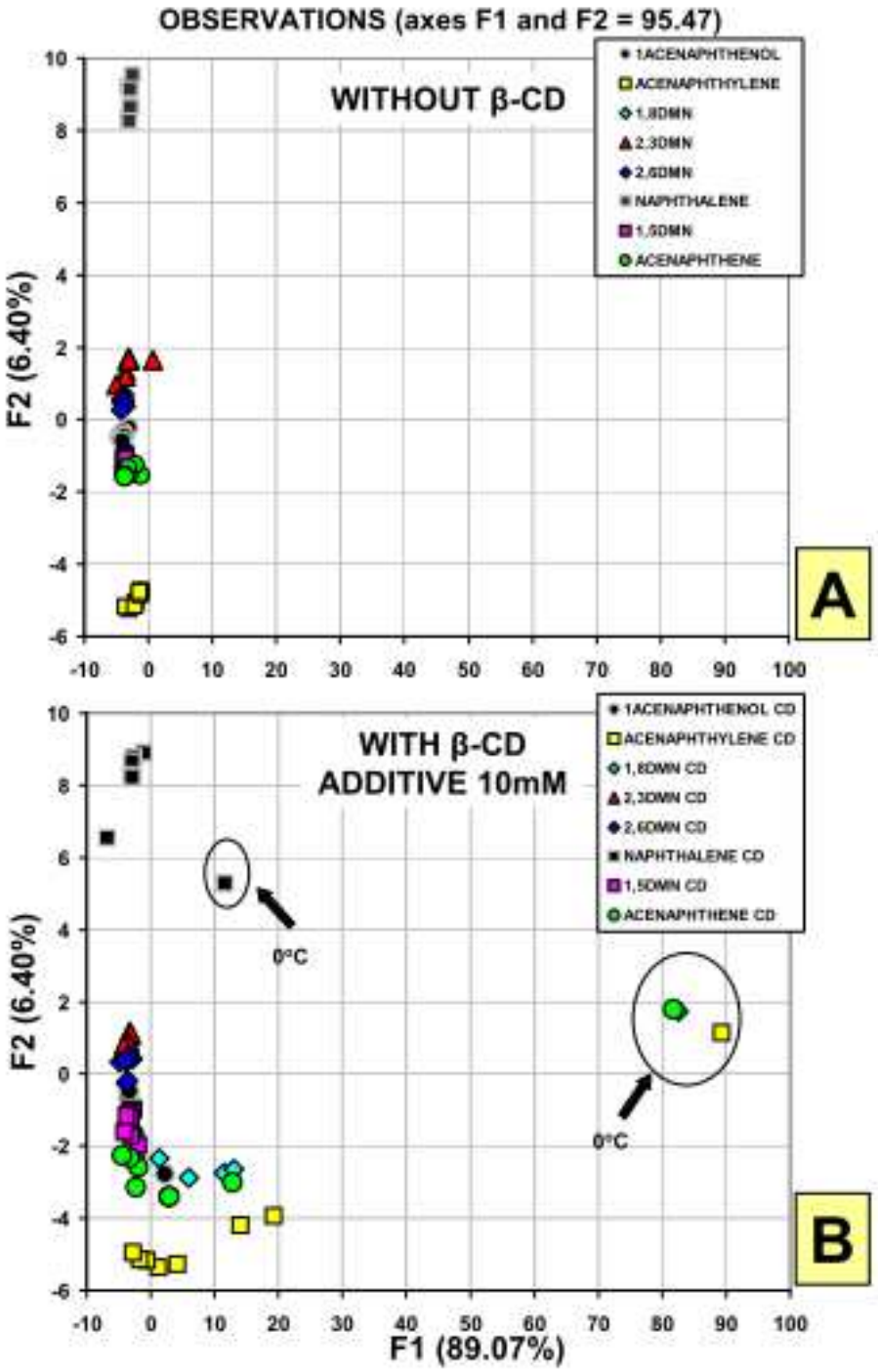


FIGURE 25. Differences in grouping of investigated objects (PAHs UV-Vis spectra from 190 to 400 nm at different temperatures) using solvents without (Graph **A**) and with β-CD additive (Graph **B**) observed within PCA factor scores 2D space.

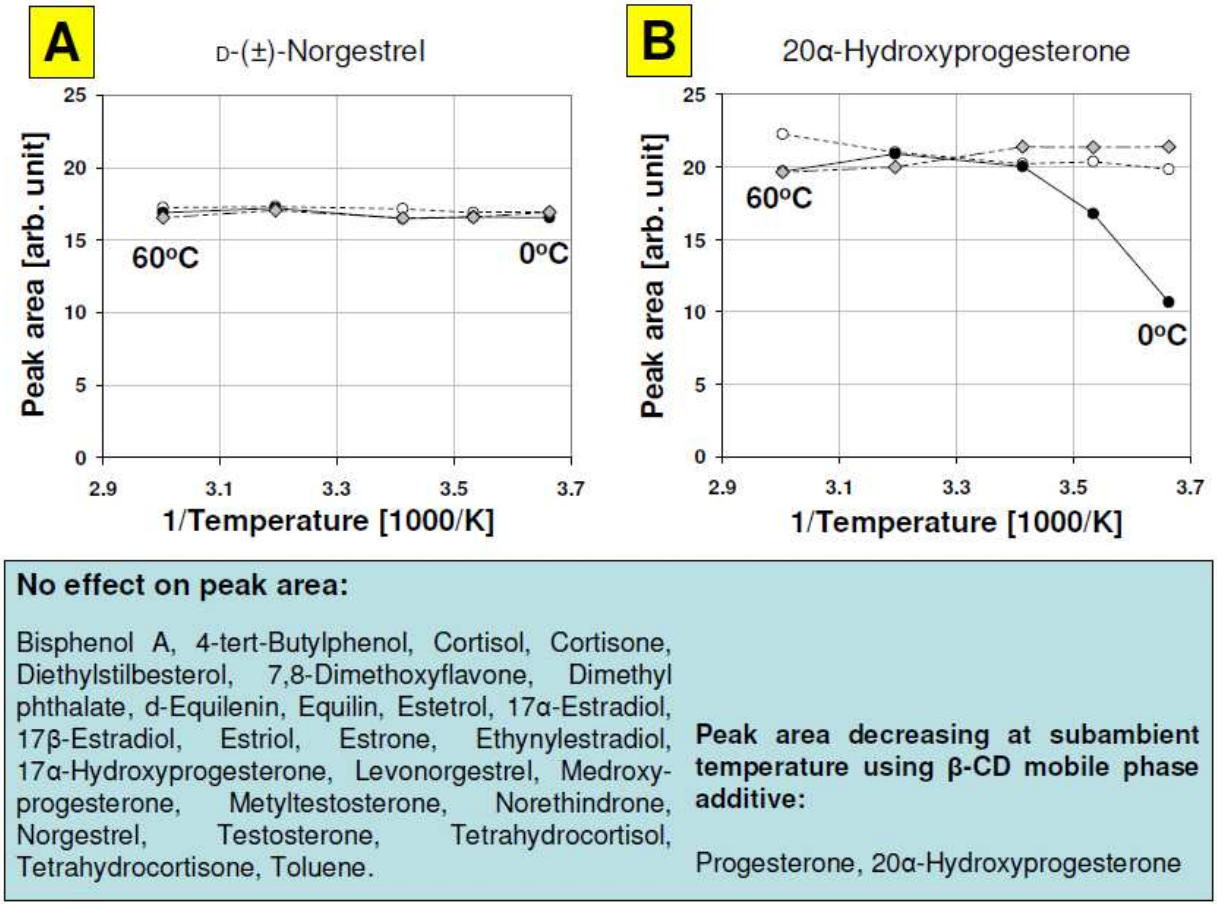


FIGURE 26. Temperature effect on peak areas of selected low-molecular mass compounds (mainly steroids) chromatographed on C-18 HPLC column using binary mobile phase composed of acetonitrile:water 35:65, v/v (white circles) and modified with β-cyclodextrin (black dots) as well as hydroxypropyl β-cyclodextrin (gray diamonds) additives at 10 mM concentration. A - no effect registered; B - peak area decreasing at low temperature using β-cyclodextrin as eluent additive. Steroids quantity injected: 20 µL of solution at concentration of 50 µg mL-1; detection: UV 240 nm Graph were based on recalculated experimental data acquired by **[Włodarczyk 2009]**.

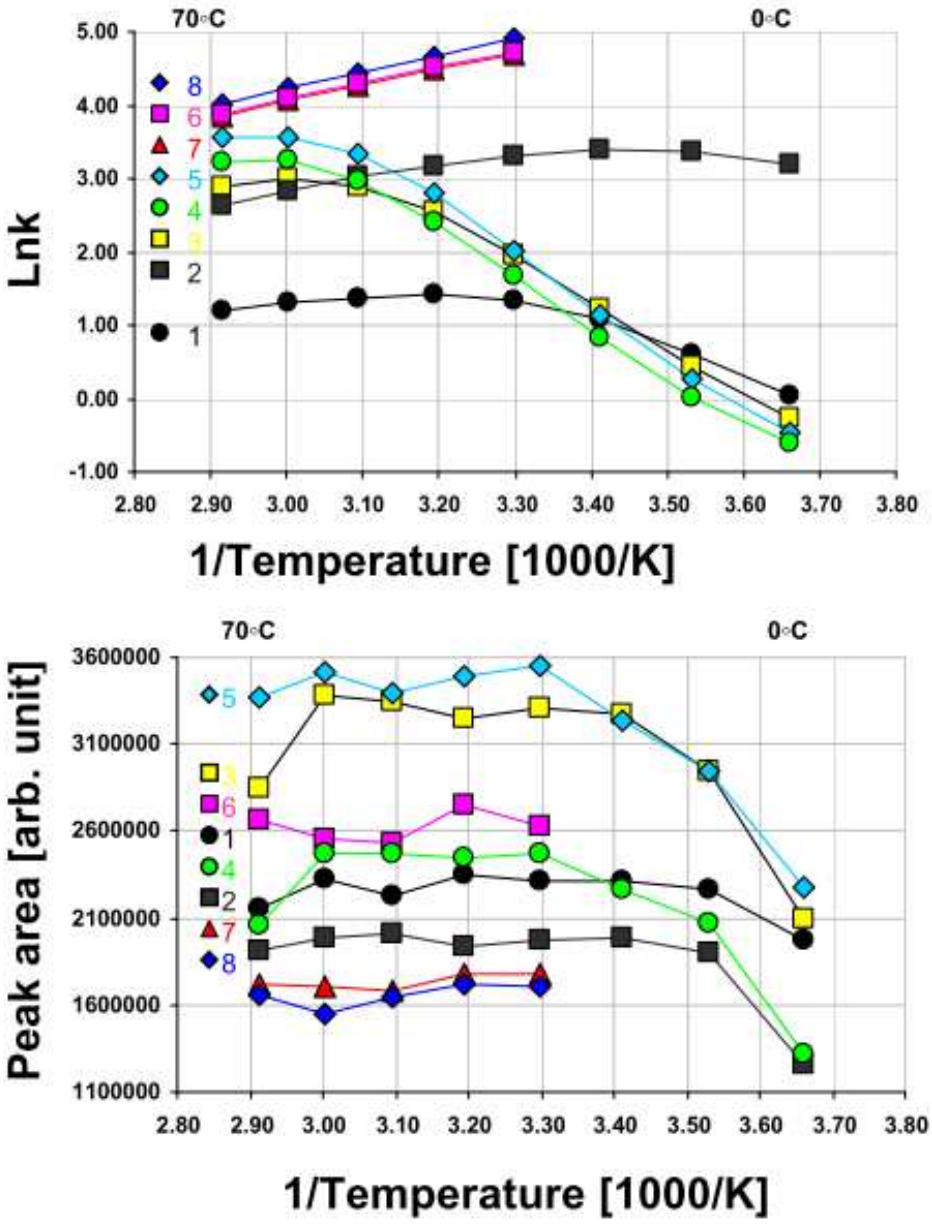


FIGURE 27. Effect of temperature and cyclodextrin additive on column chromatographic (HPLC) retention (top) and peaks areas (bottom) of PAHs investigated. Analytes labels: (**1**) 1-acenaphthenol, (**2**) naphthalene, (**3**) acenaphthylene, (**4**) acenaphthene, (**5**) 1,8-DMN, (**6**) 1,5-DMN, (**7**) 2,3-DMN and (**8**) 2,6-DMN.

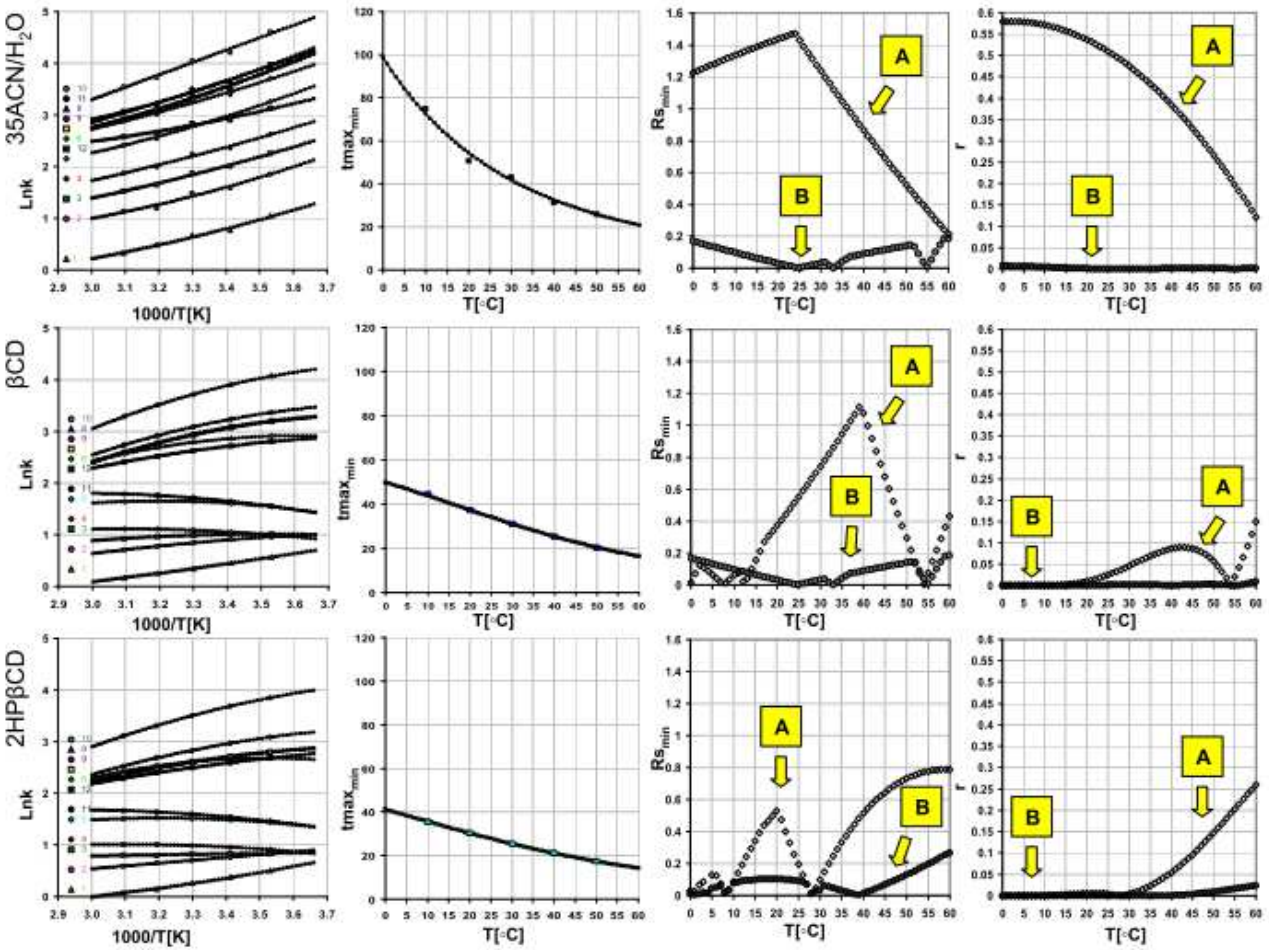


FIGURE 28. Raw chromatographic data and optimization graph concerning retention of studied bisphenols in terms of analysis time ($t_{max,min}$), resolution ($R_{s,min}$) and peaks distribution along time axis relative resolution product (r). **A** – tested bisphenol without bisphenol AF and bisphenol BP; **B** - all tested bisphenol**.**

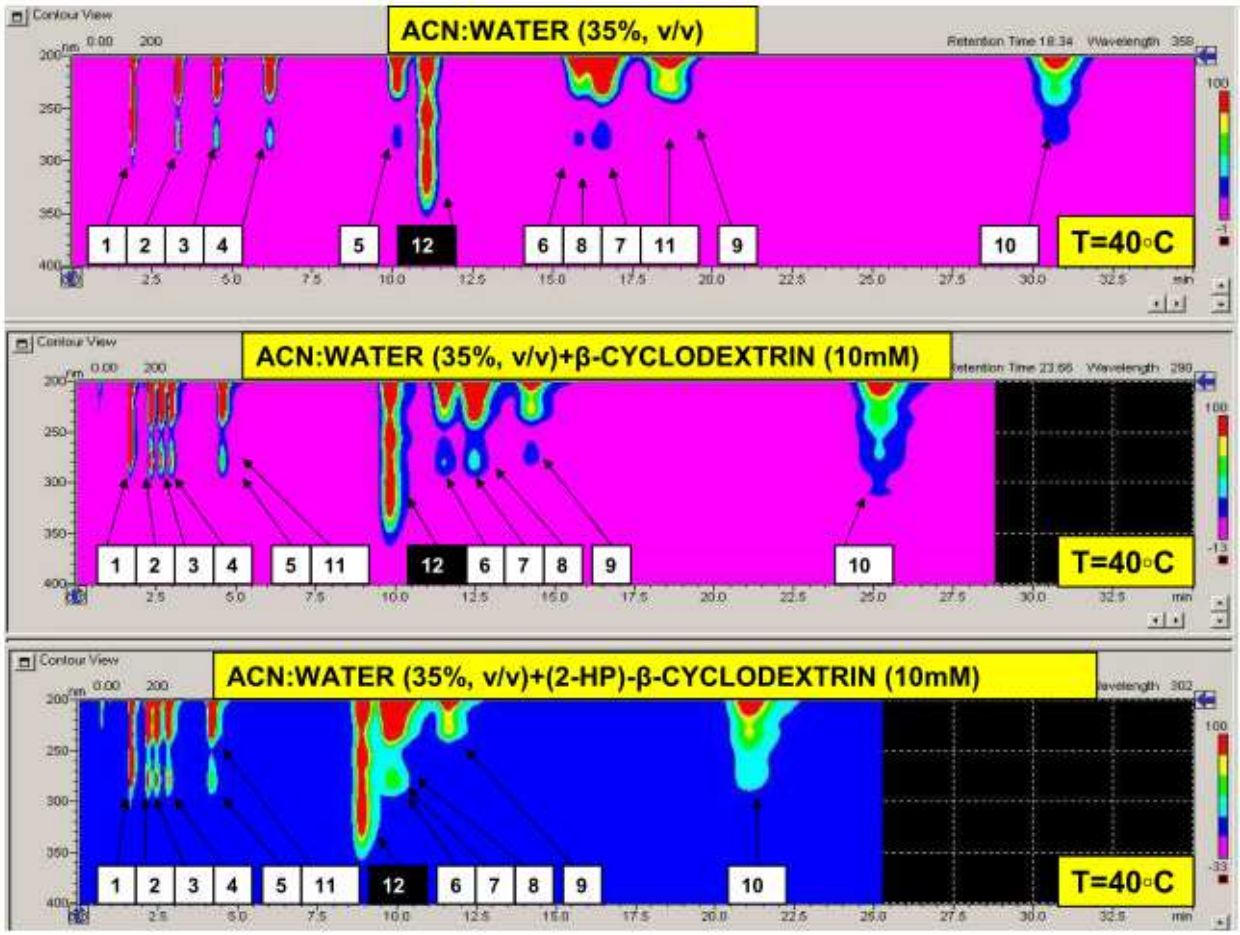


FIGURE 29. Isocratic separation of 12 substances (11 bisphenols and internal standard; analytes IDs according to data presented in **Table 4** performed on 10 cm LC-18 column at temperature of 40°C using plain binary mobile phase (top) and modified with different cyclodextrins at concentration of 10 mM (middle and bottom).

FIGURE 30. Samples of materials used in the extraction experiment. **A** wet wipes, **B** cleaning cloths, **C** rice packaging (in the experiment, bags without the contents were used), **D** sanitary towels, **E** plastic bags, **F** jelly fish baits, **G** treated wastewater from final settling tank (Jamno Wastewater Treatment Plant),
H Flushable wipes have caused problems in New York City wastewater treatment plants (https://abcnews.go.com/Business/flushability-flushable-wipes-spawns-class-action-lawsuit/story?id=22759642)

FIGURE 31. Samples hot water extraction and SPE concentration: **G** 2 g sample supplemented with 250 mL tap water, **H** heating 15 min. at 100°C, **I** cooling to room temperature, **J-K** SPE procedure (described in **3.6.** and **Figure 8**).

FIGURE 32. Selected SPE extracts of samples presented in **[Figure 30]**. Samples labels: **A1** wet wipes, **B1** cleaning cloths, **D1** sanitary towels, **E1** plastic bags, **F1** jelly fish baits, **G1** treated wastewater from final settling tank (Jamno Wastewater Treatment Plant).

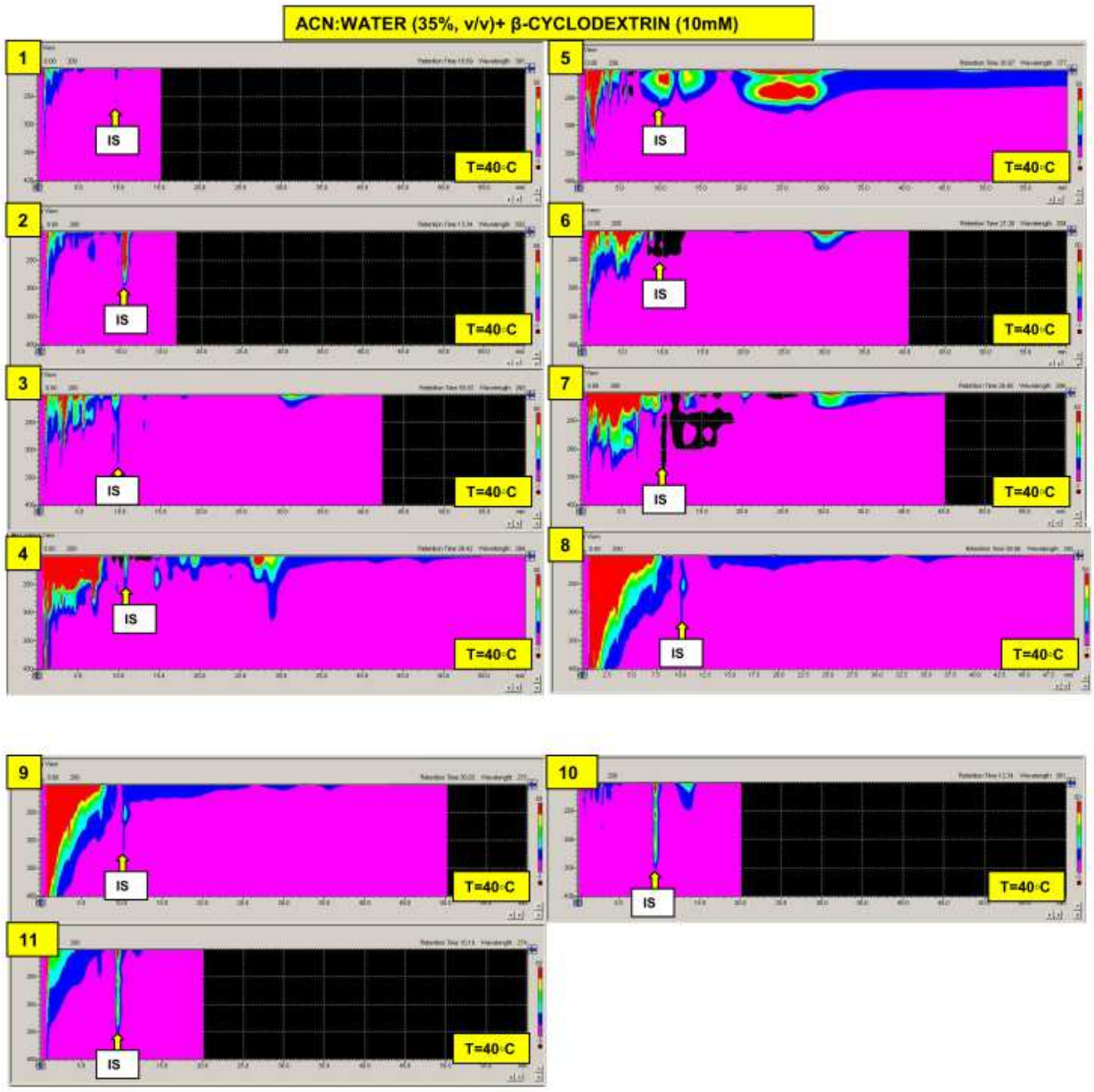


FIGURE 33. Typical DAD-UV-Vis chromatograms' of samples listed in **Table 8**. Chromatograms labels: **1** Boiled tap water, **2**. Rice bag, **3** Plastic bag**, 4** Cloth, **5** Fish baits, **6** Sanitary towels, **7** Wet wipes, **8** Boiled purified sewage, **9.** Raw purified sewage, **10.** Distilled water, **11.** Raw tap water.

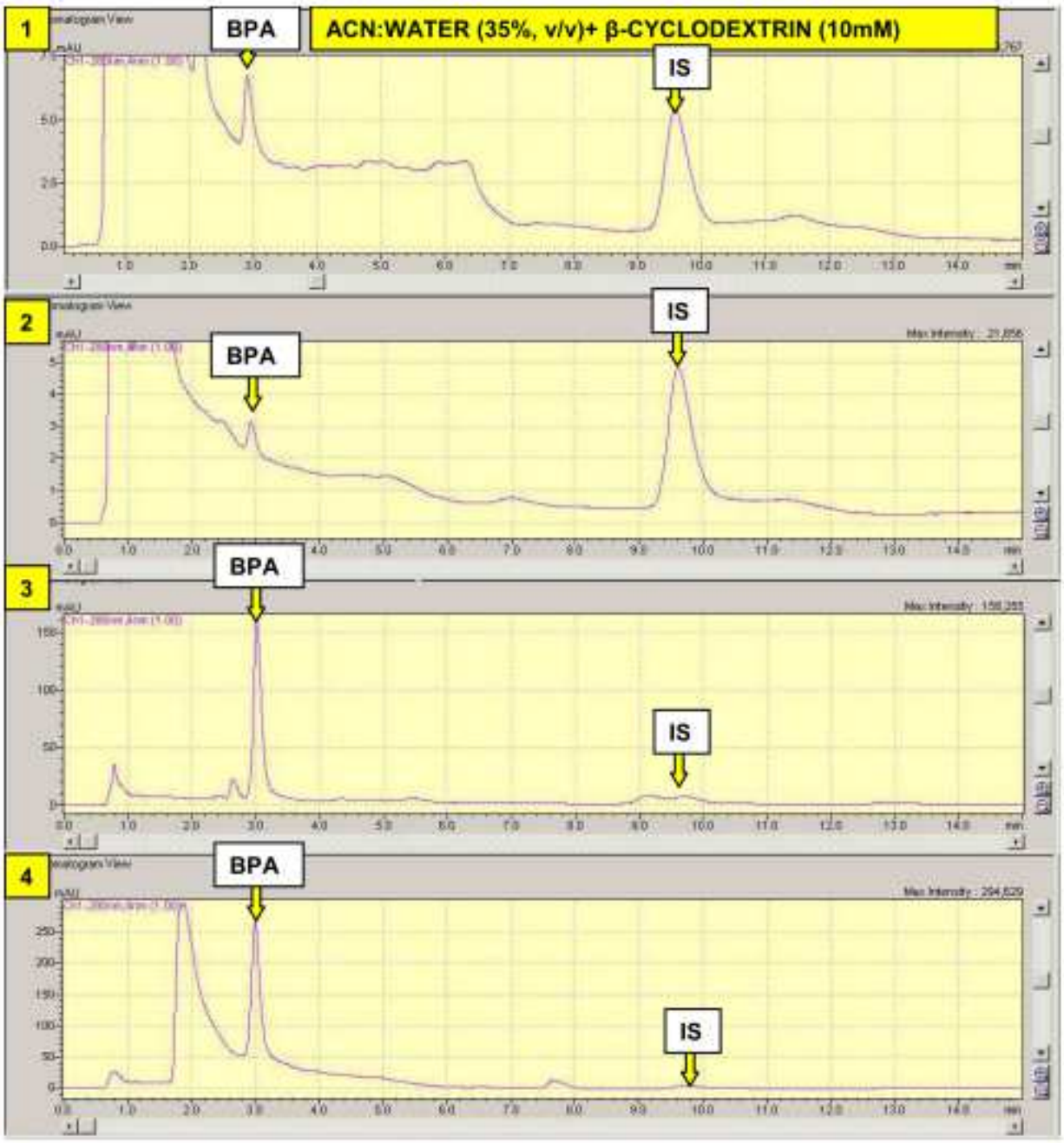
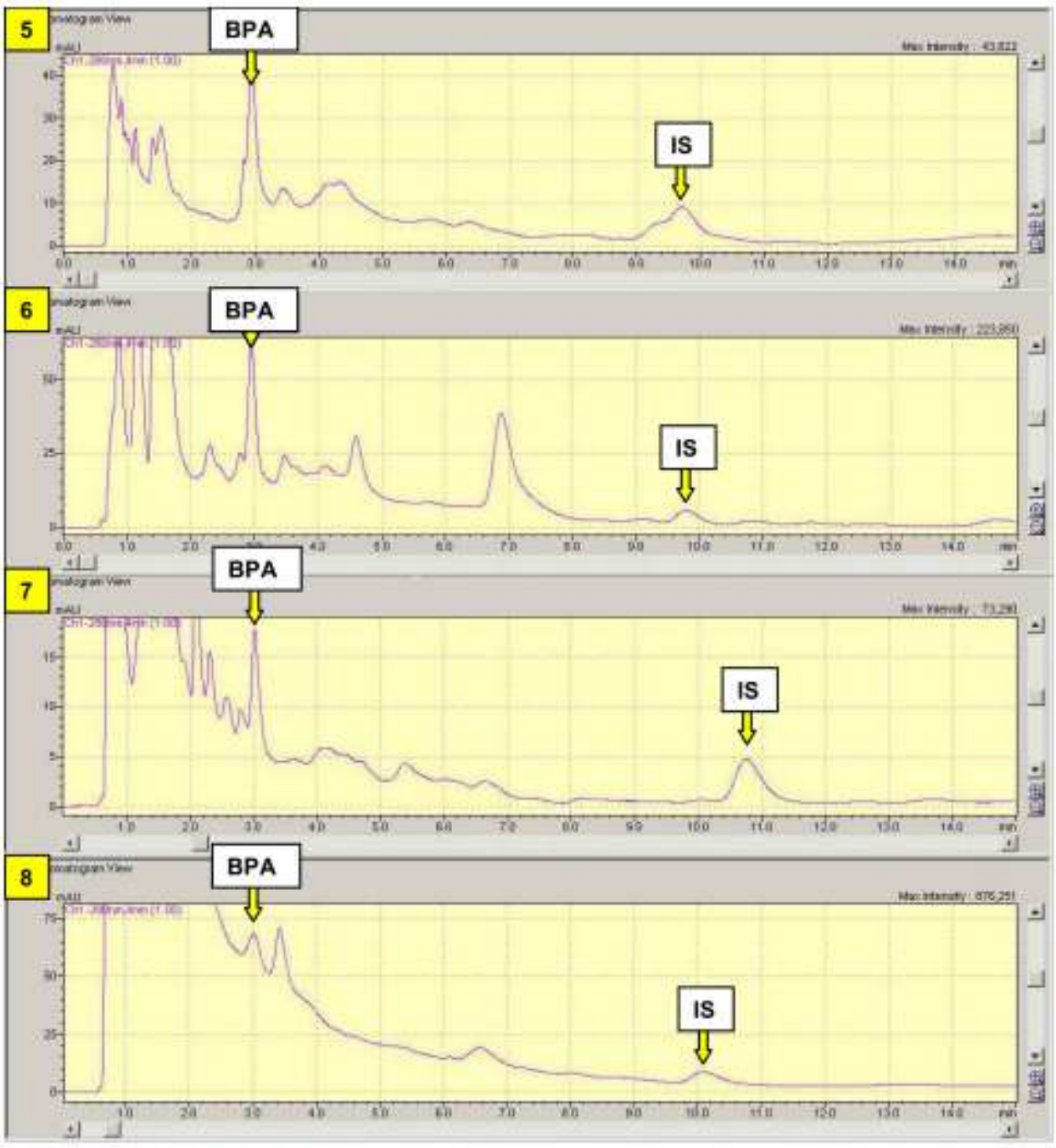
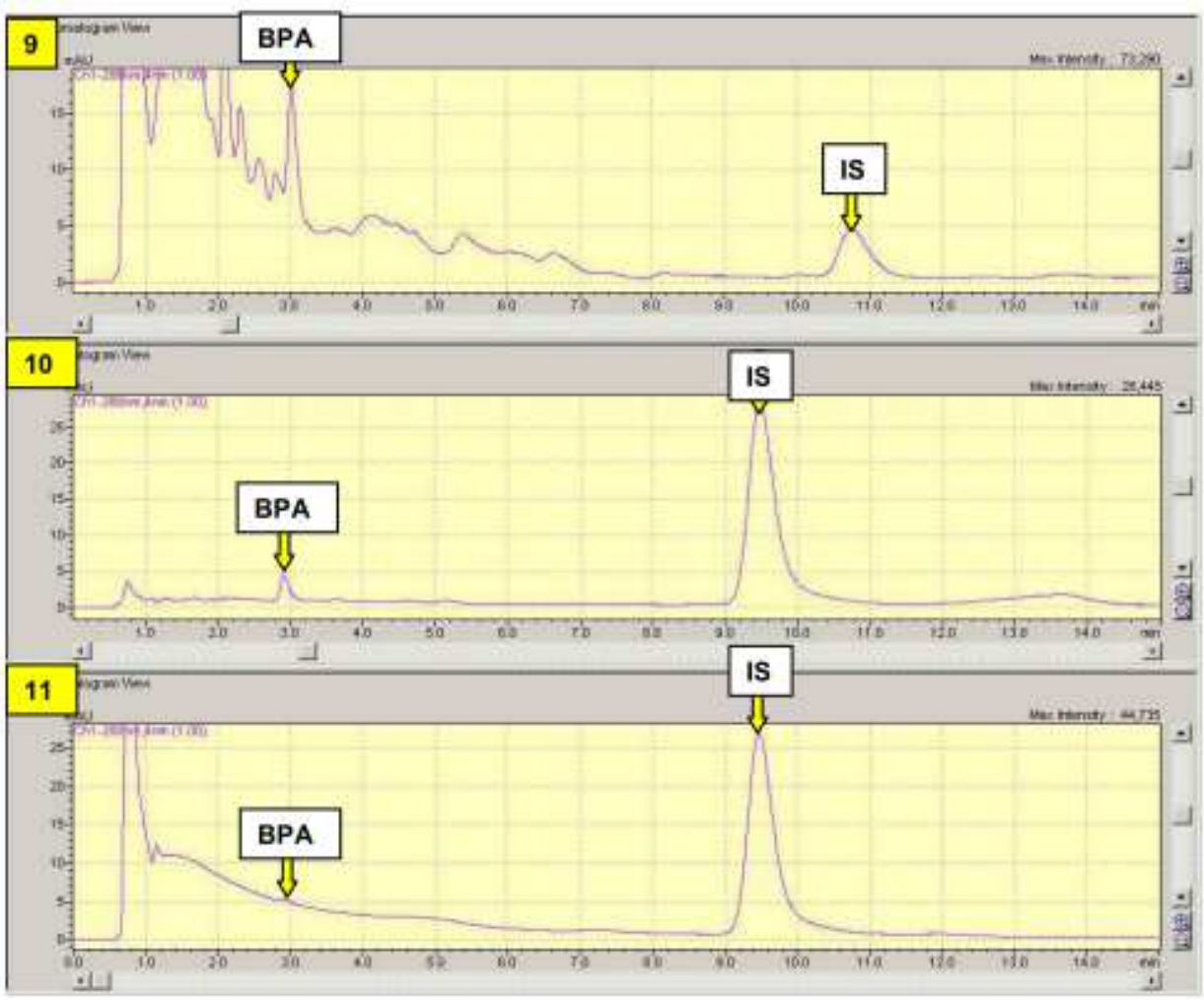


FIGURE 34. HPLC chromatograms of SPE extracts of environmental samples presented on **Figure 30** and recorded at analytical wavelength = 280 nm. Sample labels: **1** Boiled tap water and 7,8 dimethoxyflavone (IS), **2** Tap water and rice bags and 7,8 dimethoxyflavone, **3** Tap water and plastic (braeafast bags) and 7,8 dimethoxtflavone, **4** Tap water and cleaning cloths and 7,8 diethoxyflavone, **5** tap water and fish bait and 7,8 dimethoxyflavone, **6** tap water and sanitary towels and 7,8 dimethoxyflavone, **7** tap water and wet wipes and 7,8 dimethoxyflavone, **8** boiled purified sewage and 7,8 dimethoxyflavone. **9** Raw purified sewage and 7,8 dimethoxyflavone, **10** distilled water and 7,8 dimethoxyflavone, **11** Raw tap water and 7,8 dimethoxyflavone. Bisphenol A (BPA) is marked on all chromatograms.

Continuation of FIGURE 34.



Continuation of FIGURE 34.



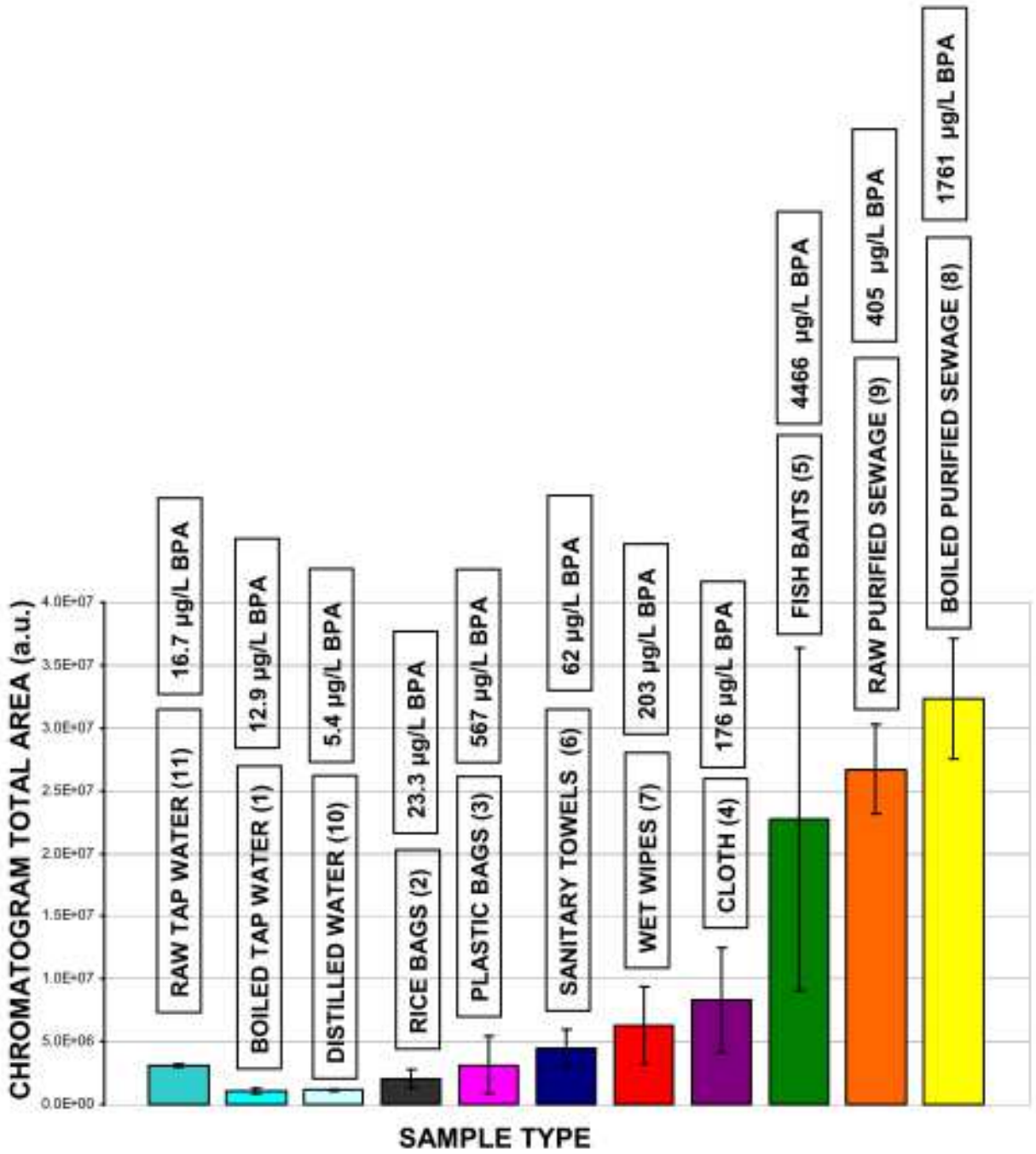


FIGURE 35. Integrated areas of all detected peaks on chromatograms (detection at 280 nm) calculated for various samples, which were prepared accordingly to analytical protocol described in **chapter 3,6**, and **Figure 8-10**. Boxes above each material type indicate the calculated value of bisphenol A detected within each sample.

Samples labeling: raw distilled water (10), raw tap water (11), boiled tap water (1), rice bags (2), various plastic bags (3), plastic fishing baits (5), various dust cloth (4), sanitary towels (6), raw purified sewage (9) boiled purified sewage (8) wet wipes (7). Numbers in parentheses are related to chromatograms numbers presented in **Figures 33,34.**

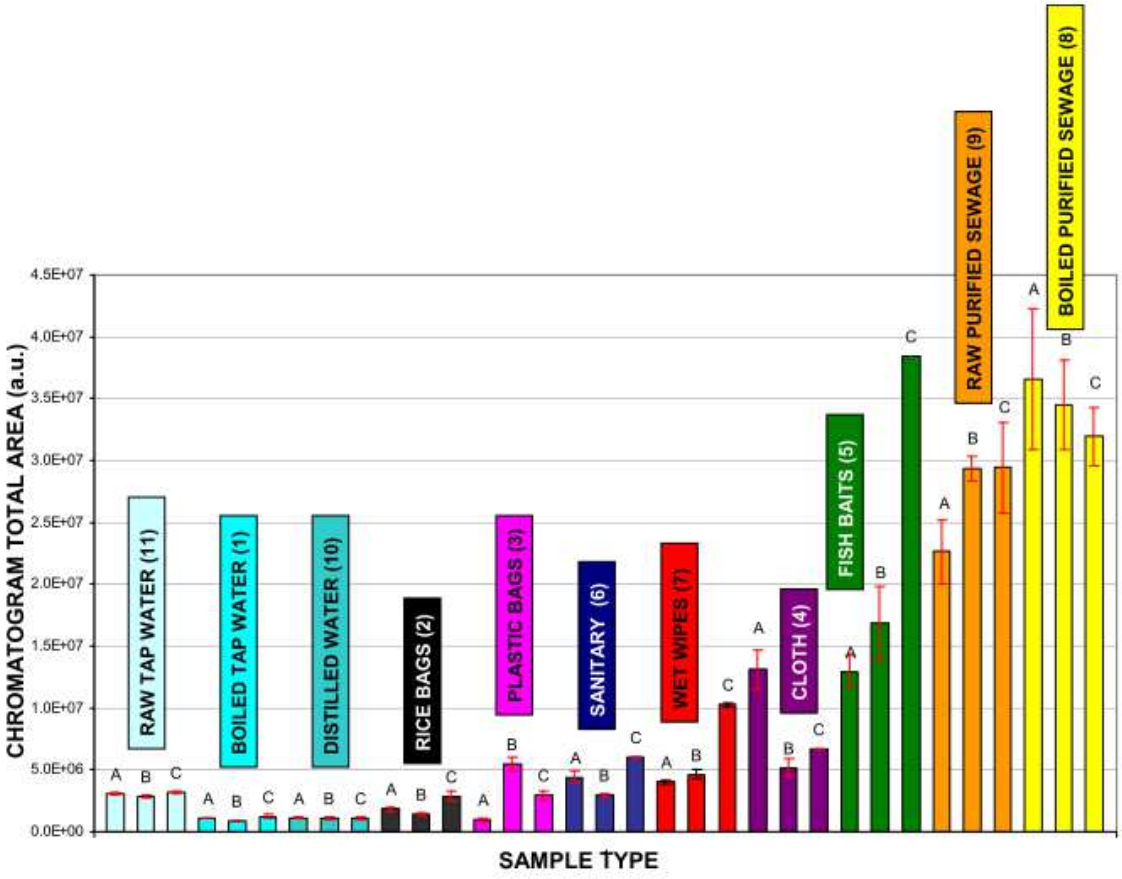


FIGURE 36. Integrated areas of all individual samples related to extracted materials presented as average bars in **Figure 35.**

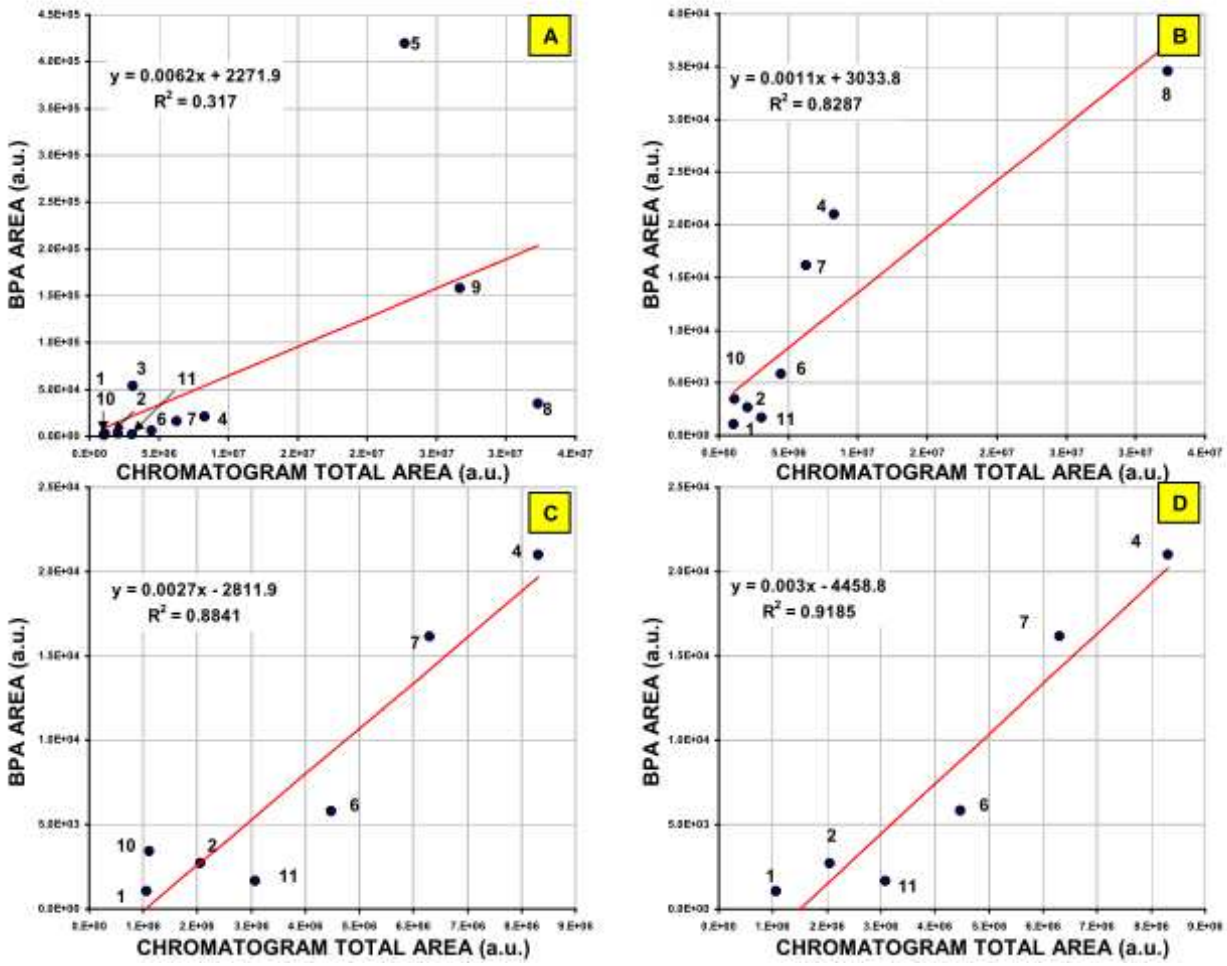


FIGURE 37. Correlation observed between SPE extracts contents (the total peaks area on UV-DAD chromatograms) and the bisphenol A peak area for each materials extracted. Samples labelling: **A** - all tested materials; **B** - without outliers 3,5 and 9; **C**- without outliers 3,5,9 and 8; **D**- without outliers 3,5,9,8 and 10. Dots numbers corresponds to material types listed in **Tables 8, 9**.

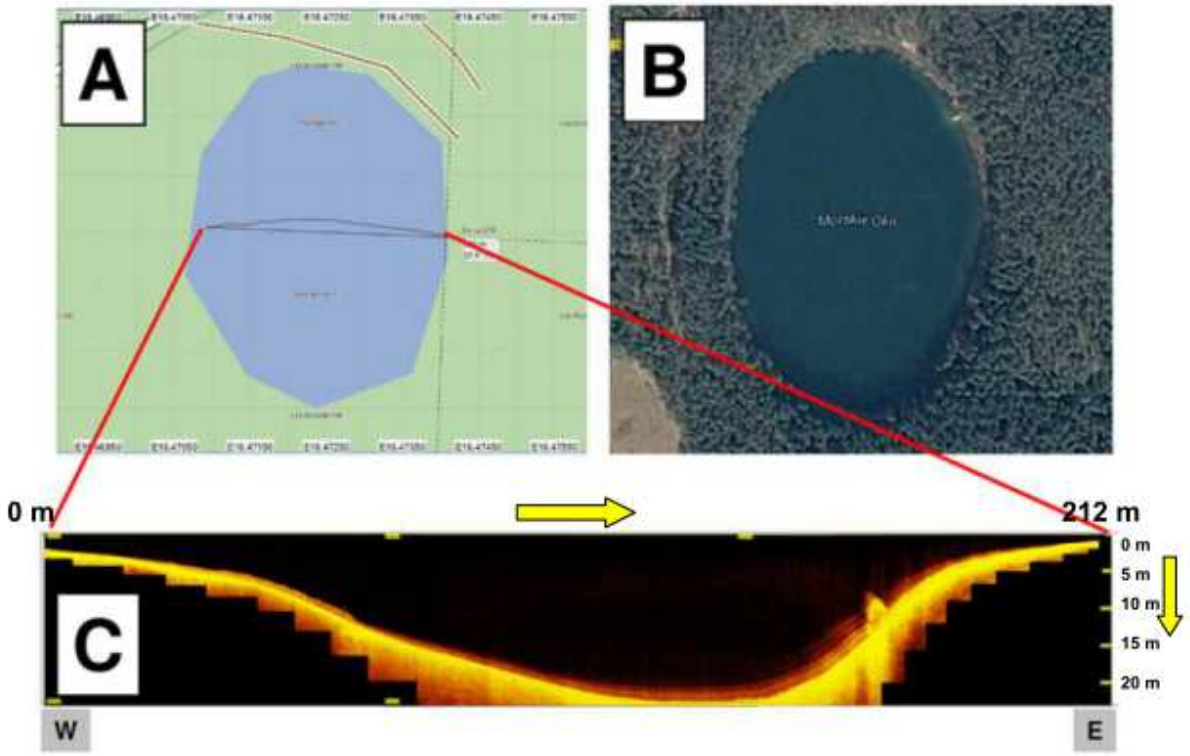


FIGURE 38. Geographical location (A,B maps provided by Garmin and GoogleMaps, respectively) and bathymetric intersection (22.03.2015) through Jezioro Morskie Oko lobelia lake. Depth profile was made using Garmin echoMAP 50dv marine chartplotter/sonar equipped with transducer GT 20 (77/200/455 kHz) working with high frequency 455 kHz (DownVü mode); lake cross-section was visualized using Home Port Ver. 2.2.1.0 2009-2015 Garmin Ltd. freeware; Copyright @ 2015 Paweł K. Zarzycki with permission; unpublished data.

FIGURE 39. Duckweed blooms in various surface water reservoirs (canals, small ponds) observed in Amsterdam City (Holland) area in September 2016 (All photography copyrights by Paweł K. Zarzycki © 2016 with permission).

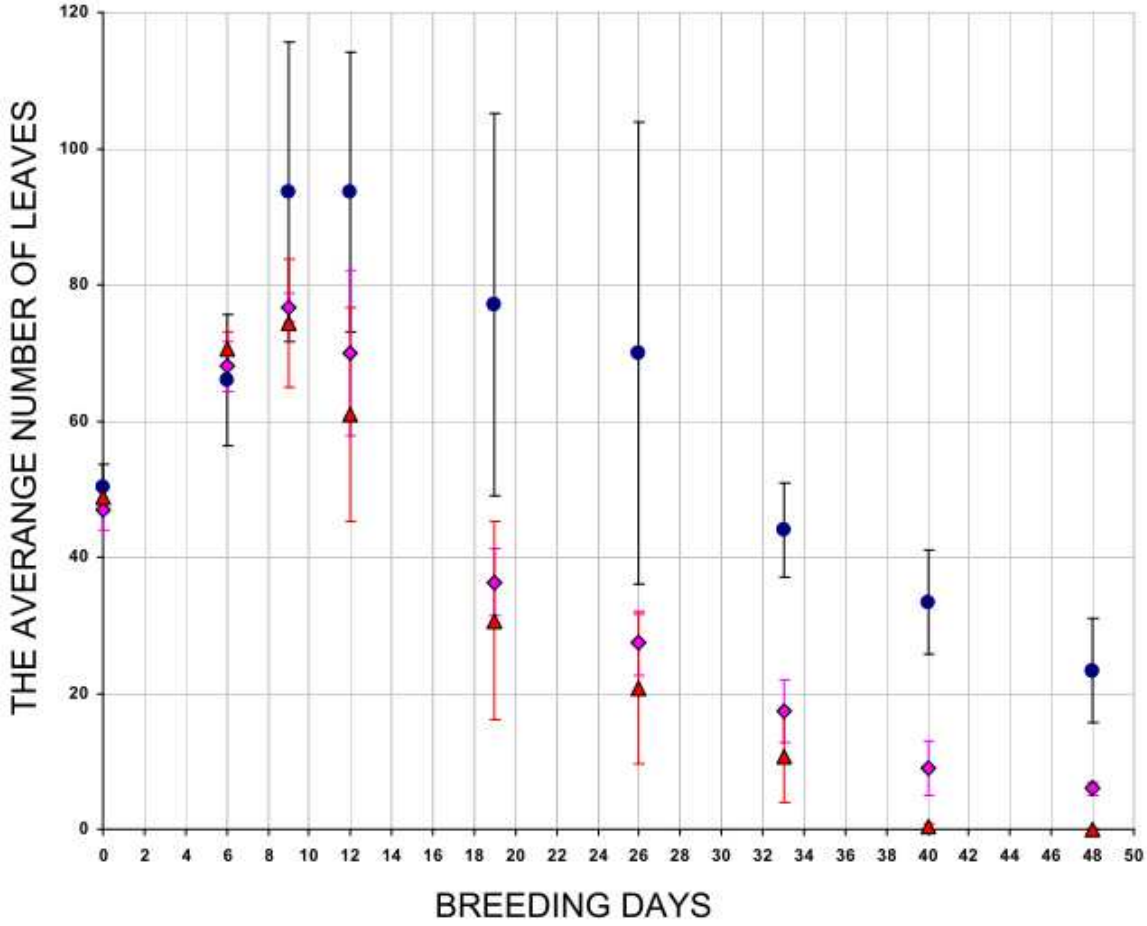


FIGURE 40. Average number of green leaflets during cultivation time depending on the liquid medium used: tap water (**blue dots**), tap water and 1 β-CD(1 mM) (**pink diamonds**) as well as tap water and glucose (7 mM) (**red triangles**).

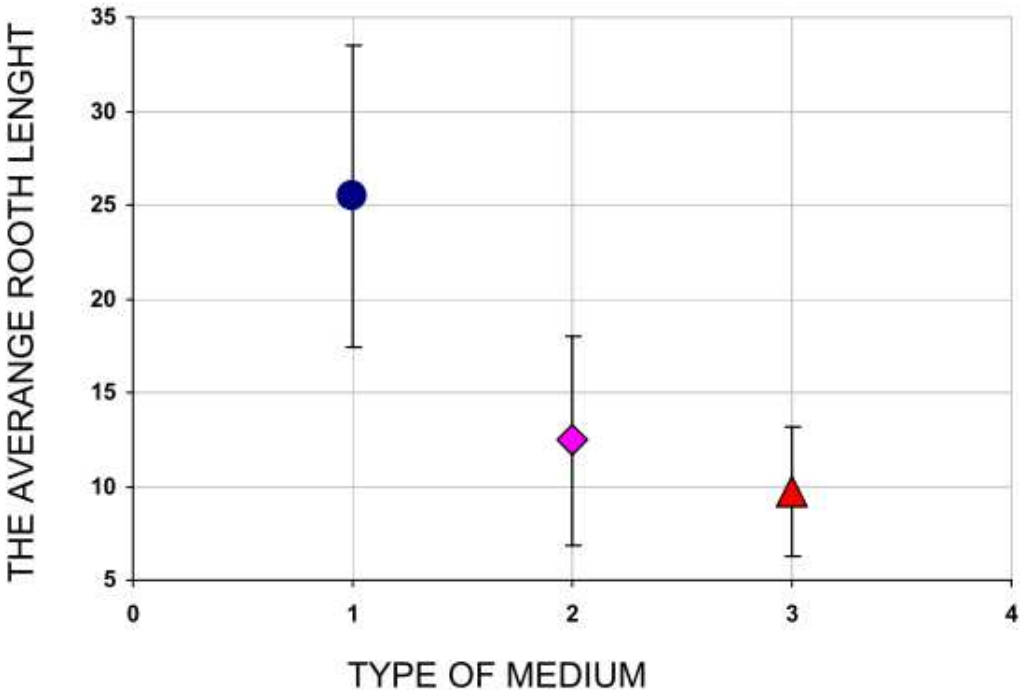


FIGURE 41. Calculated average root length (*n* = 7) of the duckweed organisms depending on the medium used and measured after 22 days of cultivation. Sample labels: **1** (**blue dot**) tap water; **2** (**pink diamond**) tap water and β-CD (1 mM), **3** (**red triangle**) tap water and glucose (7 mM).

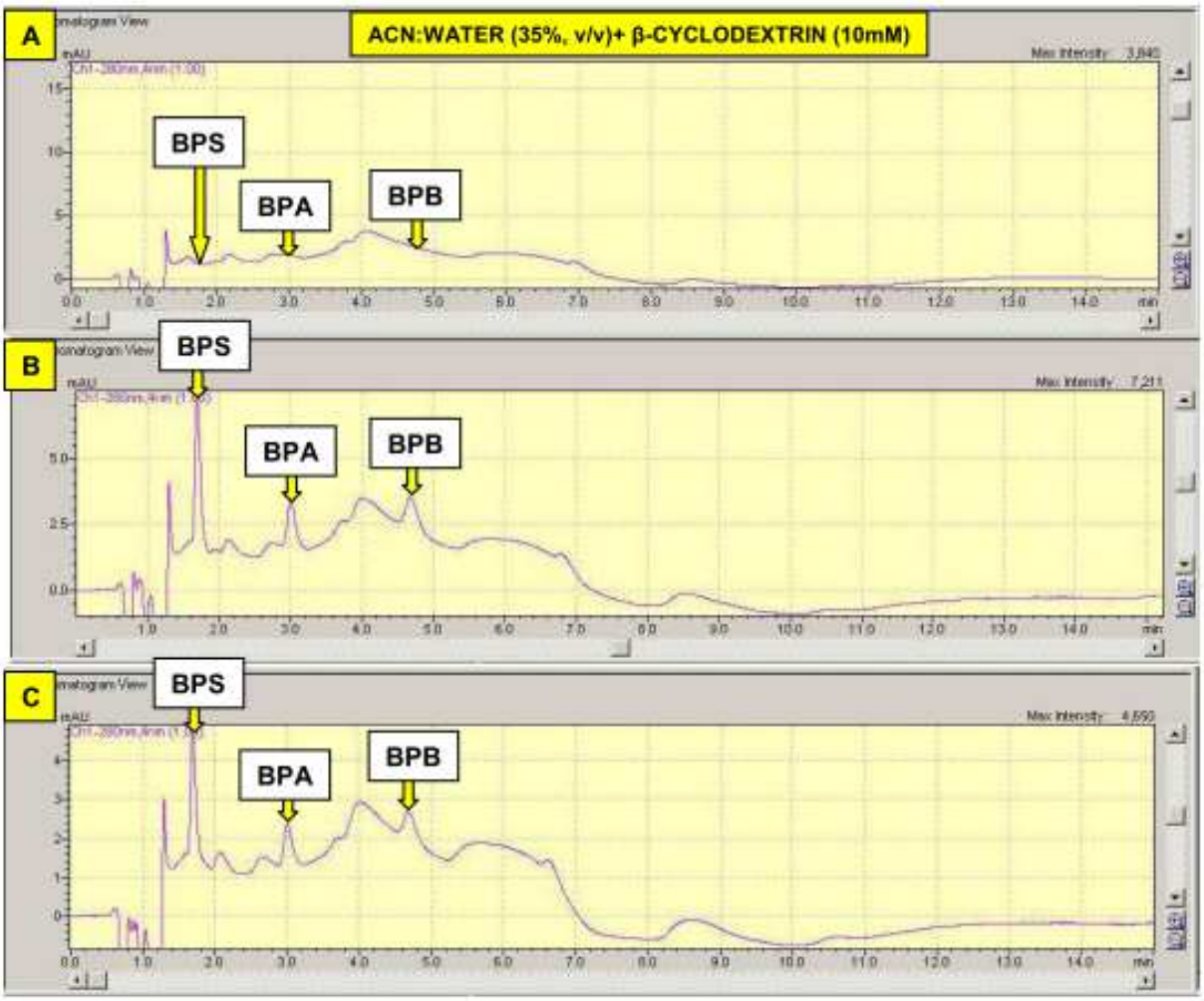


FIGURE 42. Typical chromatograms recorded at analytical wavelength = 280 nm of the reaction medium without bisphenols addition (**A;** tap water and ethanol) and with target bisphenols and cyclodextrin additive (**B**) as well as with target bisphenols, cyclodextrin and duckweed additives (**C**) measured at the beginning of degradation experiment (2h after experiment start time). Yellow arrows indicate target bisphenol A **(BPA)**, bisphenol B **(BPB)** and bisphenol S **(BPS)**;

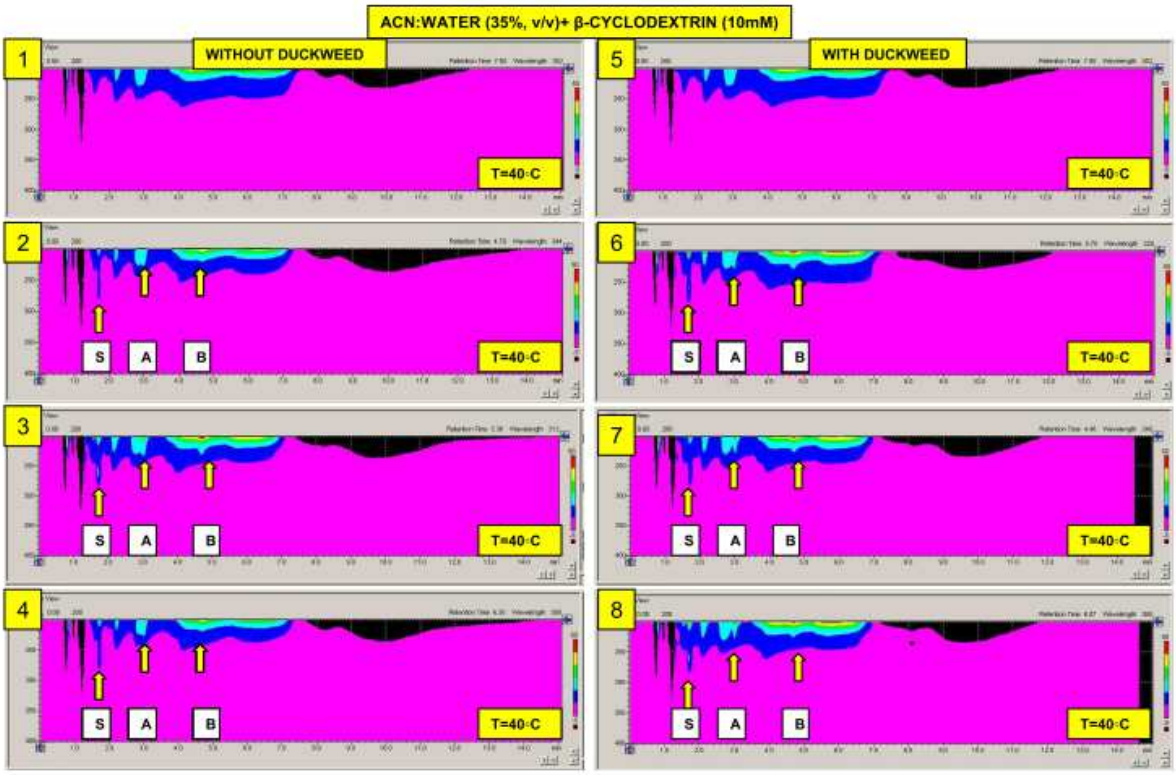


FIGURE 43. Typical chromatographic patterns (in form of DAD scans) recorded at UV range from 400 to 200 nm of all reaction media at the beginning of bisphenols degradation experiment (2h after experiment start time). Yellow arrows indicate target bisphenols (**A**, **B** and **S**); chromatograms labels: **1** and **5** - tap water and ethanol, **2** and **6** - tap water and bisphenols, **3** and **7** - tap water and bisphenols and β-CD (1 mM), **4** and **8** - tap water and bisphenols and glucose (7 mM).

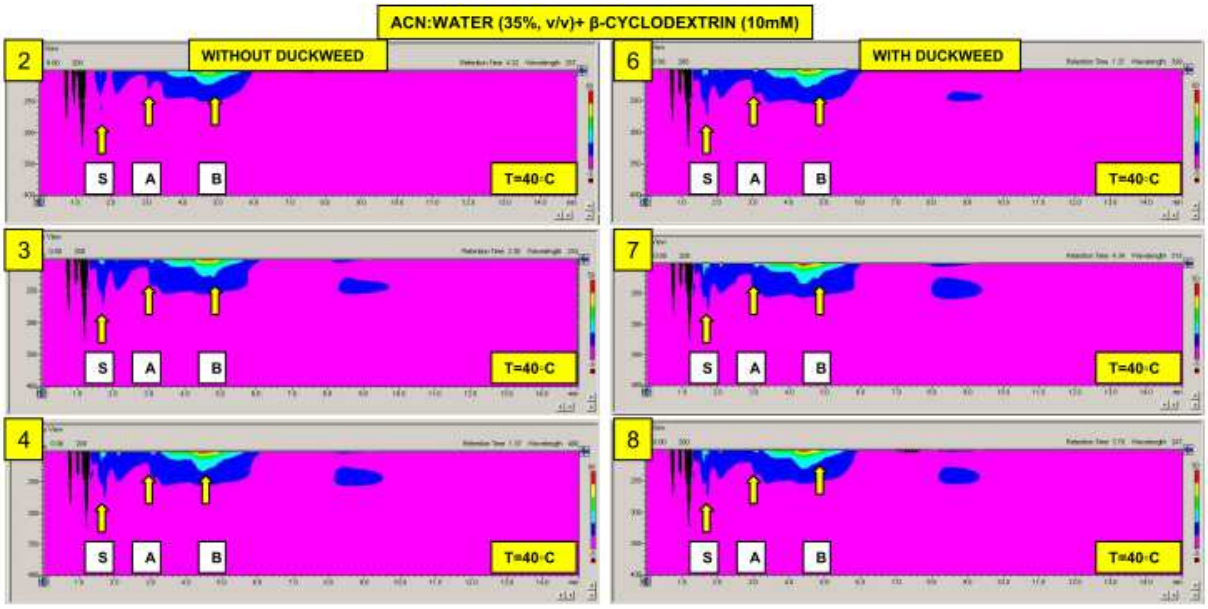


FIGURE 44. Typical chromatographic patterns (in form of DAD scans) recorded at UV range from 400 to 200 nm of all reaction media at the beginning of bisphenols degradation experiment (257h after experiment start time). Yellow arrows indicate target bisphenols (**A**, **B** and **S**); chromatograms labels: **2** and **6** - tap water and bisphenols, **3** and **7** - tap water and bisphenols and β-CD (1 mM), **4** and **8** - tap water and bisphenols and glucose (7 mM).

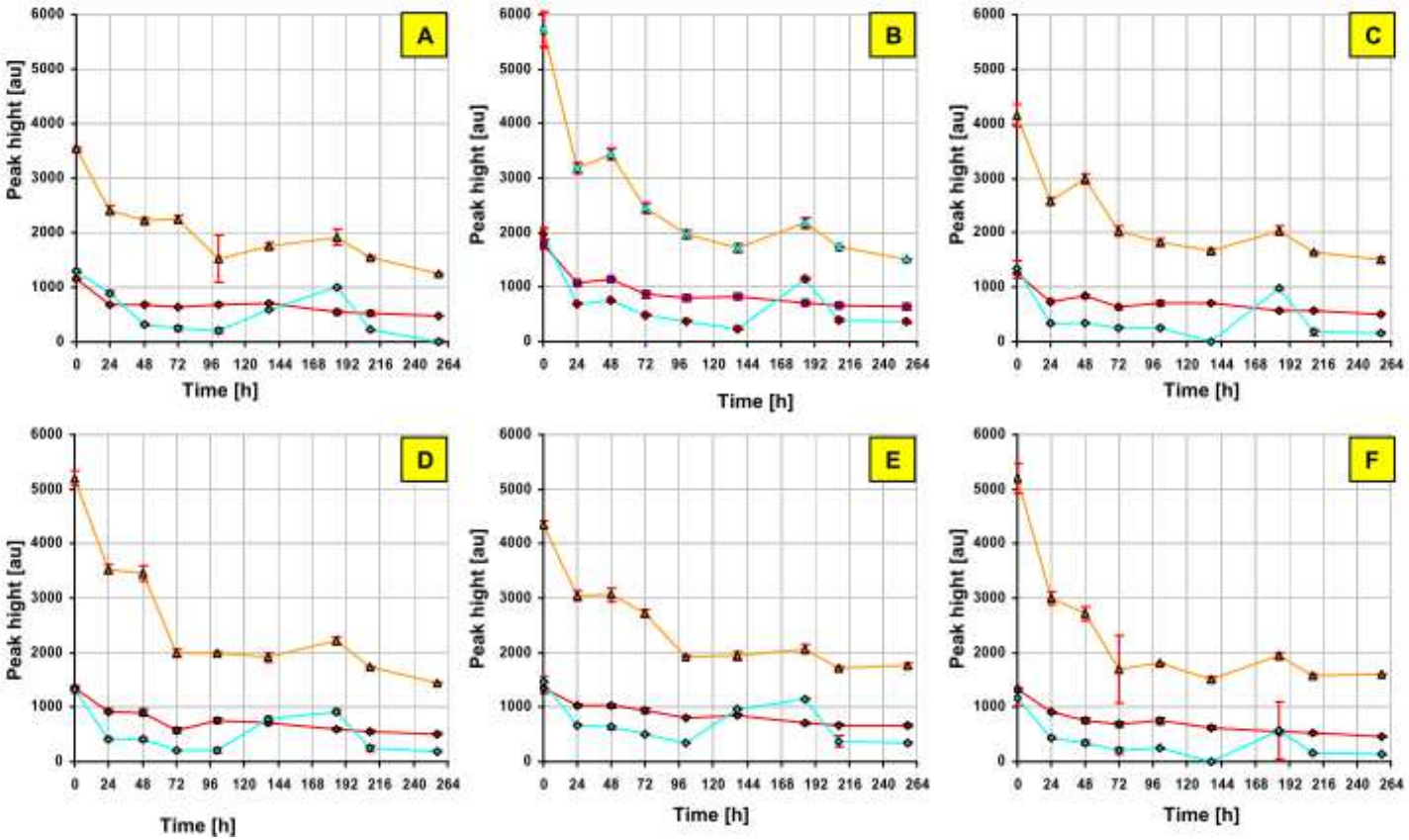


FIGURE 45. Concentration profiles of selected bisphenols in time domain. Bisphenols labels: BPS – orange triangle, BPA – red diamonds, BPB – turquoise diamonds; Reaction medium used: **A** tap water and bisphenols, **B** tap water and bisphenols and β-cyclodextrin (1 mM), **C** tap water and bisphenols and glucose (7mM), **D** tap water nad bisphenols and duckweed, **E** tap water and bisphenols and β- cyclodextrin (1 mM) and duckweed, **F** tap water and bisphenols and glucose (7 mM) and duckweed

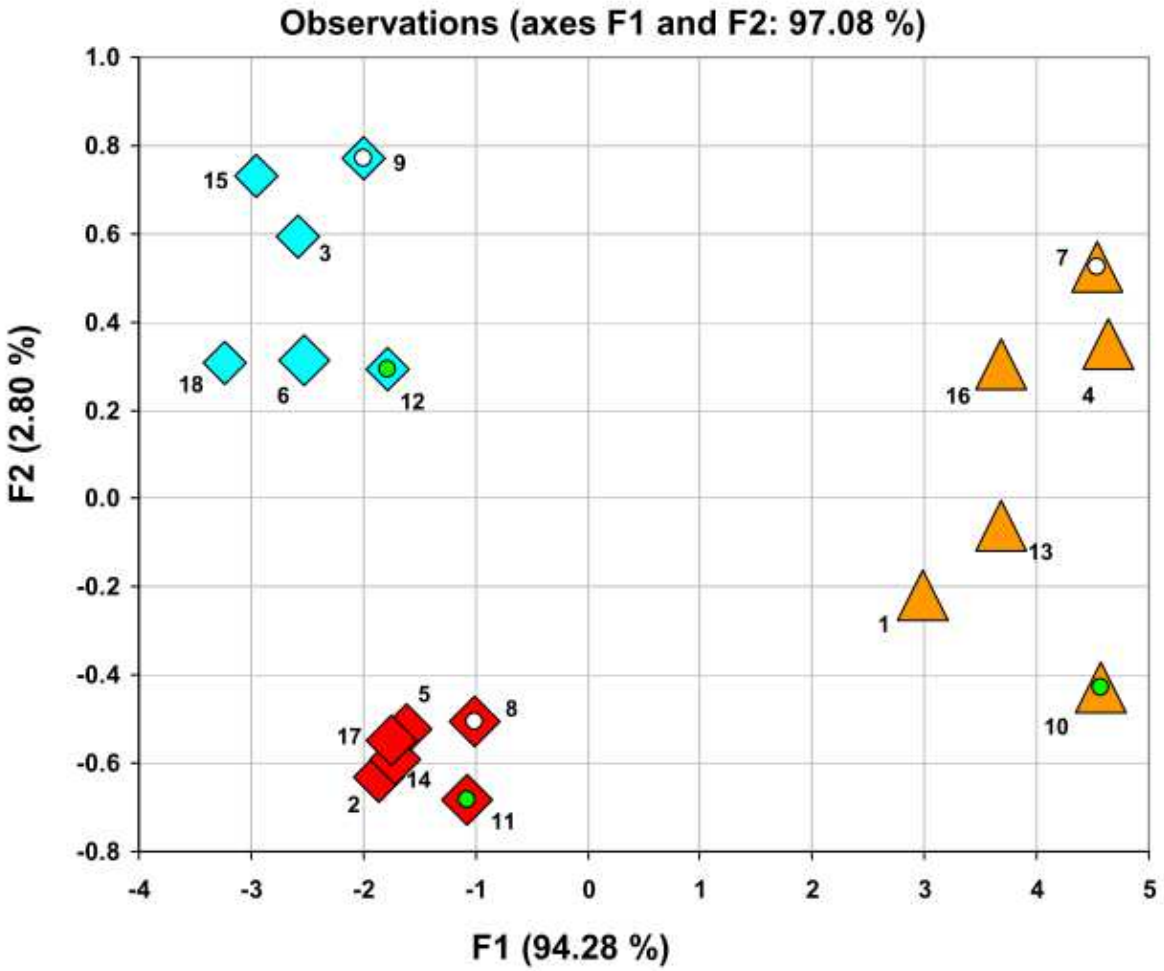


FIGURE 46. Grouping of all investigated objects (samples): bisphenol A (red diamonds), bisphenol B (turquoise diamonds) and bisphenol S (orange triangles) during degradation experiment observed within PCA factor scores 2D space. Samples with cyclodextrin additive are marked with white circles and also with green circles in case of duckweed presence; Objects labels : **1**- tap water and bisphenol S (BPS), **2-**tap water and bisphenol A (BPA), **3-** tap water and bisphenol B (BPB), **4-** tap water and duckweed and BPS, **5-** tap water and duckweed and BPA, **6-** tap water and duckweed and BPB, **7-** tap water and β-cyclodextin (β-CD) and BPS, **8-** tap water and β-CD and BPA, **9-** tap water and β-CD and BPB, **10-** tap water and β-CD and duckweed and BPS, **11-** tap water and β-CD and duckweed and BPA, **12-** tap water and β-CD and duckweed and BPB, **13-** tap water and glucose and BPS, **14-** tap water and glucose and BPA, **15-** tap water and glucose and BPB, **16-** tap water and glucose and duckweed and BPS, **17-** tap water and glucose and duckweed and BPA, **18-** tap water and glucose and duckweed and BPB.

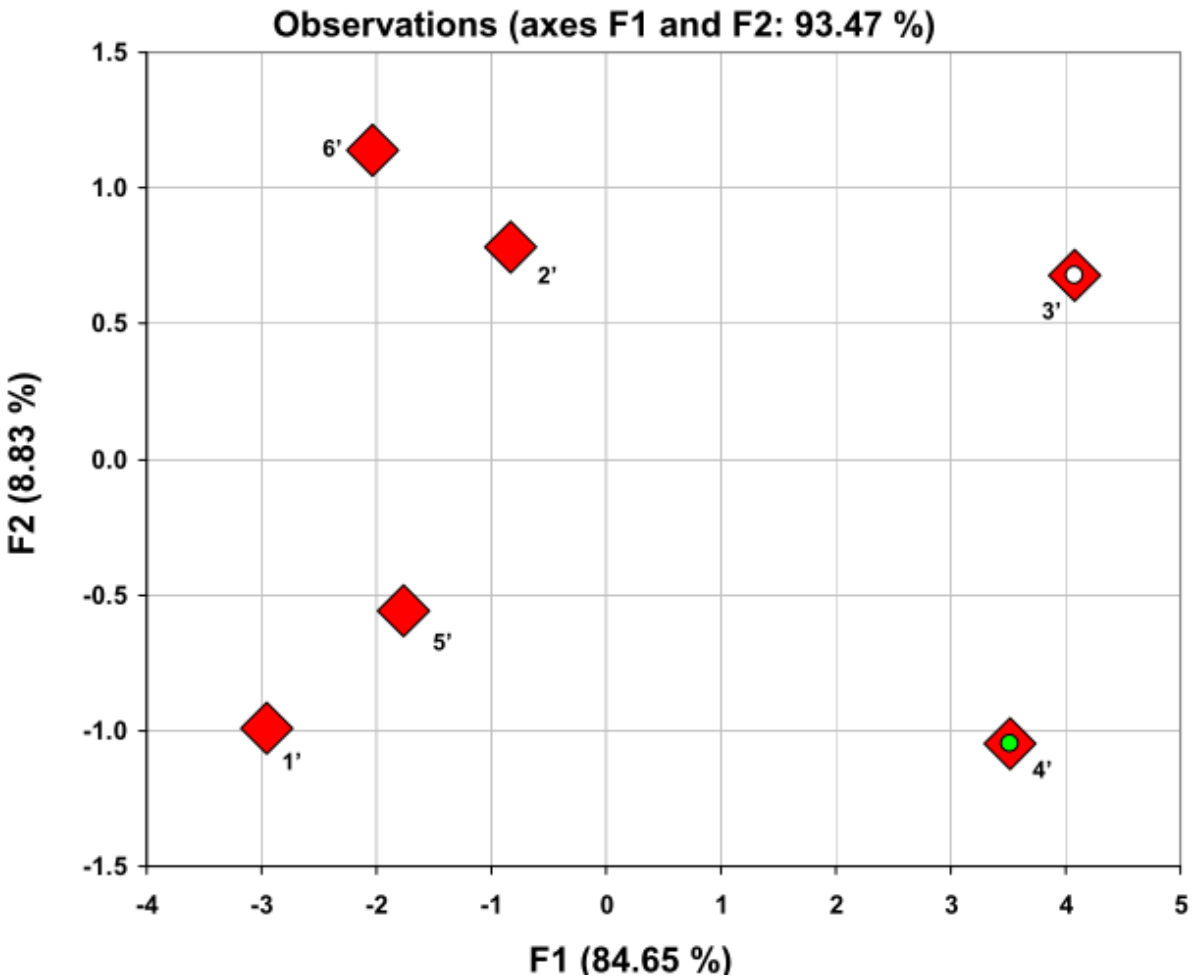


FIGURE 47. Grouping of bisphenol A samples (red diamonds) during degradation experiment observed within PCA factor scores 2D space. Samples with cyclodextrin additive are marked with white circles and also with green circles in case of duckweed presence; Objects labels: ***1'*** tap water ; ***2'*** – tap water and duckweed ; ***3'*** – tap water and β-cyclodextrin . ***4'*** – tap water and β-cyclodextrin and duckweed ***5'*** - tap water and glucose ***6'*** – tap water and glucose and duckweed.

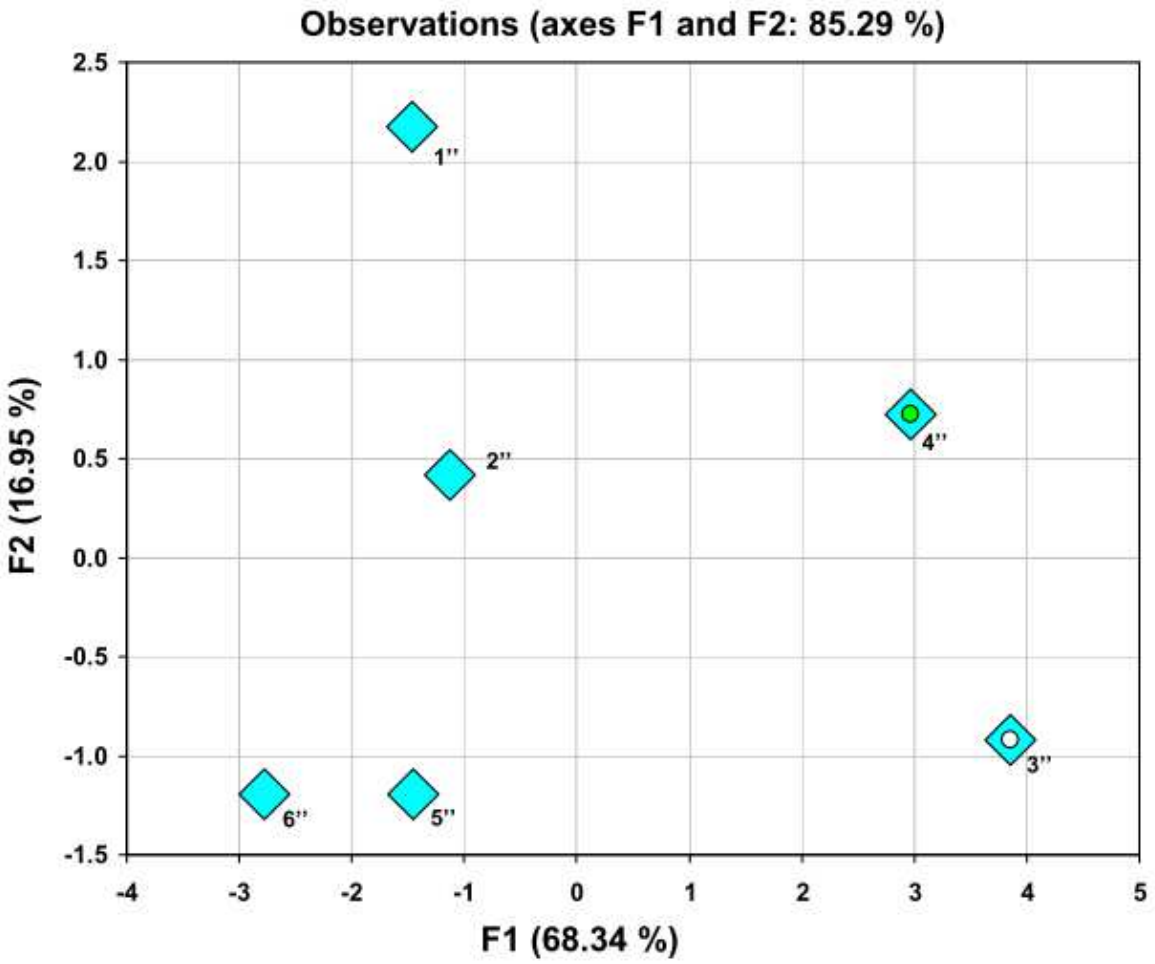


FIGURE 48. Grouping of bisphenol B samples (turquoise diamonds) during degradation experiment observed within PCA factor scores 2D space. Samples with cyclodextrin additive are marked with white circles and also with green circles in case of duckweed presence; Objects labels ; Objects labels: ***1''*** tap water ; ***2''*** – tap water and duckweed ; ***3''*** – tap water and β-cyclodextrin . ***4''*** – tap water and β-cyclodextrin and duckweed ***5''*** - tap water and glucose ***6''*** – tap water and glucose and duckweed

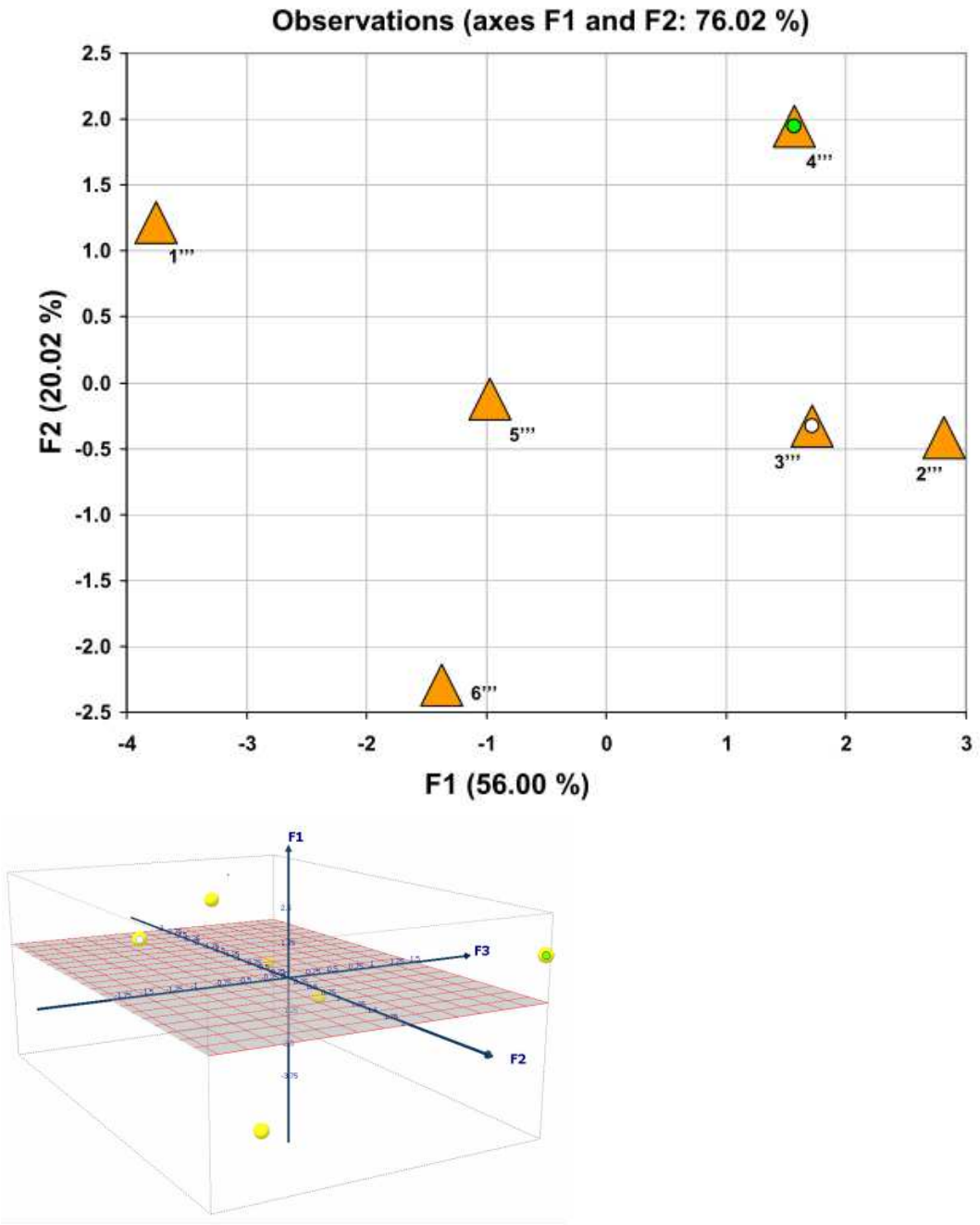


FIGURE 49. Grouping of bisphenol S samples (orange triangles) during degradation experiment observed within PCA 2D and 3D factor scores space (top and bottom graphs respectively. Samples with cyclodextrin additive are marked with white circles and also with green circles in case of duckweed presence; Objects labels ; Objects labels: ***1'''*** tap water ; ***2'''*** – tap water and duckweed ; ***3'''*** – tap water and β-cyclodextrin . ***4'''*** – tap water and β-cyclodextrin and duckweed ***5'''*** - tap water and glucose ***6'''*** – tap water and glucose and duckweed

8. LITERATURE

----------2018----------

[Świderska-Dąbrowska 2018] Świderska-Dąbrowska R., Piaskowski K., Zarzycki P.K., Preliminary Studies of Synthetic dye adsorption on iron sludge and activated carbons, Journal of AOAC International 101 (2018) 1-8.

----------2017----------

[Cheung 2017] Cheung P.K., Fok L., Characterisation of plastic microbeads in facial scrubs and their estimated emissions in Mainland China, Water Research 122 (2017) 53-61.

[Lewandowska 2017] Lewandowska L., Włodarczyk E., Fenert B., **Kaleniecka A.**, Zarzycki P.K., A Preliminary Study for the fast Prototyping of Simple Electroplanar Separation Systems Based on Various Natural Polymers and Planar Chromatographic Stationary Phases, JPC- Journal of Planar Chromatography- Modern TLC 30 (2017) 440-452.

[Ohta 2017] Ohta H., Włodarczyk E., Piaskowski K., **Kaleniecka A.**, Lewandowska L., Baran M.J., Wojnicz M., Jinno K., Saito Y., Zarzycki P.K., Unexpected differences between planar and column liquid chromatographic retention of 1-acenaphthenol enantiomers controlled by supramolecular interactions involving β-cyclodextrin at subambient temperatures, Analytical and Bioanalytical Chemistry – Springer 409 (2017) 3695-3706.

[Piaskowski 2017]. Piaskowski K., Świderska-Dąbrowska R., **Kaleniecka A.**, Zarzycki P.K., Advances in the Analysis of Water and Wastewater Samples Using Various Sensing Protocols and Microfluidic Devices based on PADs and µTAS Systems, Invited manuscript for topical, Journal of AOAC 100 (2017) 962- 970.

[Ślączka 2017] Ślączka-Wilk M.M., Włodarczyk E.,. Baran M.J., **Kaleniecka A**., Zarzycki P.K., Miniaturized Temperature-controlled Planar Chromatography (micro-TLC) as a Versatile Technique for Fast Screening of Micropollutants and Biomarkers Derived from Surface Water Ecosystems and During Wastewater Technological Processes, Invited manuscript for topical JAOAC 100 (2017) 935-949.

[Taka 2017] Taka A.L., Pillay K., Mbianda X.Y., Nanosponge cyclodextrin polyurethanes and their modification with nonmaterial's for the removal of pollutants from wastewater: A reviev, Carbohydrate Polymers 159 (2017) 94–107.

[Wang 2017] Wang Z., Zhang P., Hu F., Zhao Y., Zhu L., A crosslinked β-cyclodextrin polymer used for rapid removal of a broad spectrum of organic micropollutants from water, Carbohydrate Polymers 177 (2017) 224–231.

[Włodarczyk 2017] Włodarczyk E., Zarzycki P.K.; "Chromatographic behaviour of selected dyes on micro-TLC plates under NP and RP conditions - potential application as the internal standards substances for chromatographic and/or microfluidic systems"; Invited paper prepared for Annual Special Issue on Thin Layer Chromatography (TLC) of the JLC&RT 40 (2017) 259-281.

[Zarzycki^{A} 2017] Atta-ur-Rahman (Editor) Studies in Natural Product Chemistry (Bioactive Natural Products), Volume 54, Chapter 3, Pages 87-107: "Hopanoids in Cyanobacteria Biomass and Related Samples" by Zarzycki P.K., Kaleniecka A., Fenert B., Zarzycka M.B.,Elsevier Science Publishers, Amsterdam, the Netherlands, 2017.

[Zarzycki^{B} 2017] Zarzycki P.K., Detection and analysis of microbes, bioanalytes and micropollutants focusing on food and environmental samples, using nanoparticles based detection systems, microfluidic analytical devices and related techniques, Editorial note for Journal of AOAC International 100 (2017) 893-894.

[Xanthos 2017] Xanthos D., Walker T.R., International policies to reduce plastic marine pollution from single-use plastics (plastic bags and microbeads): A review, Marine Pollution Bulletin 118 (2017) 17–26.

----------2016----------

[Alsbaiee 2016] Alsbaiee A., Smith B.J., Xiao L., Ling Y., Helbling D.E., Dichtel W.R., Rapid removal of organic micropollutants from water by a porous β-cyclodextrin polymer, Nature 529 (2016) 190-194.

[Jin 2016] Jin H., Zhu L., Occurrence and partitioning of bisphenol analogues in water and sediment from Liaohe River Basin and Taihu Lake, China, Water Research 103 (2016) 343-351.

[Tan 2016] Tan F., Cong L., Li X., Zhao Q., Zhao H., Quan X., Chen J., An electrochemical sensor based on molecularly imprinted polypyrrole/graphene quantum dots composite for detection of bisphenol A in water samples, Sensors and Actuators B 233 (2016) 599–606.

[Yong 2016] Yong X, Wang H, Jiang Q, Zhang R., Solubility Measurement and Modeling of 4,4-Dihydroxydiphenyl Sulfone in Nine Organic Solvents from T = (278.15 to 313.15) K and Thermodynamic Property of Dissolution, Journal of Chemical and Engineering Data 61 (2016) 556−564.

[Zarzycki 2016] Zarzycki P.K., Fenert B., Głód B.K., Cyclodextrins-based nanocomplexes for encapsulation of bioactive compounds in food, cosmetics, and pharmaceuti-

cal products: principles of supramolecular complexes formation, their influence on the antioxidative properties of target chemicals, and recent advances in selected industrial applications, A. M. Grumezescu (Editor), Encapsulations, Nanotechnology in the Agri-Food Industry, Volume 2; Chapter 17717-767, Elsevier 2016.

----------2015----------

[Adhikari 2015] Adhikari U., Harrigan T., Reinhold D.M., Use of duckweed-based constructed wetlands for nutrient recovery and pollutant reduction from dairy wastewater, Ecological Engineering 78 (2015) 6–14.

[Barboza 2015] Barboza L.G.A., Garcia Gimenez B.C., Microplastics in the marine environment: Current trends and future perspectives, Marine Pollution Bulletin 97 (2015) 5–12.

[Eerkes-Medrano 2015] Eerkes-Medrano D., Thompson R.C., Aldridge D.C., Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs, Water Research 75 (2015) 63-82.

[Han 2015] Han J., Xie K. Du Z., Zou W., Zhang C., β-cyclodextrin functionalized polystyrene porous monoliths for separating phenol from wastewater, Carbohydrate polymers 120 (2015) 85-91.

[Khaoulani 2015] Khaoulani S., Chaker H., Cadet C., Bychkov E., Cherifd L., Benguedach A., Fourmentin S., Wastewater treatment by cyclodextrin polymers and noble metal/mesoporous TiO2 photocatalysts, Comptes Rendus Chimie 18 (2015) 23–31.

[Napper 2015] Napper I.E., Bakir A., Rowland S.J., Thompson R.C., Characterisation, quantity and sorptive properties of microplastics extracted from cosmetics, Marine Pollution Bulletin 99 (2015) 178–185.

[Pivnenko 2015] Pivnenko K., Pedersen G.A., Eriksson E., Astrup T.F., Bisphenol A and its structural analogues in household waste paper, Waste Management 44 (2015) 39–47.

[Pool 2015] Pool C., Instrumental Thin-Layer Chromatography. Amsterdam: Elsevier, 2015.

[Regueiro 2015] Regueiro J., Breidbach A., Wenzl T., Derivatization of bisphenol A and its analogues with pyridine-3-sulfonyl chloride: multivariate optimization and fragmentation patterns by liquid chromatography/Orbitrap mass spectrometry, Rapid Communications in Mass Spectrometry 29 (2015)1473–1484.

[Rochester 2015] Rochester J.R., Bolden A.L., Bisphenol S and F: A systematic review and comparison of the hormonal activity of bisphenol A substitutes, Environmental Health Perspectives 123 (2015) 643-650.

[Suszyński 2015] Suszyński Z., Zarzycki P.K., New approach for sensitive photothermal detection of C60 and C70 fullerenes on micro-TLC plates, Analytica chimica acta 863 (2015) 70-77.

[Yamazaki 2015] Yamazaki E., Yamashita N., Taniyasu S., Lam J., Lam P.K.S., Moon H-B., Jeong Y., Kannan P., Achyuthane H., Munuswamy N., Kanna K., Bisphenol A and other bisphenol analogues including BPS and BPF in surface water samples from Japan, China, Korea and India, Ecotoxicology and Environmental Safety 122 (2015) 565-572.

[Yin 2015] Yin Y., Yu C., Yu L., Zhao J., Sun C., Ma Y., Zhou G., The influence of light intensity and photoperiod on duckweed biomass and starch accumulation for bioethanol production, Bioresource Technology 187 (2015) 84–90.

[Yu 2015] Yu X., Xue J., Yao H., Wu Q., Venkatesan A.K., Halden R.U., Kannan K., Occurrence and estrogenic potency of eight bisphenol analogs in sewage sludge from the U.S. EPA targeted national sewage sludge survey, Journal of Hazardous Materials 299 (2015) 733–739.

[Zarzycki 2015] Zarzycki P.K., Portka J.K., Recent advances in hopanoids analysis: Quantification protocols overview, main research targets and selected problems of complex data exploration, Journal of Steroid Biochemistry & Molecular Biology 153 (2015) 3–26.

----------2014----------

[Amin 2014] Amin, M.T., Alazba, A.A., Manzoor, U., A review of removal of pollutants from water/wastewater using different types of nanomaterials, Advances in Materials Science and Engineering (2014) 1-24.

[Andrade 2014] Andrade F. I., Guedes M. I. F., Pinto Vieira I.G., Pereira Noélia Mendes F., Alves Salmito Rodrigues P., Soraya Costa Maia C., Marques Ávila M.M., de Matos Ribeiro L., Determination of Synthetic Food Dyes in Commercial Soft Drinks by TLC and Ion-Pair HPLC. Food Chem. 2014, 157, 193-198.

[Bhattarai 2014] Bhattarai B., Muruganandham M., Suri R.P.S., Development of high efficiency silica coated β-cyclodextrin polymeric adsorbent for the removal of emerging contaminants of concern from water, Journal of Hazardous Materials 273 (2014) 146–154.

[Guart 2014] Guart A., Bono-Blay F., Borrell A., Lacorte S., Effect of bottling and storage on the migration of plastic constituents in Spanish bottled waters, Food Chemistry 156 (2014) 73–80.

[Ivar do Sul 2014] Ivar do Sul J., Costa M.J., The present and future of microplastic pollution in the marine environment, Environmental Pollution 185 (2014) 352 – 364.

[Jurecska 2014] Jurecska, L., Dobosy, P., Barkacs, K., Fenyvesi, E., Zaray, G., Characterization of cyclodextrin containing nanofilters for removal of pharmaceutical residues, Journal of Pharmaceutical and Biomedical Analysis (2014) 90–93.

[Komissarchik 2014] Komissarchik S., Nyanikova G., Test Systems and a Method for Express Detection of Synthetic Food Dyes in Drinks. Food Science and Technology 58 (2014) 315-320.

[Liu 2014] Liu Q., Zhou Q., Jiang G., Nanomaterials for analysis and monitoring of emerging chemical pollutants, Trends in Analytical Chemistry 58 (2014) 10–22.

[Nagy 2014] Nagy Z.M., Molnár M., Fekete-Kertész I., Molnár-Perl I., Fenyvesi E., Gruiz K., Removal of emerging micropollutants from water using cyclodextrin, Science of the Total Environment 485–486 (2014) 711–719.

[Rezg 2014]. Rezg R., El-Fazaa S., Gharbi N., Mornagui B., Bisphenol A and human chronic diseases: Current evidences, possible mechanisms, and future perspectives, Environment International 64 (2014) 83–90.

[Sanchez 2014] Sanchez-Trujillo, M., Lacorte, S., Villaverde, J., Barata C., Morillo E., Decontamination of polycyclic aromatic hydrocarbons and nonylphenol from sewage sludge using hydroxypropyl-β-cyclodextrin and evaluation of the toxicity of leachates, Environmental Science and Pollution Research 21 (2014) 507.

[Song 2014] Song S., Song M., Zeng L., Wang T., Liu R., Ruan T., Jiang G., Occurrence and profiles of bisphenol analogues in municipal sewage sludge in China, Environmental Pollution 186 (2014) 14 -19.

[Suszyński 2014] Suszyński Z., Świta R., Łoś J., Zarzycka M.B., Kaleniecka A., Zarzycki P.K., Fast assessment of planar chromatographic layers quality using pulse thermovision method, Journal of Chromatography A 1373 (2014) 211-215.

[Wang 2014] Wang H., Wang Y., Zhou Y., Han P., Lu X., Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions, Clean Soil, Air, Water 42 (2014) 51–55.

[Yang 2014] Yang Y., Lu L., Zhang J., Yang Y., Wu Y., Shao B., Simultaneous determination of seven bisphenols in environmental water and solid samples by liquid chromatography–electrospray tandem mass spectrometry, Journal of Chromatography A, 1328 (2014) 26–34.

[Zhang 2014] Zhang J., Zhao S.Q., Zhang K., Zhou J.Q., Cd-doped ZnO quantum dots-based immunoassay for the quantitative determination of bisphenol A, Chemosphere 95 (2014) 105–110.

[Zhao 2014] Zhao Y., Fang Y., Jin Y., Huang J., Bao S., Fu T., He Z., Wang F., Zhao H., Potential of duckweed in the conversion of wastewater nutrients to valuable biomass: A pilot-scale comparison with water hyacinth, Bioresource Technology 163 (2014) 82–91.

----------2013----------

[Badruddoza 2013] Badruddoza A.Z.M., Shawon, Z.B.Z., Daniel TW.J., Hidajat K., M.S., Fe3O4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater, Carbohydrate Polymers 91 (2013) 322-332.

[Bielecka-Dasziewicz 2013] Bielicka-Daszkiewicz K., Voelkel A., Rusińska-Roszak D., Zarzycki P.K., Estimation of the breakthrough volume of selected steroids for C-18 solid-phase extraction sorbent using retention data from micro-thin layer chromatography, J. Sep. Sci. 36 (2013) 1104–1111.

[Cacho 2013] Cacho J.I., Campillo N, Viñas P, Hernández-Córdoba M., Stir bar sorptive extraction with EG-Silicone coating for bisphenols determination in personal care products by GC–MS, Journal of Pharmaceutical and Biomedical Analysis 78–79 (2013) 255–260.

[Cauwenberghe 2013] Cauwenberghe L.V., Vanreusel A., Mees J., Janssen C.R., Microplastic pollution in deep-sea sediments, Environmental Pollution 182 (2013) 495-499.

[EU 2013] DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL 2013/39 / EU of 12 August 2013 amending Directives 2000/60 / EC and 2008/105 / EC as regards priority substances in the field of water policy (Text with EEA relevance).

[Fan 2013] Fan L., Luo C., Sun M., Qiu H., Li X., Synthesis of magnetic β-cyclodextrin– chitosan/graphene oxide as nanoadsorbent and its application in dye adsorption and removal, Colloids and Surfaces B: Biointerfaces 103 (2013) 601-607.

[Lisowski 2013] Lisowski P., Zarzycki P.K., Microfluidic paper based analytical devices (μPADs) and micro total analysis systems (μTAS): development, applications and future trends, Chromatographia 76 (2013) 1201-1214.

[Rochester 2013] Rochester J.R., Bisphenol A and human health: A review of the literature, Reproductive Toxicology 42 (2013) 132–155.

----------2012----------

[Chai 2012] Chai K., Ji H., Dual functional adsorption of benzoic acid from wastewater by biological-based chitosan grafted β-cyclodextrin, Chemical Engineering Journal 203 (2012) 309-318.

[Fan 2012] Fan X., Li Y., Wu D., Ma H., Mao K., Fan D., Du B., Li H., Wei Q., Electrochemical bisphenol A sensor based on N-doped graphene sheets, Analytica Chimica Acta 711 (2012) 24–28.

[Liao 2012] Liao C., Liu F., Moon H-B., Yamashita N., Yun S., Kannan K., Bisphenol analogues in sediments from industrialized areas in the United States, Japan, and Korea: spatial and temporal distributions, Environmental Science and Technology 46 (2012) 11558 – 11565.

[Migowska 2012] Migowska N., Caban M., Stepnowski P., Kumirska J., Simultaneous analysis of non-steroidal anti-inflammatory drugs and estrogenic hormones in water and wastewater samples using gas chromatography–mass spectrometry and gas chromatography with electron capture detection, Science of The Total Environment 441, (2012) 77-88.

[Mohedano 2012] Mohedano R.A., Costa R.H.R., Tavares F.A., Filho P.B., High nutrient removal rate from swine wastes and protein biomass production by full-scale duckweed ponds, Bioresource Technology 112 (2012) 98–104.

[Song 2012] Song S., Ruan T., Wang T., Liu R., Jiang G., Distribution and preliminary exposure assessment of bisphenol AF (BPAF) in various environmental matrices around a manufacturing plant in China, Environmental Science and Technology 46 (2012) 13136–13143.

[Zhou 2012] Zhou L., Wang J., Li D., Li Y., An electrochemical aptasensor based on gold nanoparticles dotted graphene modified glassy carbon electrode for label-free detection of bisphenol A in milk samples, Food Chemistry 162 (2014) 34–40.

----------2011----------

[Andrady 2011] Andrady A.L., Microplastics in the marine environment, Marine Pollution Bulletin 62 (2011) 1596–1605.

[Cole 2011] Cole M., Lindeque P., Halsband C., Galloway TS., Microplastics as contaminants in the marine environment: A review, Marine Pollution Bulletin 62 (2011) 2588–2597.

[Srivastava 2011] Srivastava, M. High-Performance Thin-Layer Chromatography. Berlin: Springer-Verlag, 2011.

[Wang 2011] Wang Ch., Shi H., Adams CD., Timmons T., Ma Y. Investigation of pharmaceuticals in Missouri natural and drinking water using high performance liquid chromatography-tandem mass spectrometry, Water Research 2 (2011) 1818-1828.

[Xu 2011] Xu J., Shen G., Growing duckweed in swine wastewater for nutrient recovery and biomass production, Bioresource Technology 102 (2011) 848–853.

[Zarzycki^{A} 2011] Zarzycki P.K., Ślączka M.M., Zarzycka M.B., Włodarczyk E., Baran M.J.; "Application of micro-thin-layer chromatography as a simple fractionation tool for fast screening of raw extracts derived from complex biological, pharmaceutical and environmental samples" Analytica Chimica Acta 688 (2011) 168-174.

[Zarzycki^{B} 2011] Zarzycki P.K., Zarzycka M.B., Clifton V.L., Adamski J., Głód B.K., Low parachor solvents extraction and thermostated micro-TLC separation for fast screening and classification of spirulina from pharmaceutical formulations and food samples, Journal of. Chromatography A 1218 (2011) 5694-5704.

----------2010----------

[Kim 2010] Kim H.J., Lee S.D., Kwon JH., Sorption of benzimidazole anthelmintics to dissolved organic matter surrogates and sewage sludge, Chemosphere 80 (2010) 256–262.

[Oishi 2010] Oishi K., Moriuchi A., Removal of dissolved estrogen in sewage effluents by β-cyclodextrin polymer, Science of Total Environment 409 (2010) 112–115.

[Shao 2010] Shao D., Sheng G., Chen C., Wang X., Nagatru M., Removal of polychlorinated biphenyls from aqueous solutions using β-cyclodextrin grafted multiwalled carbon nanotubes, Chemosphere 79 (2010) 679–685.

[Tambosi 2010] Tambosi J.L., Felix de Sena R., Favier M., Gebhardt W.,José H.J., Schröder H.F., Regina de Fátima Peralta Muniz Moreira: Removal of pharmaceutical compounds in membrane bioreactors (MBR) applying submerged membranes. Desalination 261 (2010) 148-156.

[Yin 2010] Yin H., Zhou Y., Ai S., Chen Q., Zhu X., Liu X., Zhu L., Sensitivity and selectivity determination of BPA in real water samples using PAMAM dendrimer and CoTe

quantum dots modified glassy carbon electrode, Journal of Hazardous Materials 174 (2010) 236–243.

[Zhu 2010] Zhu R., Zhao R., Zhai M., Wei F., Cai Z., Sheng N., Hu Q., Molecularly imprinted layer-coated silica nanoparticles for selective solid-phase extraction of bisphenol A from chemical cleansing and cosmetics samples, Analytica Chimica Acta 658 (2010) 209–216.

----------2009----------

[Banerjee 2009] Banerjee, S., Sludge dewatering with cyclodextrins: a new cost-effective approach, Thirteenth International Water Technology Conference, IWTC 13 2009, Hurghada, Egypt.

[Bonenfant 2009] Bonenfant, D., Niquette, P., Mimeault M., A Furtos-Matei A., Hausler R., UV-VIS and FTIR spectroscopic analyses of inclusion complexes of nonylphenol and nonylphenol ethoxylate with β-cyclodextrin Water Research 43 (2009) 3575–3581.

[Chang 2009] Chang H-S., Choo K-H., Lee B., Choi S-J., The methods of identification, analysis, and removal of endocrine disrupting compounds (EDCs) in water, Journal of Hazardous Materials 172 (2009) 1–12.

[Fendall 2009] Fendall L.S., Sewell M.A., Contributing to marine pollution by washing your face: Microplastics in facial cleansers, Marine Pollution Bulletin 58 (2009) 1225–1228.

[Steed 2009] Steed J.W., Atwood L.J., Supramolecular Chemistry 2009 John Wiley & Sons, Ltd.

[Włodarczyk 2009] Włodarczyk E., Znaczenie i występowanie wybranych substancji typy EDCs w środowisku, PHD thesis Koszalin 2009.

[Zarzycki^{A} 2009] Zarzycki P.K., Włodarczyk E., Baran M.J., Determination of endocrine disrupting compounds using temperature-dependent inclusion chromatography I. Optimization of separation protocol, Journal of Chromatography A 1216 (2009) 7602–7611.

[Zarzycki^{B} 2009] Zarzycki P.K., Włodarczyk E., Baran M.J., Determination of endocrine disrupting compounds using temperature-dependent inclusion chromatography II. Fast screening of free steroids and related low-molecular-mass compounds fraction in the environmental samples derived from surface waters, treated and untreated sewage waters as well as activated sludge material, Journal of Chromatography A 1216 (2009) 7612–7622.

[Zarzycki^{C} 2009] Zarzycki P.K., Włodarczyk E., Zarzycka MB., Głód BK., Optimization of solid-phase extraction protocol for fractionating of selected steroids using retention data from micro thin-layer chromatography, Analytical Science 25 (2009) 935-939.

----------2008----------

[Bezuidenhout 2008] Bezuidenhout L.W., Brett M.J., Ultrathin layer chromatography on nanostruc-tured thin films, Journal of Chromatography A 1183 (2008) 179-185.

[European Union Risk Assessment Report 2012] EU; European Union Risk Assessment Report, CAS: 80-05-7 EINECS No: 201-245-8, Environment Addendum of April 2008, 4,4'-ISOPROPYLIDENEDIPHENOL (Bisphenol-A), Part 1 Environment; Available from, as of Nov 13, 2012.

[Maniero 2008] Maniero M.G., Bila D.M., Dezotti M., Degradation, estrogenic activity removalof 17β-estradiol and 17α-ethinylestradiol by ozonation and O_3 /H_2O_2 , Science of the Total Environment 407 (2008) 105–115.

[Surowiec 2008] Surowiec I., Pawelec K., Rezeli M., Kilar F., Trojanowicz M., Capillary Electrophoretic Determination of Main Components of Natural Dyes with MS Detection, Journal of separation science 31 (2008) 2457-2462.

[Yamasaki 2008] Yamasaki H., Makihata Y., Fukunaga K., Preparation of crosslinked β-cyclodextrin polymer beads and their application as a sorbent for removal of phenol from wastewater Journal of Chemical Technology and Biotechnology 83 (2008) 991–997.

[Zarzycki^{A} 2008] Zarzycki P.K., Simple horizontal chamber for thermostated micro-thin-layer chromatography. Journal of Chromatography A. 1187(2008) 250-259.

[Zarzycki^{B} 2008] Zarzycki P.K., Ohta H., Saito Y., Jinno K. Interaction of native α-cyclodextrin, β–cyclodextrin and γ -cyclodextrin and their hydroxypropyl derivatives with selected organic low molecular mass compounds at elevated and subambient temperature under RP-HPLC conditions, Analytical and Bioanalytical Chemistry 391 (2008) 2793 – 2801.

----------2007----------

[Aoki 2007] Aoki N., Kinoshita K., Mikuni K., Nakanishi K., Hattori K., Adsorption of 4-nonylphenol ethoxylates onto insoluble chitosan beads bearing cyclodextrin moieties, Journal of Inclusion Phenomena and Macrocyclic Chemistry 57 (2007) 237-241.

[Brewster 2007] Brewster M.E., Loftsson T., Cyclodextrins as pharmaceutical solubilizers, Advanced Drug Delivery Reviews 59 (2007) 645–666.

[Furuta 2007] Furuta T., Ikefuji S., Tokunaga K., Neoh T.L., Yoshii H., Enhanced effect of RM-β-cyclodextrin on biodegradation of toluene in wastewater by activated sludge, Journal of Inclusion Phenomena and Macrocyclic Chemistry 57 (2007) 21-27.

[Ko 2007] Ko E-J., Kim K-W., Kang S-Y., Kim S-D., Bang S-B., Hamm S-Y., Kim D-W., Monitoring of environmental phenolic endocrine disrupting compounds in treatment effluents and river waters, Korea, Talanta 73 (2007) 674–683.

[Lasfar 2007] Lasfar S., Monette F., Millette L., Azzouz A., Intrinsic growth rate: A new approach to evaluate the effects of temperature, photoperiod and phosphorus–nitrogen concentrations on duckweed growth under controlled eutrophication, Water Research 41 (2007) 2333-2340.

[Mőder 2007] Mőder M., Braun P., Lange F., Schrader S., Lorenz W., Determination of endocrine disrupting compounds and acidic drugs in water by coupling of derivatization, gas chromatography and negative-chemical ionization mass spectrometry, Clean 35 (2007) 444 –451.

----------2006----------

[Isobe 2006] Isobe T., Serizawa S., Horiguchi T., Shibata Y., Managaki S., Takada H., Morita M., Shiraishi H., Horizontal distribution of steroid estrogens in surface sediments in Tokyo Bay, Environmental Pollution 144 (2006) 632.

[Kowalkowski 2006] Kowalkowski T., Zbytniewski R., Szpejna J., Buszewski, B., Application of chemometrics in river water classification, Water Research 40 (2006) 744.

[O'Neil 2006] O'Neil M.J., (ed.). The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc., (2006) 212.

[Shon 2006] Shon H.K., Vigneswaran S., Snyder S.A., Effluent organic matter (EfOM) in wastewater; constituents, effects, and treatment, Critical reviews in Environmental Science and Technology 36 (2006) 327–374.

[Zarzycki 2006] Zarzycki P.K., Kulhanek K.M., Smith R., Clifton V.L., Determination of steroids in human plasma using temperature-dependent inclusion chromatography for metabolomic investigations, Journal of Chromatography A. 1104 (2006)203-208

----------2005----------

[Challa 2005] Challa R., Ahuja A.,, Ali J., Khar R.K., Cyclodextrins in Drug Delivery: An Updated Review, AAPS PharmSciTech 6 (2005) 329-357.

[Crini 2005] Crini G., Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Progress in polymer science 30 (2005) 38-70.

[Kim 2005] Kim T.U., Amy G., Drewes J.E., Rejection of trace organic compounds by high-pressure membranes, Water Science and Technology 51 (2005) 335–344.

[Liu 2005] Liu M., Li L-S., Da S-L., Feng Y-Q., High performance liquid chromatography with cyclodextrin and calixarene macrocycle bonded silica stationary phases for separation of steroids, Talanta 66 (2005) 479–486.

[Westerhoff 2005] Westerhoff P., Yoon Y., Snyder S., Wert E., Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes, Environmental Science and Technology 39 (2005) 6649–6663.

----------2004----------

[Kimura 2004] Kimura K., Toshima S., Amy G., Watanabe Y., Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, Journal of Membrane Science 245 (2004) 71–78.

[Pinkston 2004] Pinkston K.E., Sedlak D.L., Transformation of aromatic ether- and amine containing pharmaceuticals during chlorine disinfection, Environmental Science and Technology 38 (2004) 4019–4025.

[Rodriguez-Mozaz 2004]Rodriguez-Mozaz S., López de Alda M.J., Barceló D., Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction–liquid chromatography–mass spectrometry, Journal of Chromatography A 1045 (2004) 85–92.

----------2003----------

[Barceló 2003] Barceló D., Emerging pollutants in water analysis, Trends in Analytical Chemistry 22 (2003) 14-16.

[Dalu 2003] Dalu J.M., Ndamba J., Duckweed based wastewater stabilization ponds for wastewater treatment (a low cost technology for small urban areas in Zimbabwe), Physics and Chemistry of the Earth, Parts A/B/C 28(2003) 1147-1160.

[Gomes 2003] Gomes R.L., Scrimshaw M.D., Lester J.N., Determination of endocrine disrupters in sewage treatment and receiving waters, Trends in Analytical Chemistry 22 (2003) 697.

[Huang 2003] Huang H.-Y., Chiu C.-W., Sue S.-L., Cheng C.-F., Analysis of Food Colorants by Capillary Electrophoresis with Large-Volume Sample Stacking, Journal of Chromatography A 995 (2003) 29–36.

[Sherma 2003] Sherma J., Fried B., Handbook of Thin-Layer Chromatography, Marcel Dekker,New York, 2003.

[Stachel 2003] Stachel B., Ehrhorn U., Heemken O.P., Lepom P., Reincke H., Sawal G., Theobald N, Xenoestrogens in the River Elbe and its tributaries, Environmental Pollution 124 (2003) 497–507.

[Snyder 2003] Snyder S., Vanderford B., Pearson R., Quinõnes O., Yoon Y., Analytical methods used to measure endocrine disrupting compounds in water, Practice Periodical of Hazardous, Toxic, and Radioactive Waste 7 (2003) 224–234.

[Ternes 2003] Ternes T.A., Stuber J., Herrmann N., McDowell D., Ried A., Kampmann N., Teiser B., Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater, Water Research 37 (2003) 1976–198.

----------2002----------

[Fromme 2002] Fromme H., Küchler T., Otto T., Pilz K., Müller J., Wenzel A., Occurrence of phthalates and bisphenol A and F in the environment, Water Research 36 (2002) 1429–1438.

[Miao 2002] Miao XS, Koeing BG, Metcalfe CD, Analysis of acidic drugs in the effluents of sewage treatment plants using liquid chromatography- electrospray ionization tandem mass spectrometry. Journal of Chromatography A 952 (2002) 139-147.

[Nerın 2002] Nerın C., Philo M.R., Salafranca J., Castle L., Determination of bisphenol-type contaminants from food packaging materials in aqueous foods by solid-phase microextraction–high-performance liquid chromatography, Journal of Chromatography A 963 (2002) 375–380.

[Nghiem 2002] Nghiem L.D., Schafer A.I., Adsorption and transport of trace contaminant estrone in NF/RO membranes, Environmental Engineering Science 19 (2002) 441–451.

[Sorensen 2002] Sorensen L.K., Hansen H., Determination of sulfadiazine and timethoprim in marine sediment by LC-APCI-MS, Journal of Liquid Chromatography and Related Technology 25 (2002) 1063-1075.

[Ternes^{A} 2002] Ternes T.A., Andersen H., Gilberg D., Bonerz M., Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS. Analytical Chemistry 74 (2002) 3498-3504.

[Ternes[B] 2002] Ternes T.A., Meisenheimer M., Mcdowell D., Brauch H.J., Brigitte H.G, Preuss G., William U., Zulei-Seibert N., Removal of pharmaceuticals during drinking water treatment, Environmental Science and Technology 36 (2002) 3855–3863.

[Weigel 2002] Weigel S., Kuhlmann J., Huhnerfuss H., Drugs and personal care products as ubiquitous pollutants occurrence and distribution of clofibric acid, caffeine and DEET in the North Sea, Science of Total Environment 295(2002) 131-141.

[Zarzycki 2002] Zarzycki P.K., Kulhanek K.M., Smith R., Chromatographic behaviour of selected steroids and their inclusion complexes with β-cyclodextrin on octadecylsilica stationary phases with different carbon loads, Journal of Chromatography A 955 (2002) 71–78.

----------2001----------

[Ahrer 2001] Ahrer W., Buchlberger W., Analysis of acidic pharmaceutical drug residues in surface water by capillary electrophoresis- electrospray mass spectrometry, American Laboratory 33 (2001) 31-35.

[Lindsey 2001] Lindsey M.E., Meyer M., Thurman E.M., Analysis of trace levels of sulfonamide and tetracycline antimicrobials in groundwater and surface water using solid-phase extraction and liquid chromatography/mass spectrometry, Analytical Chemistry 73 (2001) 4640–4646.

[Ollers 2001] Ollers S., Singer H.P, Fassler P., Muller S.R., Simultaneous qualification of neutral and acidic pharmaceuticals and pesticides at low-ng/1 level in surface and wastewater, Journal of Chromatography A 911 (2001) 225-235.

[Ternes 2001] Ternes TA., Analytical methods for the determination of pharmaceuticals in aqueous environmental samples, Trends in Analytical Chemistry 20 (2001) 419-434.

[Zarzycki 2001] Zarzycki P.K., Smith R., Separation of steroids using temperature-dependent inclusion Chromatography, Journal of Chromatography A 912 (2001) 45–52.

----------2000----------

[Gertz 2000] Gertz C., Klostermann S., Parkash-Kochhar S., Testing and comparing oxidative stability of vegetable oils and fats at frying temperature, European Journal of Lipid Science and Technology 102 (2000) 543–551.

----------1999----------

[Bielejewska 1999] Bielejewska A., Nowakowski R., Duszczyk K., Sybilska D., Joint use of cyclodextrin additives in chiral discrimination by reversed-phase high-

performance liquid chromatography: temperature effects, Journal of Chromatography A 840 (1999) 159-170.

[Łomotowski 1999] Łomotowski J., Szpindor A. Nowoczesne systemy oczyszczania ścieków. Arkady. 1999.

[Ternes 1999] Ternes T.A., Kreckel P., Mueller J., Behaviour and occurrence of estrogens in municipal sewage treatment plants—II. Aerobic batch experiments with activated sludge, Science of the Total Environment 225 (1999) 91.

[Zarzycki 1999] Zarzycki P.K., Wierzbowska M., Nowakowska J., Chmielewska A., Lamparczyk H., Interactions between native cyclodextrins and n-alcohols studied using thermostated thin-layer chromatography, Journal of Chromatography A 839 (1999) 149–156.

----------1998----------

[Buser 1998] Buser HR, Poiger T, Muller MD, Occurrence and fate of pharmaceutical drug diclofenac in surface waters: Rapid photodegradation in a lake. Environmental Science and Technology 32 (1998) 3449-3456.

[Clemons 1998] Clemons J.H., Allan L.M., Marvin C.H., Wu Z., McCarry B. E.,. Bryant D. W., Zacharewski T. R., Evidence of estrogen-and TCDD-like activities in crude and fractionated extracts of PM10 air particulate material using in vitro gene expression assays Environmental Science and Technology 32 (1998) 1853.

[Crain 1998] Crain D.A., Guillette L.J., Pickford D.B., Percival H. F., Woodward A.R., Sex‐steroid and thyroid hormone concentrations in juvenile alligators (*Alligator mississippiensis*) from contaminated and reference lakes in Florida, USA Environmental Toxicology and Chemistry 17 (1998) 446-452.

[Gebauer 1998] Gebauer S., Friebe S., Gübitz G., Krauss G-J., High performance liquid chromatography on calixarene-bonded silica gels. II. Separations of regioand stereoisomers on p-tert-Butylcalix[n]arene phases, Journal of Chromatographic Science 36 (1998) 383-387.

[Hogenboom 1998] Hogenboom A.C., Niessen W.M.A., Brinkman U.A.T., Rapid target analysis of microcontaminants in water by on-line single- short-column liquid chromatography combined with atmospheric pressure chemical ionization ion-trap mass spectrometry, Journal of Chromatography A 794(1998) 201-210.

[Körner 1998] Körner S., Vermaat J.E., The relative importance of Lemna gibba L., bacteria and algae for the nitrogen and phosphorus removal in duckweed-covered domestic wastewater, Water Research 32 (1998) 3651-3661.

[Morin 1998] Morin N., Guillaume Y. C., Rouland J.C., A simple model for RPLC retention and selectivity of imidazole enantiomers using β-cyclodextrin as chiral selector, Chromatographia 48 (1998) 388–394.

[Uekama 1998] Uekama, K., Hirayama, F., Irie, T., Cyclodextrin Drug Carrier Systems, Chemical reviews 98, (1998) 2045-76.

[Zarzycki^{A} 1998] Zarzycki P.K., Lamparczyk H. 1998. Evidences for temperature-dependent mechanism of host-guest complexation. Chromatographia 48 (5-6): 377-382.

[Zarzycki^{B} 1998] Zarzycki, P.K., Lamparczyk, H., The equilibrium constant of beta-cyclodextrin-phenolphthalein complex; Influence of temperature and tetrahydrofuran addition, Journal of pharmaceutical and biomedical analysis 18 (1998) 165-170.

----------1997----------

[Bonomo 1997] Bonomo L., Pastorelli G., Zambon N., Advantages and limitations of duckweed-based wastewater treatment systems, Water Science and Technology 35 (1997) 239-246.

[Rivas 1997] Rivas A., Olea N., Olea-Serrano F., Human exposure to endocrine-disrupting chemicals: assessing the total estrogenic xenobiotic burden, Trends in Analytical Chemistry 16 (1997) 613.

[Van Elteren 1997] Van Elteren J.T., Slejkovec Z., Ion-exchange separation of eight arsenic compounds by high performance liquid chromatography–UV decomposition–hydride generation–atomic fluorescence spectrometry and stability tests for food treatment procedures, ournal of Chromatography A 789 (1997) 339–348.

[Zarzycki 1997] Zarzycki P.K., Nowakowska J., Chmielewska A., Wierzbowska M., Lamparczyk H., Thermodynamic study of the retention behavior of selected macrocycles using reverse-phase high-performance thin-layer chromatography plates and methanol-water mobile phase, Journal of Chromatography A 787 (1997) 227-233.

----------1996----------

[Loftsson 1996] Loftsson T., Brewster M. E., Pharmaceutical applications of cyclodextrins. 1. Drug solubilization and stabilization, Journal of Pharmaceutical Sciences 85 (1996) 1017-1025.

[Sadlej-Sosnowska 1996] Sadlej-Sosnowska N., Thermodynamic parameters of the formation of a complex between cyclodextrins and steroid hormones, Journal of Chromatography A 728 (1996) 89-95.

[Zarzycki^{A} 1996] Zarzycki P.K., Lamparczyk H. 1996. A simple experiment demonstrating the temperature effect in supramolecular chemistry. Journal of Chemical Education 73 (5): 459-460.

[Zarzycki^{B} 1996] Zarzycki P.K., Wierzbowska M., Lamparcyk H., The influence of temperature on the high performance liquid chromatographic separation of steroids using mobile phases modified with β-cyclodextrin, Journal of Pharmaceutical and Biomedical Analysis 14 (1996) 1305-1311.

----------1995----------

[Lehn 1995] Lehn J.M., Supramolecular Chemistry: Concepts and Perspectives. VCH(1995) Weinheim.

[Wittliff 1995] Wittliff J.L., Raffelsberger W., Mechanisms of signal transduction: sex hormones, their receptors and clinical utility, Journal of Clinical Ligand Assay, 1995, 18: 211-235.

[Zarzycki 1995] Zarzycki P.K., Nowakowska J., Chmielewska A., Lamparczyk H., Retention properties of cyclodextrin in reversed phase HPTLC, Journal of Planar Chromatography 8 (1995) 227-231.

----------1994----------

[Lamparczyk 1994] Lamparczyk H., Zarzycki P.K., Nowakowska J., Effect of temperature on separation of norgestrel enantiomers by high-performance liquid chromatography, Journal of Chromatography A 668 (1994) 413.

[Oron 1994] Oron G., Duckweed culture for wastewater renovation and biomass production, Agricultural Water Management 26 (1994) 27-40.

[Stone 1994] Stone R., Environmental estrogens stir debate, Science 265 (1994) 308.

----------1993----------

[Seidel 1993] Seidel V., Poglits ., Schiller K., Lindner W., Simultaneous determination of ochratoxin A and zearalenone in maize by reversed-phase high-performance liquid chromatography with fluorescence detection, Journal of Chromatography A 635 (1993) 227-235.

[Shore 1993]Shore L.S., Gurevitz M., Shemesh M., Estrogen as an environmental pollutant Bulletin of Environmental. Contamination and Toxicology. 51 (1993) 361.

----------1992----------

[Vazquez 1992] Vazquez M.L., Franco C.M., Cepeda A., Prognon P., Mahuzier G., Liquid chromatographic study of the interaction between aflatoxins and β-cyclodextrin, Analytica Chimica Acta 269 (1992), 239-247.

----------1990----------

[Berthod 1990] Berthod A., Jin H.L., Beesley T.E., Duncan J.D., Armstrong D.W., Cyclodextrin chiral stationary phases for liquid chromatographic separations of drug stereoisomers, Journal of Pharmaceutical & Biomedical Analysis 8 (1990) 123-130.

[Lepri 1990] Lepri L., Coas V., Desideri P.G., Checchini L., Separation of optical and structural isomers by planar chromatography with development by beta-cyclodextrin, Journal of Planar Chromatography 3 (1990) 311.

----------1989----------

[Aherne 1989] Aherne G. W., Briggs R., The relevance of the presence of certain synthetic steroids in the aquatic environment, Journal of Pharmacy Pharmacology 41 (1989) 735.

----------1987----------

[Connors 1987]K. A. Connors: Binding constants — the measurement of molecular complex stability, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore 1987. 411 Seiten.

[Dorn 1987] Dorn P.B., Chou C.S., Gentempo J.J., Degradation of bisphenol A in natural waters, Chemosphere 16 (1987)1501-1507.

----------1982----------

[Szejtli 1982] Szejtli J., Cyclodextrins and Their Incl. Complexes. Akademiai Kiado, Budapest, 1982.

----------1979----------

[Matsui 1979] Matsui Y., Mochida K., Binding forces contributing to the association of Cyclodextrin with alcohol in an aqueous solution, Bulletin of the Chemical Society of Japan 52 (1979) 2808–2814.

----------1975----------

[Ikeda 1975] Ikeda K., Uekama K., Otagiri M., Inclusion complexes of 13-cyclodextrin with antiinflammatory drugs fenamates in aqueous solution, Chemical and Pharmaceutical Bulletin 23 (1975) 201 - 208

----------1954----------

[Cramer 1954] Cramer F., Eischlussverbindungen (Inclusion Compounds). Springer-Verlag, Berlin 1954.

Internet pages:

[Tara Mediterranean expedition 2016]
www https://oceans.taraexpeditions.org/en/m/about-tara/les-expeditions/tara-oceans/

[EPA A 2018]EPA United States Environmental Protection Agency, Chemistry Dashboard:
https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+A
[EPA AP 2018]EPA United States Environmental Protection Agency, Chemistry Dashboard:
https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=bisphenol+AP
[Holocarbon 2012] Halocarbon; Bisphenol AF (CAS No. 1478-61-1) Data Sheet. River Edge, NJ: Halocarbon Products Corp. Available from, as of Nov 5, 2012:
http://www.halocarbon.com/halocarbon_media/BisphenolAFBPAF_224.pdf
[EPA AF 2018]EPA United States Environmental Protection Agency, Chemistry Dashboard:
https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+AF
[EPA B 2018]EPA United States Environmental Protection Agency, Chemistry Dashboard
https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+B
[EPA BP 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard
https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=bisphenol+BP
[EPA C 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard

https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+C

[Toxnet 2018] //toxnet.nlm.nih.gov/cgibin/sis/search/a?dbs+hsdb:@term+@DOCNO+8091

[EPA F 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard: https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+F

[EPA E 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID3047891

[EPA S 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard: https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+S

[EPA Z 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard: https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID4047963

[EPA FL 2018] EPA United States Environmental Protection Agency, Chemistry Dashboard: https://comptox.epa.gov/dashboard/dsstoxdb/results?utf8=%E2%9C%93&search=Bisphenol+FL

[Meti rep. 2018] http://www.meti.go.jp/english/report/downloadfiles/gED0315e.pdf Hazardassessment of Bisphenol A

[Degremont 2018] http://www.degremont.com/en/news/special-topics/what-are-micropollutants/

9. LIST OF THE OWN PAPERS

Publications related to this PhD thesis are highlighted in yellow. They contains experimental and/or review data, which were partially published in form of experimental and review papers as well as book chapters and conferences abstracts. These data were discussed in both Introduction and Experimental parts of this PhD dissertation.

[1]. Lewandowska L., Włodarczyk E., Fenert B., **Kaleniecka A.**, Zarzycki P. K., A Preliminary Study for the fast Prototyping of Simple Electroplanar Separation Systems Based on Various Natural Polymers and Planar Chromatographic Stationary Phases, JPC-JOURNAL OF PLANAR CHROMATOGRAPHY-MODERN TLC Vol 30 N05 (2017) 440-452.

[2] Atta-ur-Rahman (Editor) Studies in Natural Product Chemistry (Bioactive Natural Products), Volume 54, Chapter 3, Pages 87-107: "Hopanoids in Cyanobacteria Biomass and Related Samples" by Zarzycki P.K., **Kaleniecka A**., Fenert B., Zarzycka M.B., Elsevier Science Publishers, Amsterdam, the Netherlands, 2017.

[3] Piaskowski K., Świderska-Dąbrowska R., **Kaleniecka A.**, Zarzycki P.K., "Advances in the Analysis of Water and Wastewater Samples Using Various Sensing Protocols and Microfluidic Devices based on PADs and µTAS Systems", Invited manuscript for topical Journal of AOAC issue Vol 100 N04 (2017) 962- 970. DOI: 10.5740/jaoacint.17-0170

[4] Ślączka-Wilk M.M., Włodarczyk E., Baran M.J., **Kaleniecka A.**, Zarzycki P.K., Miniaturized Temperature-controlled Planar Chromatography (micro-TLC) as a Versatile Technique for Fast Screening of Micropollutants and Biomarkers Derived from Surface Water Ecosystems and During Wastewater Technological Processes, Invited manuscript for topical JAOAC issue; Vol 100, No 4 (2017) 935-949. DOI: 10.5740/jaoacint.17-0168

[5] Ohta H., Włodarczyk E., Piaskowski K., **Kaleniecka A.**, Lewandowska L., Baran M.J., Wojnicz M., Jinno K., Saito Y., Zarzycki P.K., Unexpected differences between planar and column liquid chromatographic retention of 1-acenaphthenol enantiomers

controlled by supramolecular interactions involving β-cyclodextrin at subambient temperatures Analytical Bioanalytical Chemistry 409 (2017) 3695-3706 (Springer) DOI: 10.1007/s00216-017-0313-y

[6] Suszyński Z., Świta R., Łoś J., Zarzycka M.B., **Kaleniecka A.**, Zarzycki P.K., Fast assessment of planar chromatographic layers quality using pulse thermovision method, Journal of Chromatography A 1373 (2014) 211-215.

[7] **Kaleniecka A.,** Zarzycki P.K., Pharmaceuticals in the acquatic environment: sources, effects, treatment methods, Arch. Physiother. Glob. Res. 19 (3) (2015) 39-52.

[8] Kurhalyuk N., Hetmański T., Antonowicz J., Kasprzak M., **Kaleniecka A.,** Tkachenko H., Milewczyk M. "Ocena antyoksydacyjnego bilansu we krwi gołębi (Columba livia) z różnych środowisk północnej Polski" Słupskie Prace Biologiczne, 4, (2007) 43-51.

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10. LIST OF CONFERENCES PRESENTATIONS PUBLISHED IN FORM OF ABSTRACTS IN CONFERENCES PROCEEDINGS

[1] Zarzycki P.K., **Kaleniecka A.**, Włodarczyk E., "Development of new protocols for monitoring of micropollutants and biomarkers in surface water ecosystems: chromatographic analysis of bisphenols" XIXth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 16-19 November 2017, Jastrzębia Góra, Poland.

[2]. Zarzycki P.K, Lewandowska L., Fenert B., **Kaleniecka A.**; "Electronic nose on small sailing yacht" XIXth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 16-19 November 2017, Jastrzębia Góra, Poland.

[3] Zarzycki P.K., Lewandowska L., **Kaleniecka A.**, Fenert B., Piaskowski K., Włodarczyk E., Baran M.J., Wojnicz M., Świderska-Dąbrowska R., Ohta H., Saito Y., Jinno K.; "Development of new protocols for monitoring of micropollutants and biomarkers in surface water ecosystems: hybrid electoplanar separation of dyes and micro-TLC analysis of host-guest supramolecular complexes" XIXth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 16-19 November 2017, Jastrzębia Góra, Poland.

[4] **Kaleniecka A.**, Włodarczyk E., Zarzycki P.K., "Separation and analysis of various bisphenols involving supramolecular complexes with macrocyclic oligosaccharides". EMN (Energy, Materials, Nanotechnology) Meeting on Biomaterials, August 14-18, Milan, Italy.

[5] Ohta H., Włodarczyk E., Piaskowski K., **Kaleniecka A.**, Lewandowska L., Baran M.J., Wojnicz M., Jinno K., Saito Y., Zarzycki P.K., "Adjustment of phenomenological model describing liquid chromatography retention controlled by supramolecular interactions with natural cyclodextrins" EMN (Energy, Materials, Nanotechnology) Meeting on Biomaterials, August 14-18, Milan, Italy.

[6] Zarzycki PK., Baran M.J., Lewandowska L., Włodarczyk E., Świderska-Dąbrowska R., Piaskowski K., Wojnicz M., Nowak R., **Kaleniecka A.**, Fenert B., "Wyniki Wstępnych badań batymetrycznych oraz metodologii poboru prób wody i osadów dennych

wybranych ekosystemów wód powierzchniowych Pomorza Środkowego"; XVIIIth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 24-27 November 2016, Jurata, Poland.

[7] Fenert B., Wróblewska-Krepsztul J., **Kaleniecka A.**, Baran M.J., Włodarczyk E., Zarzycki P.K., "Rola cyjanobakterii w ekosystemach wodnych oraz ich wykorzystanie praktyczne". XVIIth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 28-29 December 2015, Lidzbark Warmiński, Poland.

[8] Włodarczyk E., **Kaleniecka A.**, Fenert B., Wróblewska-Krepsztul J., Baran M.J., Zarzycki P.K., "Estrogenne modulatory hormonalne w ekosystemach wód powierzchniowych". XVIIth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 28-29 December 2015, Lidzbark Warmiński, Poland.

[9]. Baran M.J, **Kaleniecka A.**, Wróblewska-Krepsztul J., Fenert B., Włodarczyk E., Zarzycki P.K., "Wybrane problemy poboru i obróbki próbek ciekłych oraz stałych z ekosystemów wodnych dla celów analiz chromatograficznych". XVIIth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 28-29 December 2015, Lidzbark Warmiński, Poland.

[10] **Kaleniecka A.**, Fenert B., Wróblewska-Krepsztul J., Baran M.J., Włodarczyk E., Zarzycki P.K., "Wykorzystanie kompleksów supramolekularnych w eliminacji substancji typu EDCs z wód powierzchniowych oraz w trakcjie procesów technologicznych oczyszczania ścieków". XVIIth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 28-29 December 2015, Lidzbark Warmiński, Poland.

[11] Zarzycki P.K., **Kaleniecka A.**, Fenert B., Wróblewska-Krepsztul J., Baran M.J., Włodarczyk E., "Hopanoidy jako biomarkery procesów hydrobiologicznych". XVIIth Annual meeting of the Polish Hyperbaric Medicine and Technology Society, 28-29 December 2015, Lidzbark Warmiński, Poland.

[12] Wróblewska-Krepsztul J., Fenert B., **Kaleniecka A.**, Baran M.J., Włodarczyk E., Zarzycki P.K., "Mikroukładowe metody analizy zanieczyszczeń wody". XVIIth Annual

meeting of the Polish Hyperbaric Medicine and Technology Society, 28-29 December 2015, Lidzbark Warmiński, Poland.

11. ABBREVIATIONS

AOP- advanced oxidation process
BAC- biological activated carbon
CE- Capillary electrophoresis
EC- Emerging contaminants
EDC's- endocrine disrupting compounds
HPLC- high-performance liquid chromatography
MBR- membrane bioreactor
MF- microflitration
NF- nanofiltration
UF- ultrafiltration
PCP- personal care product
PPCP- pharmaceutical and personal care product
RO- reverse osmosis
SPE- solid phase extraction
TLC- thin layer chromatography
WWTP- wastewater treatment plant

12. SUPPLEMENTS LIST

[S1] Kaleniecka A., Zarzycki P.K., Pharmaceuticals in the acquatic environment: sources, effects, treatment methods, Arch. Physiother. Glob. Res. 19 (3) (2015) 39-52.

[S2] Ohta H., Włodarczyk E., Piaskowski K., Kaleniecka A., Lewandowska L., Baran M.J., Wojnicz M., Jinno K., Saito Y., Zarzycki P.K.; "Unexpected differences between planar and column liquid chromatographic retention of 1-acenaphthenol enantiomers controlled by supramolecular interactions involving β-cyclodextrin at subambient temperatures" Anal. Bioanal. Chem. 409 (2017) 3695-3706 (Springer) DOI: 10.1007/s00216-017-0313-y

13. ABSTRACT

Investigation of supramolecular encapsulation as potential tool for analysis and removal of selected micropollutants from liquid phases

Presented PhD thesis concerns experimental work that is focusing on investigation of supramolecular encapsulation processes driven by cyclodextrins additives as the potential tool for analysis and removal of selected organic micropollutants from liquid phases. Particularly, several aspects of host-guest complexation were studied including: ***(i)*** basic research related to formation of supramolecular complexes (molecular encapsulation) between macrocyclic compounds (β-cyclodextrin and its more water soluble derivative: 2-hydroxypropyl-β-cyclodextrin) and selected host molecules, which may exist in drinking water, wastewater and surface water ecosystems as micropollutants and act as hormonal modulators (EDCs), including PAHs and bisphenols; ***(ii)*** screening, quantification and classification of selected organic fractions, mainly focusing on bisphenols group that may be present in various products of daily use and may act as the micropollutants in surface water ecosystems and/or released directly to the environment form a municipal treatment plant (Jamno, Koszalin) as well as ***(iii)*** conducting of preliminary multivariate biological research that was carried out using aquatic organisms containing chlorophyll, particularly, duckweed (*Lemna minor L*), which may work as an active biomass for the elimination of bisphenols micropollutants from water. Moreover it was hypothesized that the initial data set obtained from the multivariate experiment involving duckweed (and combined with supramolecular complex formation data calculated from chromatographic experiments) enable designing of further experiments focusing on the development of green chemistry technology of micropollutants purification. Consequently, the results may be used for creation of novel systems for the efficient removal of low-molecular mass micropollutants using classical technological wastewater treatment processes modified by biomass and macrocyclic additives.

Generally, the results of the research conducted have revealed the high potential of host-guest complexation based on cyclodextrin molecules for analytical and further technological wastewater treatment applications. The addition of given macrocycles, namely native β-cyclodextrin and its hydroxypropyl derivative, to the liquid phase significantly changes the retention behavior of the target (guest) molecules including poly-

cyclic aromatic hydrocarbons (naphthalene, its methyl derivatives and acenaphthenol optical isomers) as well as a battery of selected bisphenols (A, B, C, E, F, S, Z, AF, AP, BP, FL) in the liquid phase, both under static (solutions) and dynamic (chromatographic separation) conditions. It has been found that chromatographic retention data obtained from planar chromatography may be used as a guide for target components and host molecules selection to design of selective extraction systems for the removal of PAHs residues various liquid phases. Appropriate mechanism enabling complexes creation was proposed and discussed in comparison with literature data. On the other hand, the column chromatographic experiment focusing on the separation efficiency of selected bisphenols in the presence of macrocyclic additives clearly indicated that such modifiers can significantly improve analysis time and selectivity of the isocratic system at the given temperature for simultaneous determination of various bisphenols mixtures in complex matrices. Quantification protocol invented, due to its simplicity, may be applied for highly selective monitoring of micropollutants during technological wastewater treatment processes. It has been demonstrated that a whole range of low-molecular mass compounds (with polarity ranging from estetrol to progesterone), which may be detected using UV-Vis detector, can easily be emitted from various in daily use products. This issue must be seriously taken into account in the case of the presence of micropollutants in treated wastewater, water ecosystems and plastic waste utilization *via* technological wastewater treatment processes, especially in terms of microplastics originated pollutants, acting as endocrine disrupters. Obtained results from multivariate biological experiments involving duckweed biomass and native β-cyclodextrin additive clearly indicated that β-CD and/or combined β-CD/duckweed system have an effect on bisphenols elimination from water.

The experimental data presented in this doctoral dissertation should be treated as an initial platform and starting point for designing of the further experiments, which may improve the effectiveness and selectivity of low-molecular mass micropollutants removal during technological processes of wastewater treatment, involving biomass and/or supramolecular encapsulation driven by the presence of macrocyclic oligosaccharides in the liquid phase.

14. STRESZCZENIE

Badanie enkapsulacji supramolekularnej, jako potencjalnego narzędzia do analiz i usuwania wybranych mikrozanieczyszczeń z fazy ciekłej

Przedstawiona rozprawa doktorska dotyczy pracy eksperymentalnej poświęconej badaniom enkapsulacji supramolekularnej, prowadzonej w oparciu o cząsteczki cyklodekstryn, jako potencjalnego narzędzia analizy i usuwania wybranych mikrozanieczyszczeń organicznych z fazy ciekłej. W szczególności, badano szereg problemów związanych z tworzeniem kompleksów typu gość-gospodarz, włączając w to: ***(i)*** badania podstawowe dotyczące tworzenia kompleksów supramolekularnych (tzw. enkapsulacja molekularna) pomiędzy związkami o strukturze makrocyklicznej (β-cyklodekstryna i jej pochodna 2-hydroksypropylo-β-cyklodekstryna) oraz wybranymi cząsteczkami "gośćmi", które mogą występować w wodzie pitnej, ściekach i ekosystemach wód powierzchniowych, jako mikrozanieczyszczenia i działać, jak modulatory hormonalne (EDCs). Szczególnie zwrócono uwagę na wielopierścieniowe węglowodory aromatyczne (PAHs) oraz bisfenole; ***(ii)*** badania przesiewowe, oznaczanie ilościowe oraz klasyfikacja wybranych frakcji organicznych, z uwzględnieniem bisfenoli, które mogą być składowymi różnych produktów codziennego użytku. Występujące, jako mikrozanieczyszczenia ekosystemów wód powierzchniowych, uwalniane do nich poprzez ścieki oczyszczone np. z Oczyszczalni Jamno (Koszalin); oraz ***(iii)*** przeprowadzenie wstępnych biologicznych eksperymentów wielowariancyjnych z wykorzystaniem wodnego organizmu chlorofilowego - rzęsy wodnej (*Lemna minor L*), odgrywającej rolę aktywnej biomasy eliminującej mikrozanieczyszczenia (bisfenolami) z fazy wodnej. Dodatkowo, założono, iż uzyskanie wstępnych danych ilościowych poprzez eksperyment wielowariancyjny z użyciem rzęsy wodnej oraz w obecności cyklodekstryny, jak również danych chromatograficznych z tworzenia kompleksów supramolekularnych, umożliwi projektowanie przyszłych badań dotyczących tzw. zielonych technologii usuwania mikrozanieczyszczeń, jako uzupełnienie do obecnych procesów usuwania mikrozanieczyszczeń, głównie mineralnych.

Rezultaty badań wskazują na wysoki potencjał kompleksowania typu gość-gospodarz z wykorzystaniem cyklodekstyn dla celów analitycznych oraz technologicznych w doczyszczaniu ścieków. Wykazano, iż dodatek do fazy ciekłej wybranych makrocykli, w tym β-cyklodekstryny oraz jej hydroksypropylowej pochodnej, wpływa zna-

cząco na retencję analitów (cząsteczki "goście") takich jak: wielopierścieniowe węglowodory aromatyczne (naftalen i jego pochodne: metylowane naftaleny oraz izomery optyczne 1-acenaftenolu), jak również wybrane bisfenole (A, B, C, E, F, S, Z, AF, AP, BP, FL), zarówno w systemach statycznych (roztwory) oraz dynamicznych (układy chromatograficzne). Przedstawiono dane eksperymentalne oraz zaproponowano możliwy mechanizm kompleksowania wskazujący na potencjalne zastosowanie danych retencyjnych uzyskiwanych z chromatografii planarnej do projektowania selektywnych systemów ekstrakcji pozostałości WWA z faz ciekłych. Ponadto, dokonano optymalizacji procesu rozdzielania bisfenoli w oparciu o metodologię wysokosprawnej chromatografii cieczowej (pracującej w trybie zależnej od temperatury chromatografii inkluzyjnej), dla celów oznaczeń ilościowych w/w analitów w próbkach złożonych. Opracowany schemat oznaczeń ilościowych, ze względu na swoją prostotę (system izokratyczny), może być z powodzeniem stosowany w analizowaniu mikrozanieczyszczeń bisfenoli w złożonych matrycach organicznych, w szczególności dla celów monitorowania procesów technologicznych oczyszczania ścieków komunalnych. W badaniach wykazano, iż szereg organicznych substancji niskocząsteczkowych o polarności w zakresie estetrol - progesteron, może być emitowanych z produktów codziennego użytku, szczególnie w warunkach podwyższonej temperatury. Problem ten powinien być brany pod uwagę w projektowaniu procesów oczyszczania ścieków komunalnych, również w kontekście tzw. mikroplastików. Wyniki eksperymentu wielowariancyjnego z użyciem rzęsy wodnej oraz cyklodekstryny wskazują na możliwość użycia biomasy organizmów wodnych do redukcji ilości mikrozanieczyszczeń w fazie ciekłej.

Przedstawione dane eksperymentalne prezentowane w niniejszej rozprawie doktorskiej można traktować, jako punkt wyjścia do projektowania dalszych eksperymentów, które mogą poprawić skuteczność i umożliwić wysoką selektywność usuwania mikrozanieczyszczeń organicznych w trakcie technologicznych procesów oczyszczania ścieków, w tym z udziałem biomasy i/lub enkapsulacji supramolekularnej związanej z obecnością makrocyklicznych oligosacharydów w fazie ciekłej.