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Detection and mapping of per- and polyfluoroalkyl substances in the drinking water supply of Budapest.

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1. Introduction:

Water is the most important natural resource and is essential for life. Unfortunately, it is becoming increasingly contaminated by human activities (Vorosmarty et al. 2010). Industrialization has led to the direct or indirect introduction of emergent pollutants into water supply sources, affecting the environment and human health (Schwarzenbach et al. 2010). An example of these pollutants that are being used in several industrial processes are the per- and polyfluoroalkyl substances (PFAS). These substances have been produced and introduced into the environment for decades, and one of the main sources of exposure to humans is through drinking water (Boiteux et al., 2012; Ericson et al., 2009; Hu et al., 2019).

It is well established that the majority of PFAS substances are bio-accumulative and resistant to complete mineralization under natural conditions and resistant to several forms of degradation due to high chemical stability, making PFAS the most environmentally persistent substances among the organic chemicals (Wang et al., 2017; Boiteux et al., 2012; Kucharzyk K.H et al., 2017). The higher hydrophobicity of long-chain PFAS, in comparation with short-chain PFAS, increases their affinity for particles and lends to their considerably greater bioaccumulation potential (Martin et al., 2003; Ahrens et al., 2010).

PFAS has been detected in the bloodstream of the majority of the world's populations in developed nations, a consequence from the prolonged environmental durability and biological half-lives of these compounds (Kato et al. 2011; Khalil et al. 2016; Stubleski et al. 2016; Jian et al. 2018). Several effects of PFAS substances on human health have been determined, such as thyroid disease, increases in cholesterol levels, breast cancer, liver damage, kidney cancer, inflammatory bowel disease, testicular cancer, and increased time to pregnancy (European Environmental Agency, 2019).

In the production of drinking water, various types of PFAS can co-occur, including PFOA, PFOS, PFNA, PFHxS, PFBS, and GenX chemicals. These PFAS can be present in the piping materials utilized for water transport, such as Polyethylene (PE), Polyethylene of Raised Temperature Resistance (PE-RT), Polypropylene (PP), and Chlorinated Polyvinyl Chloride

(CPVC). These materials are chosen for their ability to withstand heat, water, and oil, making them commonly used in water treatment and distribution systems. Consequently, PFAS can leach into the water supply from these pipes and potentially impact human health. (US EPA, 2024)

2. Objectives:

PFAS are a group of concerning substances for the environment and human health due to their chemical nature. It is important to understand these substances better and to improve on our detection of them in the water supply. The objective of this work was to analyze the drinking water of the city of Budapest, Hungary at various points and create a map of the sampling sites with the corresponding detected PFAS. With the results of this work, it is hoped that it will be possible to compare the sample sites, their influence on each other and estimate the type and concentration of PFAS.

3. Literature Review:

Water is the perfect solute for all carbon-based life. Water has several important physical properties that make it very useful, such as high heat retention, surface tension and dielectric constant. The ability to contain salts essential for life is facilitated by its high density. Also, water facilitates the polymerization and the formation of the structure of organic molecules (Westall and Brack, 2018). Water is the most important resource for life, and it has been contaminated by natural sources or human-made processes. Contaminated water can cause several health problems, and providing safe drinking water is a challenge (Shannon et al., 2008; Sharma and Bhattacharya, 2017).

Water pollution can be associated with four types of contaminants: biological, which includes pathogens like, virus, bacteria and parasites that can cause issues like diarrhea and fever; radiological, when water is contaminated by radioactive compounds, it has potential to emit ionizing radiation, posing risk of cancer and other severe health problems; inorganic compounds, like metals, salts and other compounds without carbon, which can cause health concerns at high levels and organic compounds, like pesticides, herbicides and even artificial chemical substances like PFAS (Sharma and Bhattacharya, 2017).

Some examples of water contamination over the world help us to understand the consequences of what can happen when the main source of life is polluted, and also what are the possibilities and limitations for remediating the water. The Walkerton E. coli outbreak in Canada, 2000 (Vicente and Christoffersen, 2006), Fukushima Daiichi nuclear disaster in Japan, 2011 (Funabashi and Kitazawa, 2012), the flint water crisis in USA, 2014 (Pauli, 2020) and the Camp Lejeune water contamination incident in USA, 1982 (Jung et al, 2022) are just some of the examples of the water crisis around the world on how this events lead to several harmful consequences to human health and, even after some years, the long-term effects can be detected.

It is important to highlight that most of the water crises and water bodies pollution could be completely avoided or minimized if the right precautions, measures, or knowledge were used to prevent major disasters and long-term contaminations, that affect the environment and the human health (Elleuch el al., 2018). From the past decades, several artificials chemical compounds have been manufactured, the possible effects on the environment of them are being investigated by scientist, but meanwhile these substances are being release in the environment and their consequences are not completely understood (Badmus et al., 2021; Adeola, 2020). Poly and perfluoroalkyl substances are part of this group of new artificial substances that need to be fully understood, in order to prevent more emissions in the environment that may impact human health (Nayak et al., 2023; Ambaye et al., 2022).

Poly and perfluoroalkyl substances, known as PFAS, are a group of man-made organic chemical substances globally used in industries that have been the focus of attention for their unique chemical properties and environmental concern (European Commission, 2020). An alkyl group is a functional group that contains only carbon and hydrogen atoms, and on the PFAS substances many or all the hydrogen atoms have been replaced by fluorine attached to a functional group, like carboxylic or sulfonic acids, called perfluorooctanoic acid and perfluorooctane sulfonate (PFOA and PFOS) (European Commission, 2020; Fàbrega et al., 2014). PFOA and PFOS contain a long hydrophobic chain with eight carbons, saturated with fluorine and a hydrophilic functional group (Prevedouros et al., 2006).

The high carbon-fluorine chemical bonding strength (485 KJ/mol) makes PFAS thermodynamically stable and highly resistant to several forms of degradation, such as hydrolysis, metabolism, and photolysis, making them persistent in the environment and difficult to remediate

(Boiteux et al., 2012; Kucharzyk K.H et al., 2017). This high stability and lipid and water repelling properties contributed to their former use in surfactant applications (Rayne and Forest, 2009; USEPA, 2012). The term surfactant describes the tendency of these compounds to adsorb at the between two immiscible fluid phases (Rahman et al., 2014).

These characteristics attract wide use of PFAS for several purposes, making PFAS manufactured massively for the industry for example, paper industry, medical devices, oil, pesticides, leather, metallurgical, mining and packing, and also for the use of costumers like, cosmetics, paints, inks, cooking utensils, aqueous film forming foams (AFFFs), carpets and several waterproof products (Buck et al., 2011; Fujii et al., 2007; Houtz et al., 2013; Prevedouros et al., 2006; Gagliano et al., 2020; Ji et al., 2020; Wang et al., 2017; Lu et al., 2017; Kotthoff et al., 2015). The main objective of using PFAS in consumer products is to extend the service life and durability, but this practice results in a longer exposure of humans, wildlife, and environment due to the persistent characteristic of PFAS (Herzke et al., 2012).

PFAS has been widely utilized since 1950s, but it was only in the beginning of 2000s that scientifical research accelerated on the properties, occurrence, future of environment, and toxicology (Cousins, 2015). The wide use of PFAS made them become an emergent contaminant in the environment and for their monitoring is very important to understand regulations and develop techniques to facilitate environmental management and remediation (Al Amin et al.,2020). There is still much to learn about the physicochemical properties, transport of PFASs in groundwater and their ultimate fate. For the treatment of PFOA and PFOS, several traditional methods are ineffective, such as air stripping, heat treatment, soil vapor extraction, and hydroxyl-based chemical oxidation (Kucharzyk K.H et al., 2017). PFAS and others related chemical compounds have been targeted by regulations during the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001. These regulations started to be effective from May 2004, with the objective of restricting the production and use of POPs (Nadal and Domingo 2019).

Understanding how PFAS behaves in the environment is very important and it is influenced by various factors, for example, organic carbon content, temperature, salinity, and concentration of atmospheric oxidants. Short-chain PFAS tend to be hydrophilic and more mobile in hydrological systems, while long-chain PFAS exhibit higher hydrophobicity, binding to particles and showing a relevant bioaccumulation potential (Martin et al., 2003; Inoue et al., 2012).

One of the notable traits of PFAS, regarding the environmental impact, is their mobility within the environment (Kwiatkowski et al., 2020). This mobility, in addition to their persistence, leads to the accumulation of PFAS in water, sources of drinking water, plants and the atmosphere. Contaminations cases affecting water, drinking water and soil in both European Union and globally, brings the attention to the widespread presence of PFAS (WHO, 2017; Nordic Council of Ministers, 2019). PFAS can be introduced in the environment through various sources, such as industrial and municipal wastewater treatment plants, landfills, recycling, and incineration facilities, end the reuse of contaminated sewage sludge.

An example of the PFAS introduction in the environment is the detection of perfluorooctanoicacid (PFOA) in drinking water near a fluorochemical industry in Washington, in concentrations 190 times greater in amount than the limit recommended for the Environment Protection Agency of 70 ng/L, where PFOA was used for the manufacturing of fluoropolymer (Hoffman et al., 2011). Also, several airports and military fire training areas have been contaminated by PFAS. The origin of this contamination can be related to the aqueous film-forming foams (AFFFs), which are used in firefighting training activities and contain PFAS. The surface and groundwater of the surroundings of these sites presented concentrations of PFAS three to four times higher than the advisory level of drinking water indicated by EPA (70 ng/L) (Ahrens et al., 2015; Moody et al., 2003). In addition, wastewater plants can also be a source of PFAS contamination, since these substances are not removed by the standards treatment methods (Schultz et al., 2006).

In Europe the number of possible sites of emissions of PFAS is approximately 100,000 (Goldenman et al., 2019). During all their lifecycle (production, distribution, product usage, and disposal), PFAS substances are released in aquatic environment (Buck et al., 2011) The majority of these emissions, over 95%, directly enter aquatic ecosystems, while atmospheric emissions are considered relatively minimal, less than 5% of the total emissions (Paul et al, 2009; Prevedouros et al., 2006).

PFAS has the capacity to bioaccumulate in humans, animals, and plants, and many of them are considered toxic after examinations (Cousins et al., 2017). Some PFAS are categorized as persistent, bioaccumulative, and toxic (PBT) or very persistent and very bioaccumulative (vPvB) under Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations

(European Environmental Agency, 2019). Several adverse health effects are associated with PFAS exposure, including thyroid disease, high cholesterol levels, effects on reproduction and fertility, immunotoxicity, liver damage, kidney, and testicular cancer, immunotoxicity and endocrine effects. Also, the European Food Safety Agency (EFSA) links PFOS and PFOA to the reduced antibody response to vaccination (European Environmental Agency, 2019).

A previous work provided evidence that suggests an increase in the concentration of PFAS in plasma through tap water consumption between 1989 to 1990 and 2013 to 2015. This increase refers to the estimated levels of persistent PFAS compounds (such as PFOS, PFOA, PFNA, and PFHxS), which have been extensively utilized over time. It was estimated that the tap water contributes to the plasma concentrations for the five PFAS analyzed in 1989–1990 in values between 2.2% and 34% (Hu et al., 2019).

The drinking water distribution system (DWDS) is the most important factor for ensuring a safe drinking water for populations around the world, and the deterioration of the water quality usually occurs in the DWDS (Cerrato et al., 2006; Kim et al., 2011; Li et al., 2019a; Chen et al., 2021). The environment of the drinking water distribution system affects the transportation characteristics of PFAS. It has been reported that PFAS, especially long-chain PFAS, tend to accumulate in loose deposits on pipe walls, resulting in a constant decrease of concentration though the distribution process (Chen et al., 2019).

A study in South Korea made by Park et al, 2018, investigated the levels of PFAS contamination in tap water based on its origin, whether is from river water, lake, or reservoir water. The results of this work reveled a significant higher level of PFAS in tap water samples sourced from river water, when compared to tap water samples sourced from lake or reservoir, indicating a potential contamination from industrial facilities along the river. PFHxS emerged as a major risk for its high concentrations. From the eight cities investigated in this study, Daegu and Busan City showed the highest PFAS levels in tap water. The presence of industrial facilities like electronics, textile, and chemical industries midstream of the Nakdong River basin may strongly affect tap water contamination (Park et al., 2018)

The ban on PFOS in 2012 in South Korea, seemed to have influenced PFAS contamination downstream, leading to a change in the type of PFAS usage to a short-chained PFASs like PFHxS, as evidenced by increased proportions in the mainstream of Nakdong River water compared to lake/reservoir water. Evidence of this change is the increasing proportions of PFHxS and PFPeA, from 1.9% to 33% and 4,4% to 12% respectively, and decreased proportions of PFOS and PFOA, 6.3% to 0.42% and 31% to 20% respectively, compared to a previous study conducted in South Korea (Park et al., 2018; Heo et al., 2014).

The same study investigated the daily intake via tap water and compared it with the daily intake from bottled water. It was found that tap water consumption was significantly more influential to PFAS exposure than bottled water consumption. The daily intake from tap water was approximately 70 times higher than bottled water, the values were 48.6 ng/L per person per day for tap water and 0.721 ng/L per person per day for bottled water, and in Busan city this difference was even higher, 140 times higher, were 33.3 ng/L per person per day for tap water and 0.237 ng/L per person per day for bottled water. These findings highlight the urgent need for further research and regulations for PFAS. Banning one type of PFAS does not effectively mitigate exposure, instead, it leads to a shift towards the usage of other types, highlighting the need for comprehensive regulatory actions. (Park et al., 2018).

The levels of PFAS in tap water can be influenced by the pipeline distribution process. Short-chain PFAS exhibit greater stability in the water phase, allowing them to migrate towards the end of the pipeline (Chen et al., 2019). The structure of the drinking water distribution system is usually divided into two types of pipes networks, branched pipeline, and loop pipe network. For small-scale towns and municipalities, the branched pipeline is usually used for water supply, and this structure is made of long pipelines, for a small population, low consumption, and long hydraulic retention time (Ma et al., 2019; Yu et al., 2019). For the urban water supply with a large coverage area, where the consumption and the concentration of the population is higher, the looped pipe network is mostly used, which has a better hydraulic condition and the water quality is more uniform (Li et al., 2011).

There is no world consensus regarding the standards for PFAS limit concentration in drinking water. In 2009, the United States Environmental Protection Agency (EPA), set a standard for drinking water health recommendations of 200 ng/L and 400 ng/L for perfluorooctanesulfonic acid (PFOS) and PFOA. In 2013, the standards were changed to a lower value for the concentrations of PFOS and PFOA, alone or in mixture, the new limit concentration was 70 ng/L (EPA, 2013; Qin., et al 2024).

The European Commission reviewed the directive of drinking water legislations, as a result standards of drinking water were introduced. For the individual PFAS types: PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDS, perfluoroundecane sulfonic acid, perfluorododecane sulfonic acid, perfluorotridecane sulfonic acid the limit value for drinking water is 0.1 µg/L or 100 ng/L. And for total PFAS concentration is 0.5 µ/L or 500 ng/L (European Commission, 2020).

However, the Environment Protection Agency (EPA) is suggesting a National Primary Drinking Water Regulation to set thresholds, known as Maximum Contaminant Levels (MCLs), for six PFAS substances in drinking water. For PFOA and PFOS the proposed MCL is 4.0 parts per trillion (4 ng/L) (Environmental Protection Agency, 2023).

Some of techniques used for the determination of Poly and perfluoroalkyl substances in water were published by the United States Environmental Protection Agency (EPA), like the Method 537.1 using Solid Phase Extraction and liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) (Shoemaker and Tettenhorst, 2018) and the Method 533 using Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (Rosenblum and Wendelken, 2019).

The need for uncontaminated water led to the creation of several techniques of water treatment aiming to remove or mitigate a contaminant; according to the final objective different types of techniques can be applied. Some of the most common water purification techniques are sedimentation, settling, boiling, distillation, chemical treatment, disinfection, and filtration. These processes provide different approaches and results according with the target to be removed (Sharma and Bhattacharya, 2017). For example, chlorination is a technique that uses a strong form of chlorine, like chlorine oxide, to disinfect water, having a good efficiency against bacteria and protozoa (Gala-Gorchev, 1996). One limitation for the use of chlorine is the formation of potential harmful and carcinogenic by-products, like trihalomethanes and haloacetic acids (Univ. Florida Report 1998).

Another form of water treatment is the use of adsorbent. The activated carbon is the most common and used adsorbent. The difference between charcoal and activated carbon is the high porous character of the activated carbon, making it much more efficient. The origin of the activated carbon can be of petroleum coke, bituminous coal, lignite, wood products, and coconut/peanut shells, and when exposed to high temperatures, parts of the carbon are transformed into CO2 and steam, the gases leave the structure by micro fractures and pores are created, increasing the surface area of the activated carbon, making a good material for the removing of contaminants (Baudu et al. 1991; Yang and Benton 2003; Sharma and Bhattacharya, 2017). According to the particle size and diameter, activated carbon can be in two different forms, the granular activated carbon (GAC) or powder activated carbon (PAC). The activated charcoal is efficient against carbon-based impurities, it has a good cost efficiency and a long life (Sharma and Bhattacharya, 2017).

Ozone (O3) is an unstable form of oxygen and has an important role of protection against ultra-violet radiation. When added to drinking water it can be an effective disinfectant (VonGunten 2003 a, b). The use of ozone in drinking water is good against biological contaminants causing a rupture in the cells and immediate death. Also, ozone is useful to transform soluble Fe and Mn, that cannot be filtered into insoluble form, which can be filtered. The downside of the use of ozone as disinfectant are a significant air pollution, risk of explosion, can irritate skin, eyes, respiratory tract, and mucous membrane, and if there is bromine in the treated water, it can produce carcinogenic substances (Sharma and Bhattacharya, 2017).

Another type of water treatment technique is nanofiltration. This technique is used to remove at molecular level contaminants in water. It consists in passing the water through a membrane with pores of size of nanometer scale, which can filter almost all organic molecules and viruses. Nanofiltration is effective on removing micropollutants like disinfecting by-products, arsenic and can be used to remove PFAS (Guo et al., 2022). The use of nanofiltration worldwide has increased because the several advantages and for being an alternative for reverse osmosis. The advantages of nanofiltration are low operating pressure, high flux, high retention of multivalent anion salts and organic matter, relatively low investment and low operation and maintenance costs.

The removal of PFAS from water proved to be a challenge, and only a few techniques are efficient. The conventional drinking water treatment like aeration, sand filtration, sedimentation, ozonation and chlorination were found to be ineffective to remove the PFAS. After the process of ozonation, an increase of certain PFAS concentration was even detected. The technique that presented satisfactory results by removing all the analyzed PFAS was nanofiltration. Some authors found that the activated carbon was efficient to remove the PFAS from water, however other authors found this technique inefficient (Boiteux et al., 2017; Takagi et al., 2011; Domingo et al., 2019).

Hungary is located in Central Europe and is home to the capital city of Budapest. Budapest, often referred to as the “Queen of the Danube,” is not only the political and administrative heart of the nation but also its cultural pulse. The city of Budapest was officially created on November 17, 1873, through the unification of three neighboring cities: Buda, Pest, and Óbuda. Budapest stands as a testament to Hungary’s historical evolution, from its Celtic roots and Roman occupation to the rise as a significant city within the Austro-Hungarian Empire.

The city is divided into two parts by the Danube River: Buda, with its hilly terrain and historic buildings, and Pest, the flat counterpart where the government and commercial sectors are located. Together, they form a metropolis that accommodates approximately one-fifth of Hungary’s population. As the commercial center of Hungary, Budapest plays a crucial role in the country’s economy. It is also an educational hub, with more than half of Hungary’s university students attending institutions within the city. This concentration of knowledge and commerce makes Budapest a dynamic place where tradition and innovation intersect (Péter, L. Encyclopedia Britannica, 2024).

The origin of the drinking water supply of Budapest is from bank filtration wells situated on the Szentendrei and Csepel Islands, two banks of the Danube River. The benefit of bank filtration is that it produces large amounts of high-quality water that only need to be chlorinated before usage. Because of the excellent hydrological conditions and the good quality of the Danube River, no post-treatment is required other than disinfection for the drinking water treatment. Previous study reassures the premise that the water treatment process in Budapest is effective, even considering extreme changes in the weather (Homonnay el al., 2008; Makk et al., 2010; Nagy-Kovács et al., 2019).

Despite the good water treatment in the city of Budapest, PFAS can be detected in the water of Danube River and tributaries rivers and highest concentrations were detected in the Alz River. The use of compounds like PFOA and PFOS, that have clearly been shown to be harmful, are already banned, but they can still be detected in rivers. Other similar substances came to substitute these compounds, such as ADONA, which shows the highest concentration in the Danube River data. Values of 45-219 ng/L for PFOA and 300-4246 ng/L for ADONA were measured during 2022 and 2023 (Prager, Sica, & Kohrs, 2024).

The high concentration values in Alz River, can be probably explained due to the fact of a working activity of the company Dyneon, the American Minnesota Mining and Manufacturing Company, that manufactures fluoropolymers in the Gendorf Chemiepark industrial park. Even if the activities of the company stop, the environment has been polluted on a considerable scale, by industry activities, household emission and another major cause of PFA pollution is diffuse, hard-to-determine sources. This means that large amounts of the contaminant will remain in the waters for a very long period. In addition, sewage treatment facilities are not required to filter out inherited chemicals from water. Because of this, PFA chemicals are present in wastewater from wastewater treatment plants even after the process of treatment, and these compounds are subsequently washed into rivers (Prager, Sica, & Kohrs, 2024).

4. Materials and Methods:

Sampling and sample preparation:

In October 2023, thirty-two samples were collected from different points in the Budapest Water Works and stored in 250 mL narrow-mouth polypropylene bottles. To maintain sample integrity, these bottles underwent a thorough cleaning process involving rinsing with de-ionized water and two washes with MeOH before being filled with water from the respective sampling locations. The samples were refrigerated at a constant temperature of 5°C until analysis, which occurred within two weeks of collection.

To concentrate and extract per- and polyfluoroalkyl substances (PFAS) from the drinking water samples, weak anion exchange solid-phase extraction tubes were utilized. Prior to extraction, the samples were acidified using acetic acid to 0.1%, and 10µl of SUR standard solution was added for recovery monitoring. Manual liquid loadings were administered at a flow rate of one drop per second. Conditioning of the SPE cartridges commenced with sequential steps: 4 mL of 5 v/v% NH4OH solution in MeOH, followed by 4 mL of MeOH, 4mL of water, and finally, 4 mL of 1% acetic acid. The tubes were dried followed by the elution of analytes using a specific solvent (4 ml of 5 v/v % NH4OH solution in MeOH). After evaporation by nitrogen gas, the residuals were redissolved with a solvent mixture (495 µL MeOH with 4% of H2O and 5 µL of IS standard solution).

For instrumental analysis:

An Agilent 1290 Infinity II HPLC system equipped with an Ultivo triple quadrupole, and an ESI ion source was used. Chromatographic separation was achieved using a Zorbax Eclips RRHD column and gradient elution, using a mix of ammonium-hydrogen-carbonate and acetic acid (0.01%) along with methanol as mobile phases was used at 40°C. For the run, 3 µL of the sample was injected on the column and the total time of one run was 30 minutes. The mass spectrometer operated in dynamic multiple reaction monitoring mode (dMRM) for precise measurement of PFAS, filtering one precursor and two products of PFAS. The mass spectrometer used nitrogen as the collision and nebulizing gas.

Method validation:

According to established guidelines, SANTE/11312/2021 and USA EPA Method nr. 537.1 version 2.0 (European Comission, 2021, USA EPA 2020), including determining the limit of detection, linearity range, recovery, precision, and limit of quantification. Calibration curves from range of 0 to 50 ng/ml in 10 steps were constructed, and recovery measurements were conducted to ensure method accuracy and reliability. Additionally, identification and quantification of analytes were verified through ion ratio and retention time comparison with standards. Where the signal-to-noise ratio of the chromatogram was at least three were used to determine the LOD, as the lowest concentration. Linearity was evaluated by assessing the residuals along with the r2 of the calibration curves. Recovery measurements were conducted by spiking 250ml tap water samples at two levels: 80.0 ng/L and 16.0 ng/L, with 6 repetitions each. Recovery was calculated using the equation:

$$REC\ (\%) = \frac{measured\ concentration\ (\frac{ng}{L})}{spiked\ concentration\ o\ (\frac{ng}{L})}\ x$$

Precision was expressed as the relative standard deviation (RSD) of the replicates. To assess method applicability, the guidance of USA EPA 537.1 method was followed, requiring mean recovery between 70% and130% with RSD smaller than 20% for satisfactory results. LOQ was measured similarly but with spike levels at much lower concentrations (1 and 3 ng/L). Due to the measurement of very low concentrations (ppt level), it was noted that procedural blanks and solvent blanks contained trace levels of detectable analytes. For validation reasons, tap water samples with the lowest concentrations were utilized, and the validation data were not adjusted for measured contamination.

Identification, Quantification, and Quality Assurance:

For identification reasons, the ion ratio of the secondary mass transition to the primary mass transition and retention time were recorded for each compound. The criteria chosen was +- 30% deviation for ion ratio and 0.1min deviation for retention time of analytes in samples compared to standards. In order to monitor background contamination from various sources in the laboratory, solvent blank and procedural blank samples were injected. For analyte quantification, internal standard calibration was used. Calibration curves with range of concentrations from 0 to 20 ng/ml with 6 points were constructed, with a regression coefficient (r2) greater than 0.99 for all curves.

Map construction:

We generated maps to visualize the types of PFAS identified at each sampling site. The actual PFAS concentration values are not shown in this work because they are part of a future published article. To generate the map images, the software QGIS (version 3.28.12) was utilized, using the coordinates of the sampling sites with Google maps and Google roads map services. After that, the interpolation tool, Distance Weighting (IDW), was used. This method presupposes that each input point carries a local impact that gradually diminishes with distance. It assigns greater weight to points in proximity to the prediction location compared to those farther away. The settings for the symbology were: Interpolation: Discrete; Mode: Equal Interval; Classes: 7. This process was used on each type of PFAS detected.

5. Results:

The outcomes of the image construction process utilizing QGIS (version 3.28.12), a geographic information system software, are presented in this section. These images were specifically crafted to illustrate the sampling locations (Figure 1) and facilitate a comprehensive comparison of the concentration and presence of the 11 PFAS (Total PFAS, PFOS, PFOA, ADONA, GenX, PFBS, PFHpA, PFHxA, PFHxS, PFNA and PFDA) detected in this study (Figures 2 - 12). Using the interpolation tool, the analysis aimed to identify samples/regions with heightened concentrations of specific PFAS types, when compared with the other samples/regions. The gradual color gradient, indicative of concentration levels, offers valuable insights for estimating PFAS concentrations in the regions surrounding the sampling sites.

The sample sites spanned across 32 locations and included the urban center of Budapest: Districts I, III, IV, X, XII, XIII, XIV, XVIII, XXI and XXII; and several surrounding municipalities: Biatorbágy, Budakeszi, Budaörs, Százhalombatta, Halásztelek, Szigetszentmiklós, Tököl, Ráckeve, Dunabogdány, Kisoroszi, Tahitótfalu, Pócsmegyer-Surany and Szigetmonostor (Figure 1). The colors of the interpolated maps (Figure 2- 12) represent higher (darker color) or lower (lighter color) concentrations of the respective PFAS in the samples, when compared to the concentration of the other samples results. The same color pattern in the map represents a similar value between the samples, which means that those samples have a very close level of concentration when compared with other samples.

The Total PFAS represents the sum of all PFAS detected in each sample. The north part of Budapest in the regions of Dunabogdány, Kisoroszi, Pócsmegyer-Surany and Tahitótfalu had the highest concentration of Total PFAS, followed by district III, XIII and XII. This can be seen by the darker color gradient in this region, indicating that the concentrations detected in this region were higher than the other samples. The other regions show a lighter color, indicating a lower concentration of Total PFAS, with the south-west region of Budapest and the municipalities of Százhalombatta and Ráckeve having the lowest Total PFAS concentrations (Figure 2).

The concentration of PFOS was higher in the north of Budapest. The municipalities Dunabogdány, Tahitótfalu and Pócsmegyer-Surany show a darker color, indicating that the concentration of PFOS was higher than the other regions. The municipality of Halásztelek and district XXI also had a high concentration of PFOS. The center of Budapest and Százhalombatta indicates a lower concentration of PFOS. The south-west regions of Budapest indicate an intermediate concentration of PFOS (Figure 3).

PFOA concentrations in all samples were mostly similar, which is indicated by the same color gradient for the majority of the map area. With some exceptions for a darker color in Dunabogdány, indicating a higher concentration in this municipality than the others, and a lighter color in Biatorbágy, in district XVIII, south and south-west regions of Budapest, indicating a lower concentration for those regions (Figure 4).

The ADONA concentration shows higher values (darker color) in the center of Budapest, in district XIII, district XII and district X. Also, in some regions in the north of Budapest, Kisoroszi and Tahitótfalu, a darker color can be seen. In the majority of the north and south-west of Budapest, an intermediate color can be seen, indicating similar concentration values. In Százhalombatta and Halásztelek the ADONA concentration is lower than the other regions (Figure 5).

The GenX (HFPO-DA) concentration shows intermediate colors in the majority of the map, indicating similar concentrations. Although, in the region of Dunabogdány, the concentration of GenX was higher than the others. In the south and south-west of Budapest, the concentration of GenX was lower than the other regions. In the center of Budapest, the concentrations remain similar, with only a darker color in district XIII (Figure 6).

The PFBS concentration was much higher in district III than the rest of the map. This is indicated by the darker color in district III that diminishes with distance. The other regions in the center of Budapest, the south, the south-east regions of Budapest, Pócsmegyer-Surany and Szigetmonostor exhibit a lighter color, indicating a lower concentration of PFBS. An intermediate color can be seen in the center of Budapest, north, north-west, and east of Budapest (Figure 7).

The PFHpA concentrations in the center and north of Budapest were similar, showing a similar intermediate color. In district XIII and Dunabogdány, a darker color can be seen, indicating a higher PFHpA concentration. In the south and south-west of Budapest a lighter color can be seen, indicating that in those regions the concentration of PFHpA is lower than the others (Figure 8).

The PFHxA concentration was higher in the center of Budapest, showing a darker color in district XIII, district XII and also in the municipalities of Dunabogdány, Budakeszi and Budaörs. The south and south-west of Budapest indicate a lighter color, meaning a lower concentration of

PFHxA in those regions, the lowest was the municipality Százhalombatta. The north of Budapest showed an intermediate concentration (Figure 9).

The concentration of PFHxS showed a darker color in three regions, district XVIII, Biatorbágy and Dunabogdány, indicating a higher concentration of PFHxS in these three regions. The other regions showed an intermediate color, trending to a light color, with the exception for Százhalombatta that trended to a darker color and Ráckeve with the lighest color of the map, that means that this region has the lowest concentration of PFHxS when compared to the others (Figure 10).

The PFNA concentration is shown by a lighter color for the regions of Tahitótfalu, district III, district X, Biatorbágy, district XI, and Százhalombatta, indicating that the concentration of PFNA was lower than other regions. A darker color can be seen in the regions of Dunabogdány and Szigetmonostor, indicating that in those regions the highest concentration of PFNA was detected compared with the others. In the other regions, an intermediate color can be seen, meaning that the concentration in those regions was similar, with the exception for Budakeszi and Ráckeve, which showed a slightly darker color (Figure 11).

The PFDA concentration was lower for the region of Kisoroszi and Tahitótfalu, represented by the lighest color in the map. The regions of Budaörs, Biatorbágy, Budakeszi, Halásztelek, Szigetmonostor, and Ráckeve showed a darker color, indicating that the concentration of PFDA was higher in those regions. In the other regions, an intermediate trend toward a darker color can be seen, indicating that the concentration of PFDA in those regions was slightly lower than the darker ones (Figure 12).

Sampling Location:

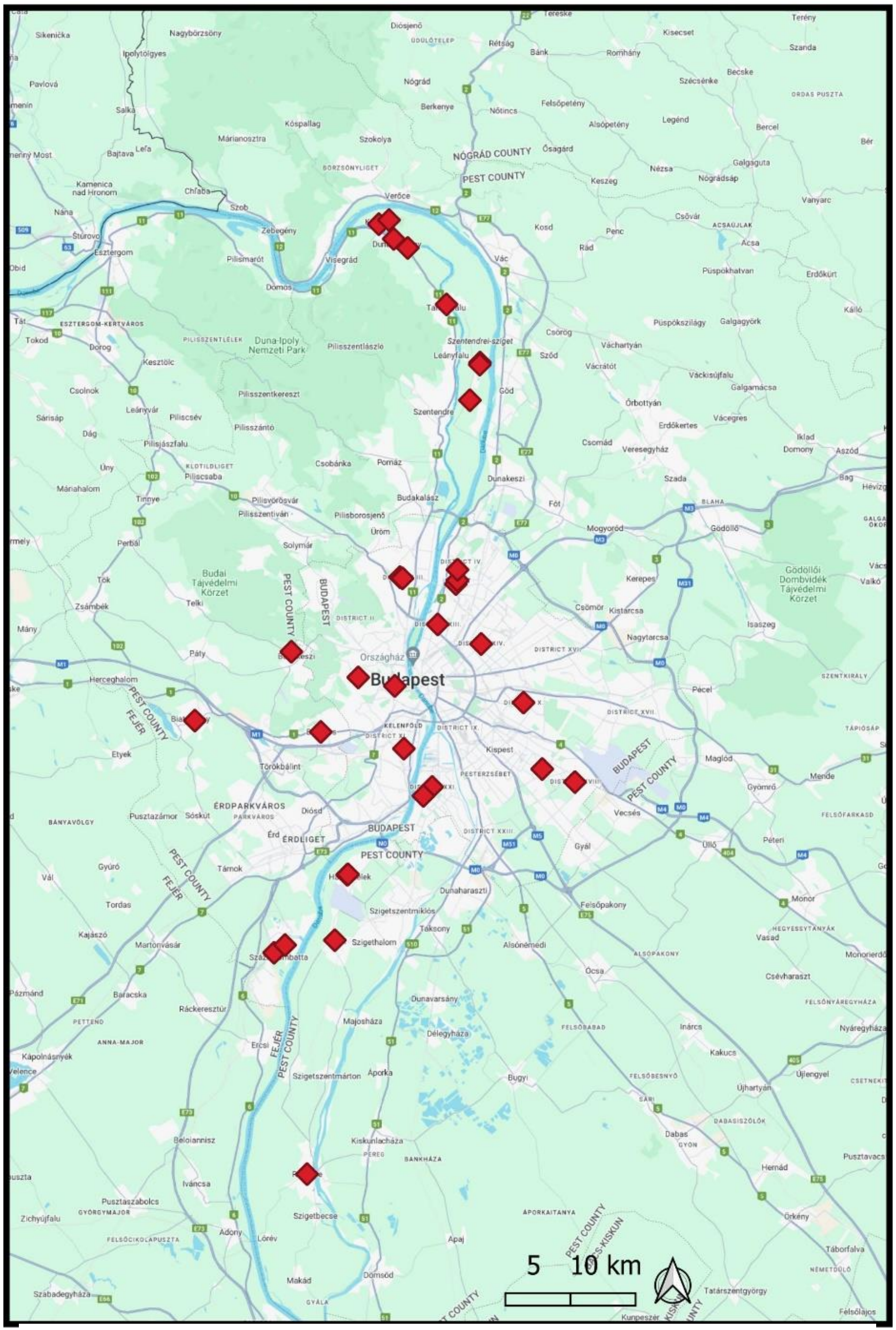

Figure 1: Sampling Map Locations. The map shows the 32 sampling locations in Budapest.

Total PFAS:

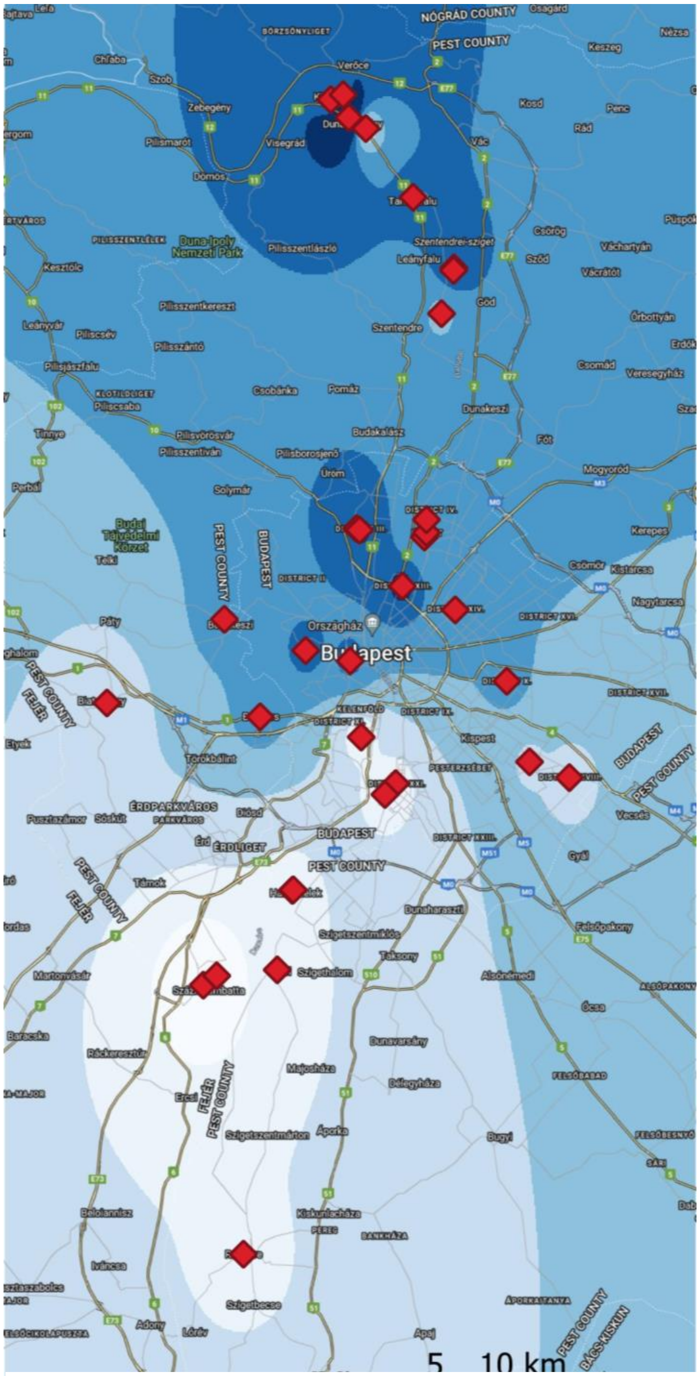

Figure 2: Total PFAS Interpolation. This map shows the interpolation of total PFAS concentration for each sample (sum of all PFAS detected)

PFOS:

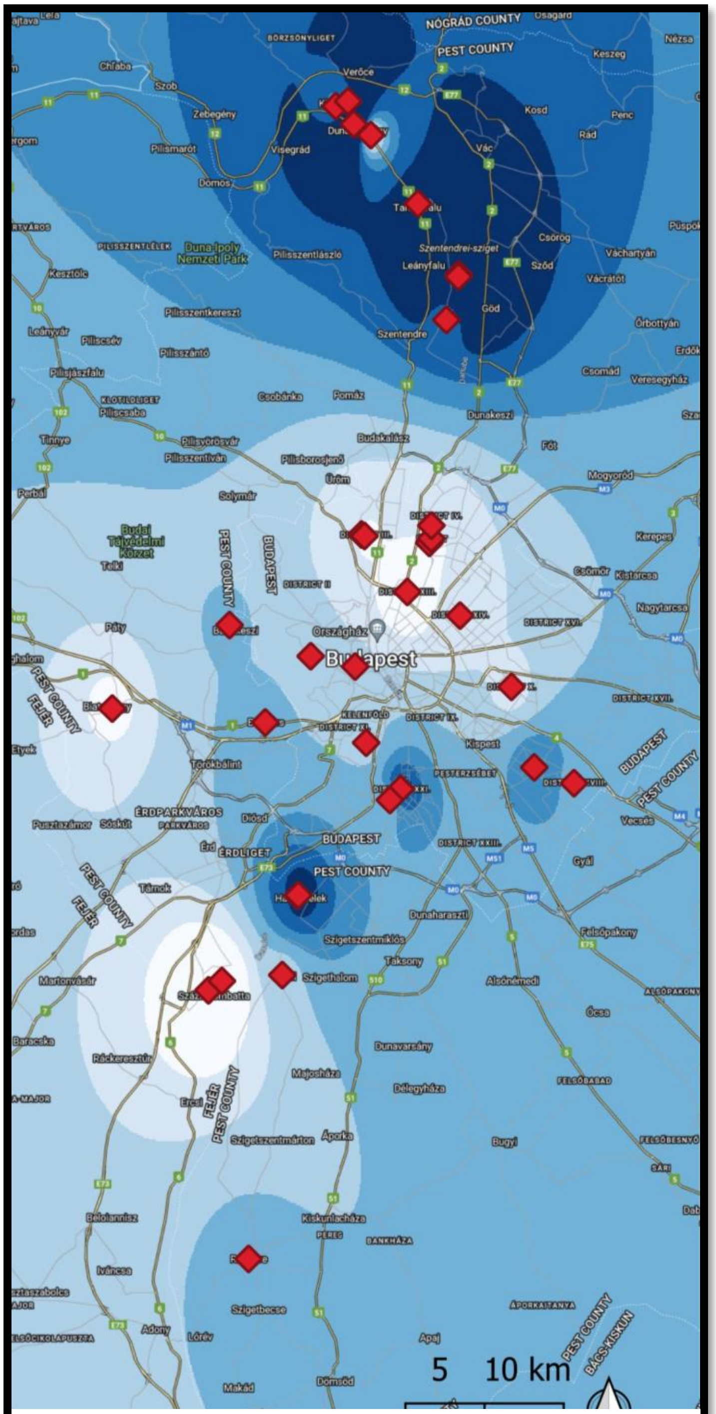

Figure 3: PFOS Interpolation map. This map shows the interpolation of PFOS concentrations for each sample.

PFOA:

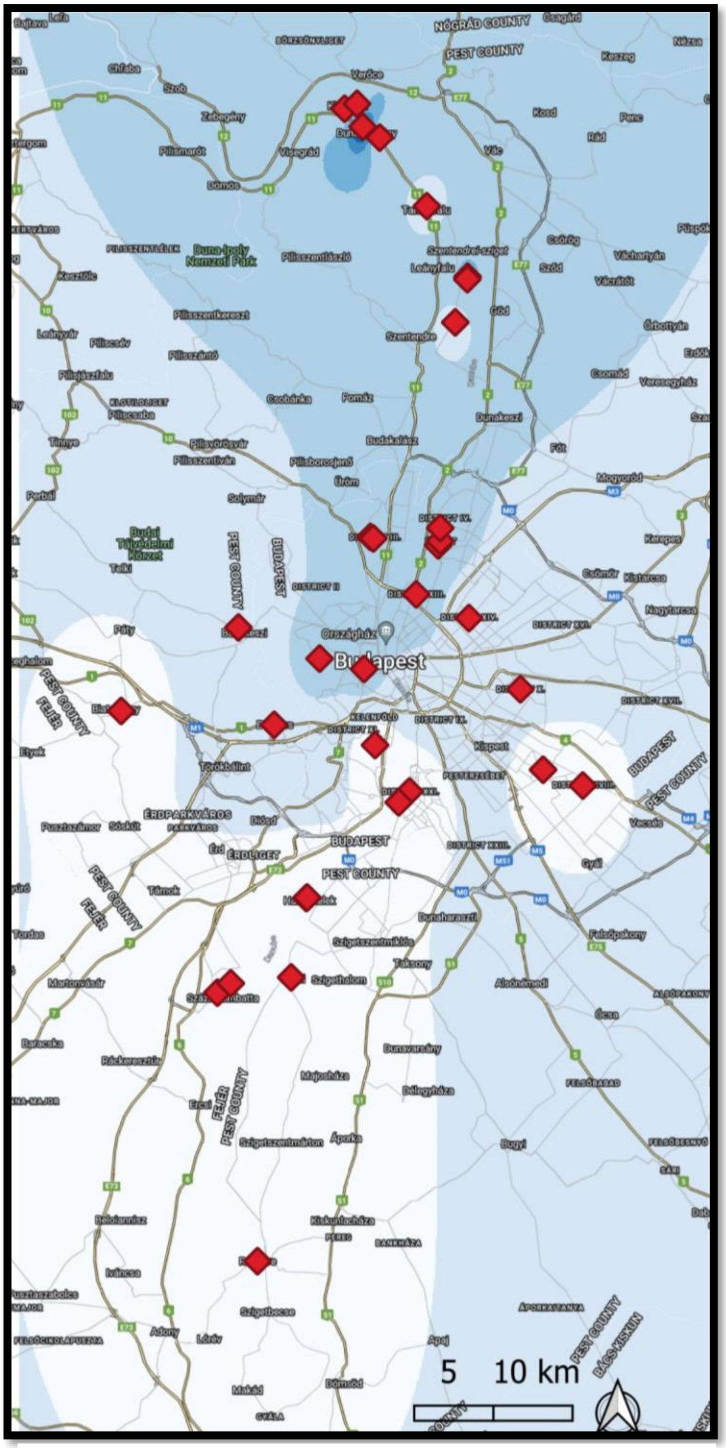

Figure 4: PFOA Interpolation map. This map shows the interpolation of PFOA concentrations for each sample.

ADONA:

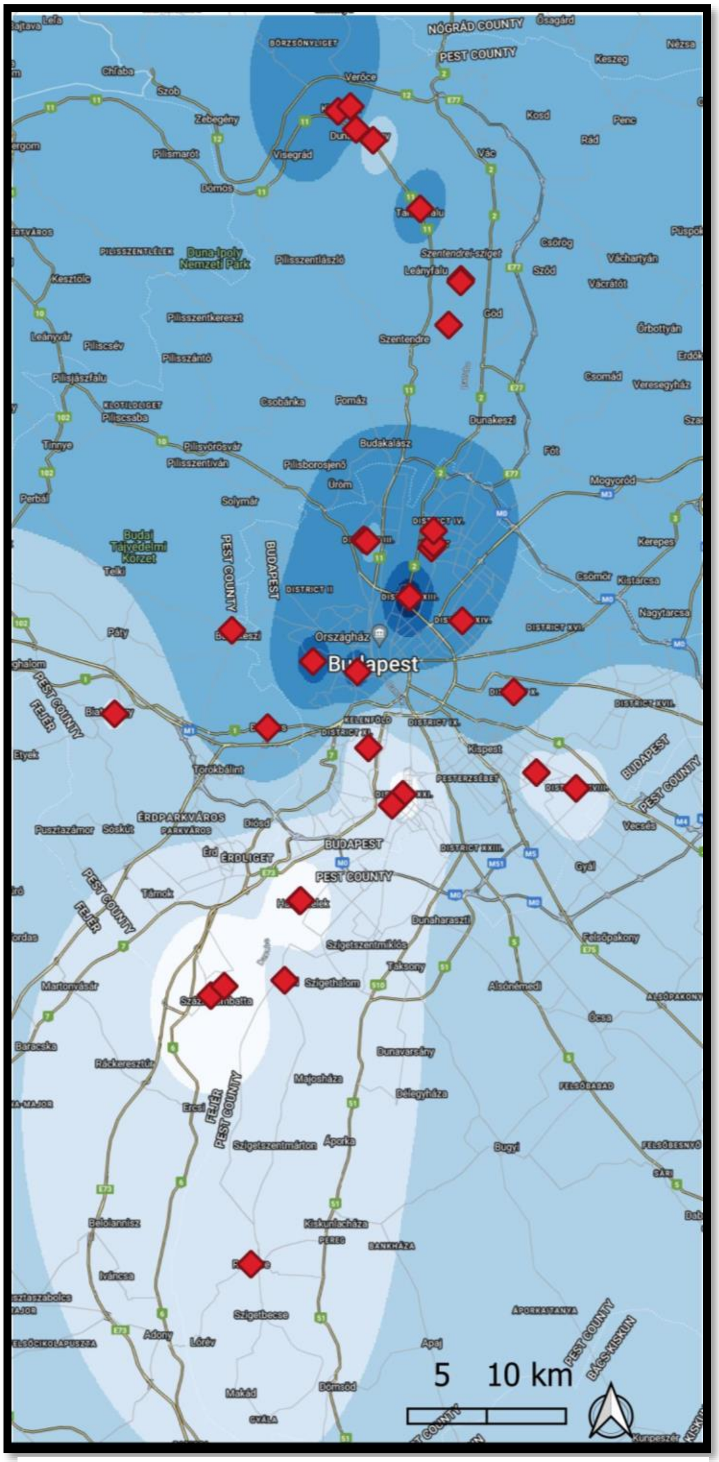

Figure 5: ADONA Interpolation map. This map shows the interpolation of ADONA concentrations for each sample.

GenX:

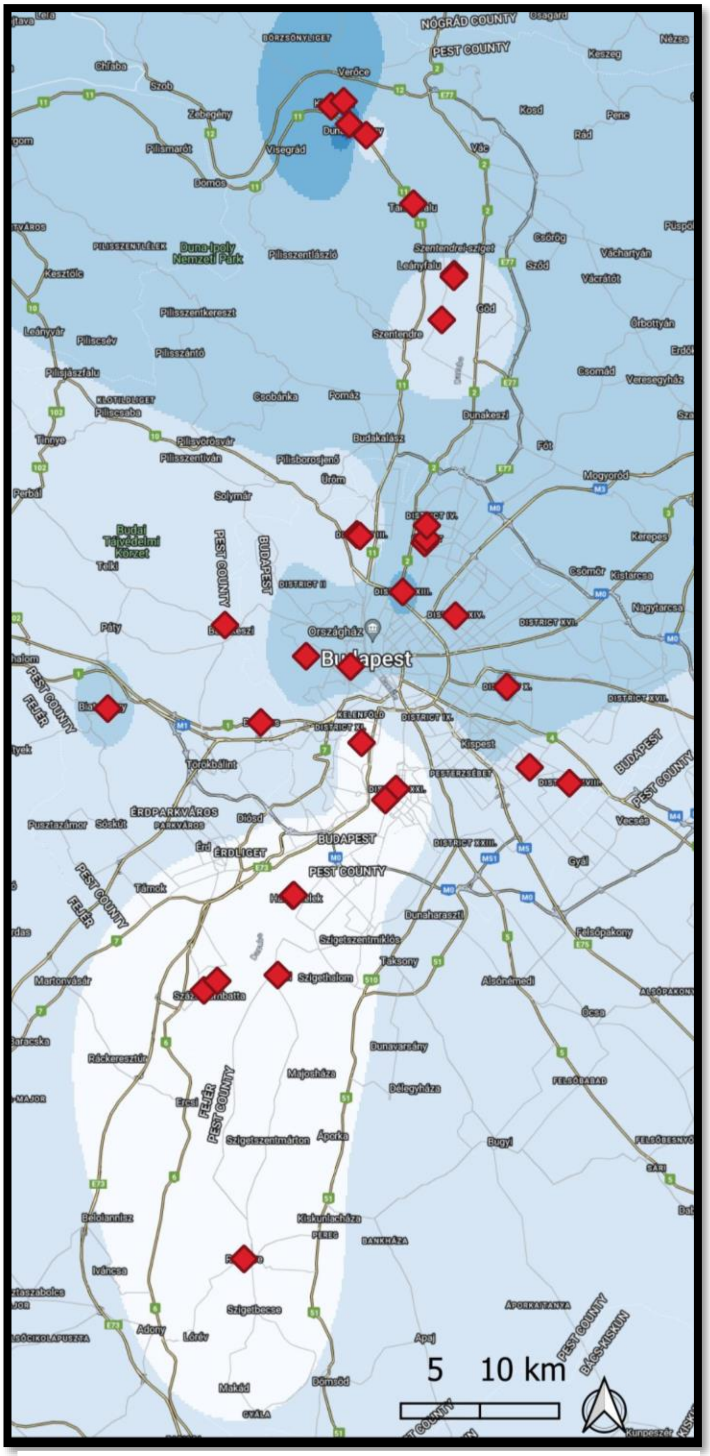

Figure 6: GenX Interpolation map. This map shows the interpolation o GenX concentrations for each sample.

PFBS:

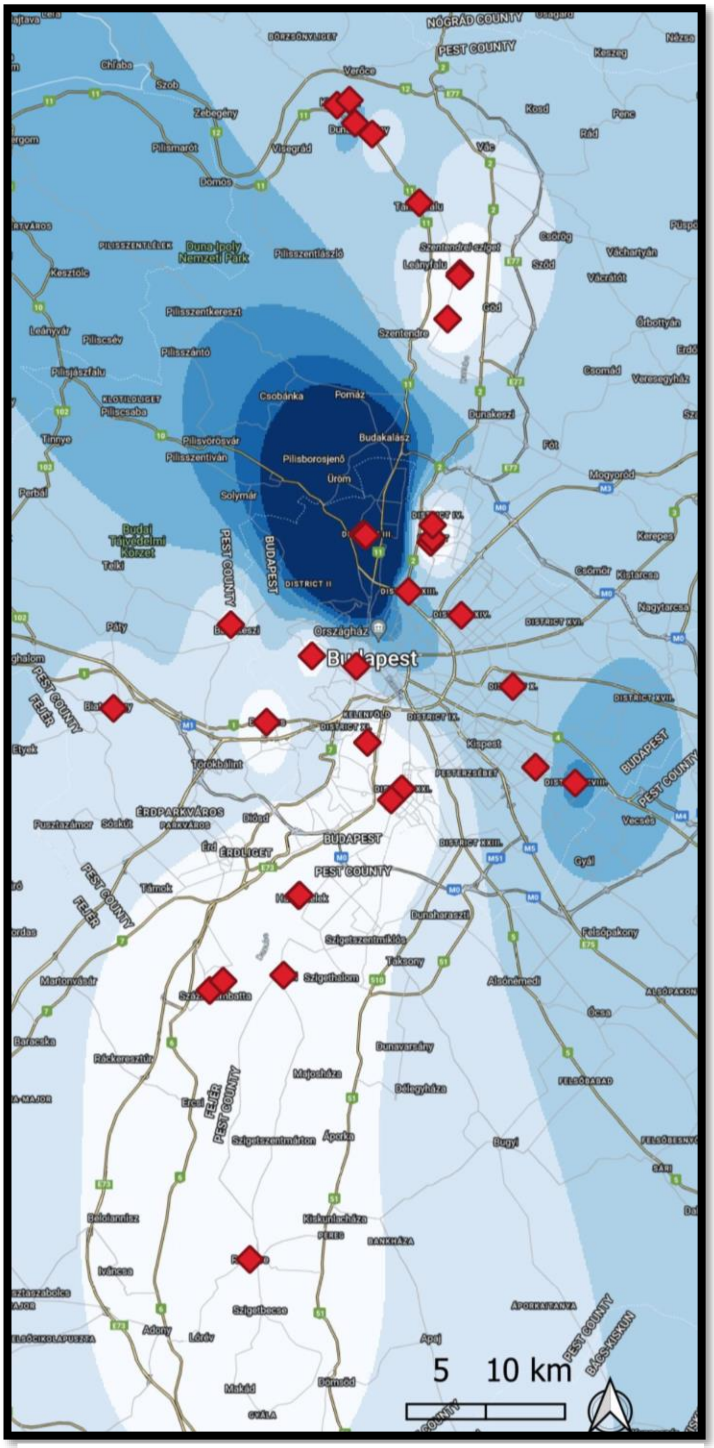

Figure 7: PFBS Interpolation map. This map shows the interpolation of PFBS concentrations for each sample.

PFHpA:

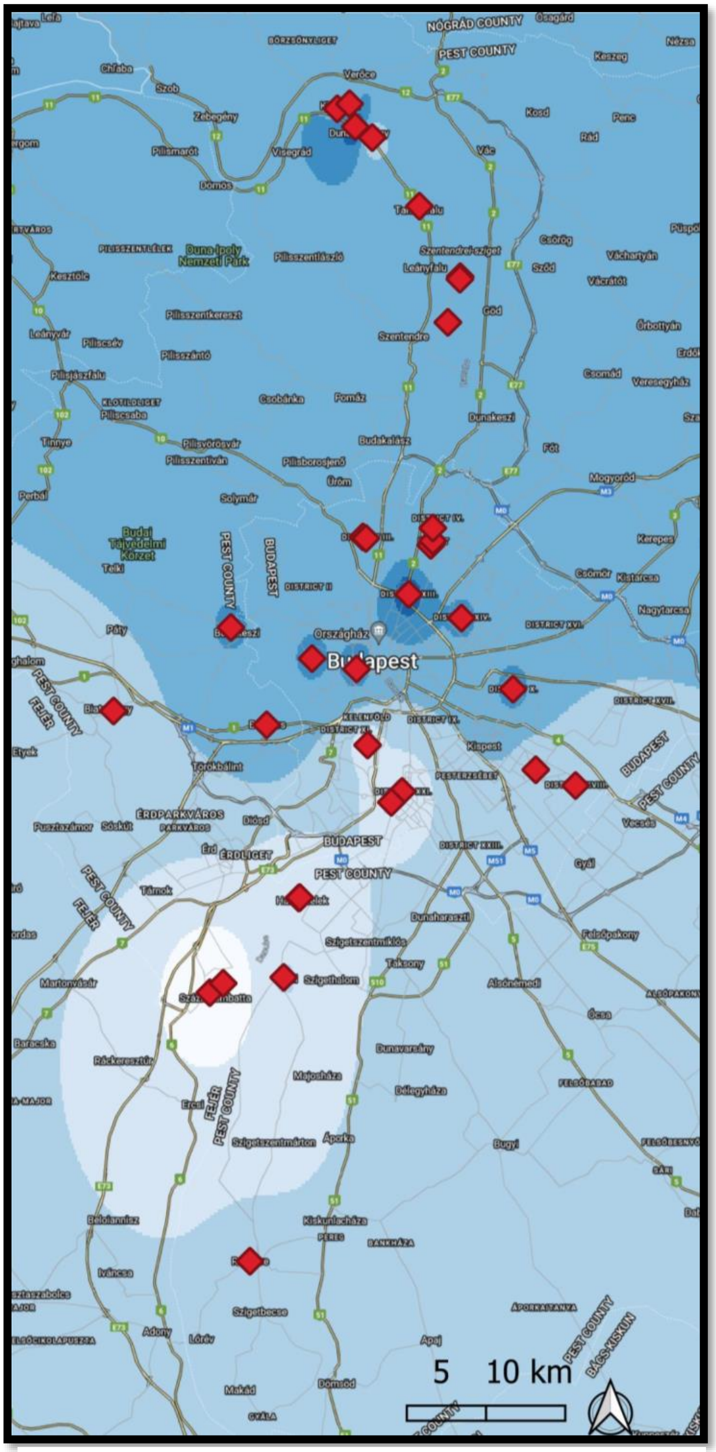

Figure 8: PFHpA Interpolation map. This map shows the interpolation of PFHpA concentrations for each sample.

PFHxA:

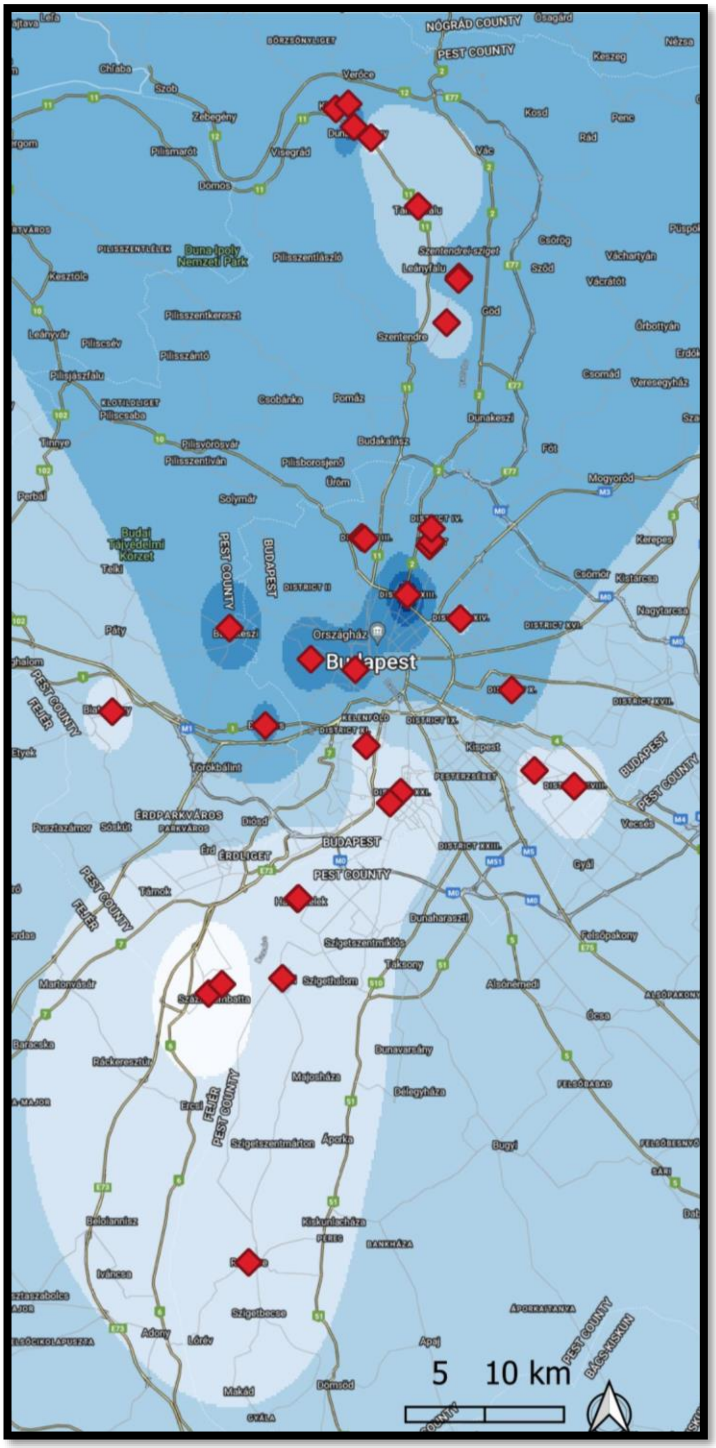

Figure 9: PFHxA Interpolation map. This map shows the interpolation of PFHxA concentrations for each sample.

PFHxS:

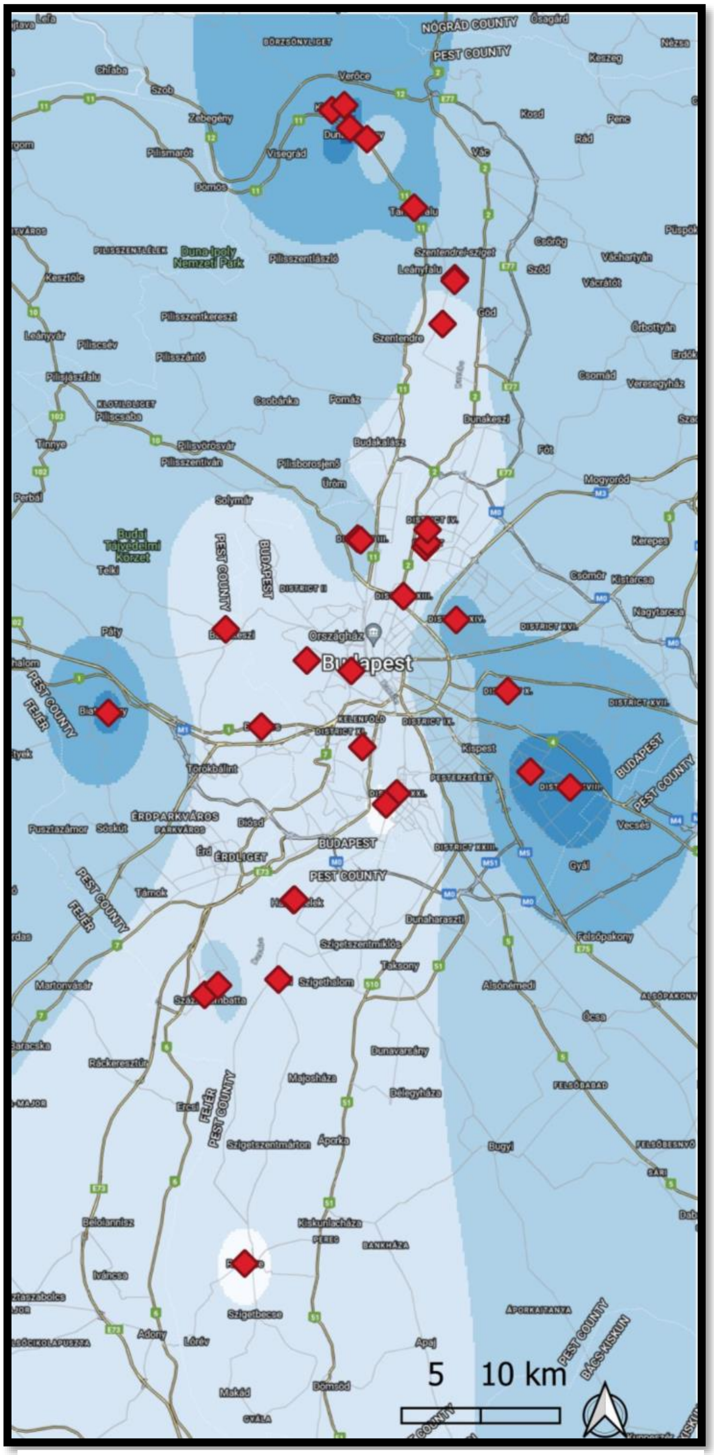

Figure 10: PFHxS Interpolation map. This map shows the interpolation of PFHxS concentrations for each sample.

PFNA:

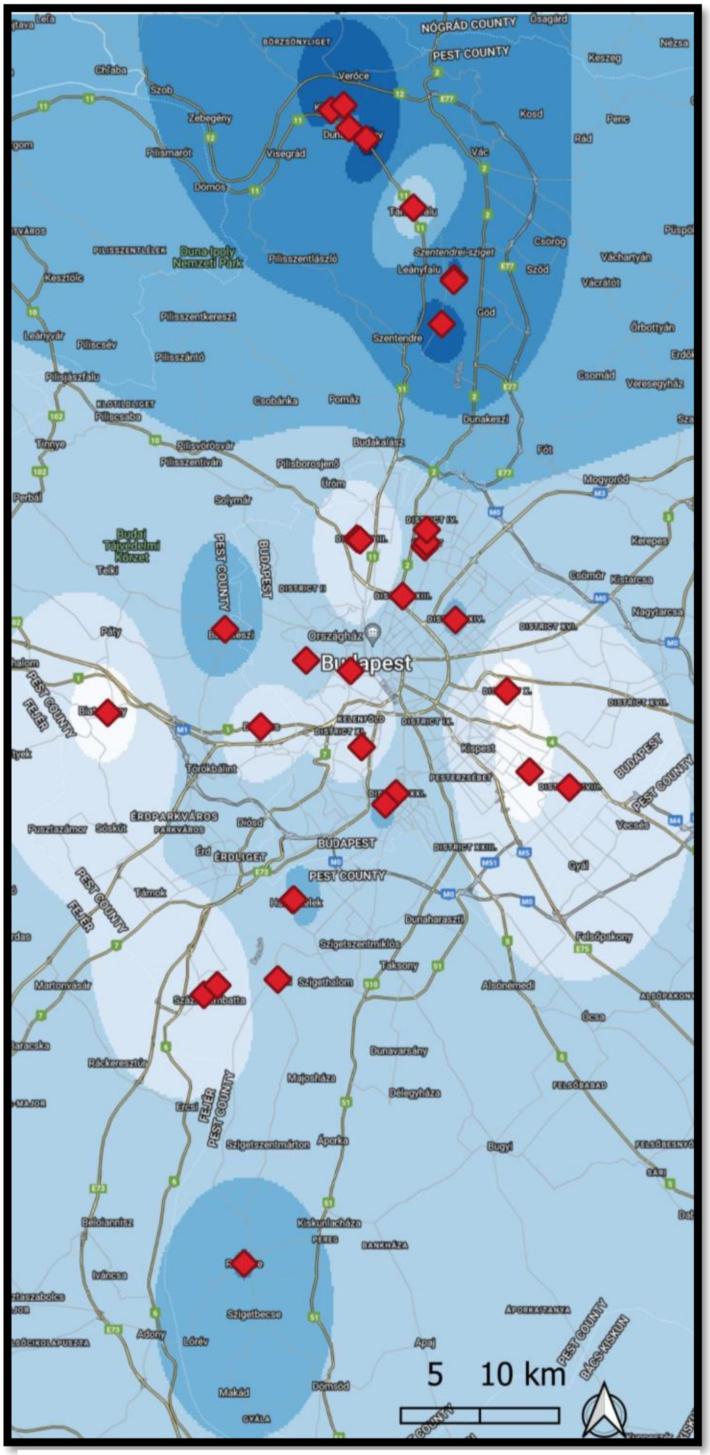

Figure 11: PFNA Interpolation map. This map shows the interpolation of PFNA concentrations for each sample.

PFDA:

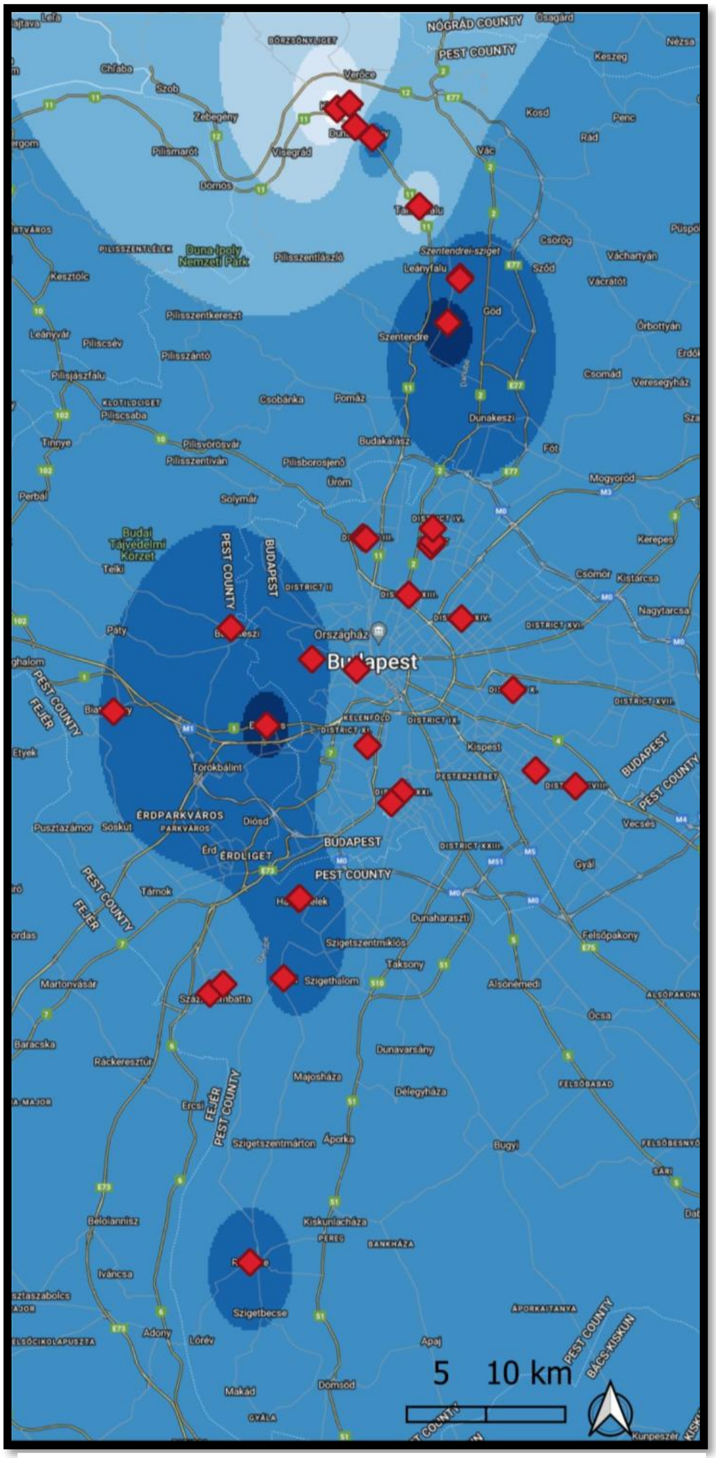

Figure 12: PFDA Interpolation map. This map shows the interpolation of PFDA concentrations for each sample.

6. Discussion:

The analysis of the figures generated using the interpolation tool reveals a complex distribution of PFAS across various regions of Budapest and several neighboring municipalities. The color variation indicates how higher (darker) or lower (lighter) the concentration of a certain PFAS can be when compared with all the other samples. The concentration levels of different PFAS vary noticeably across different locations, with certain regions showing higher values of a certain PFAS compared to others.

In the northern part of Budapest, that includes areas such as Dunabogdány, Kisoroszi, Pócsmegyer-Surany, and Tahitótfalu, there is a consistent trend of darker colors across multiple PFAS compounds. This indicates higher concentrations of certain PFAS in these regions than other regions. Notably, Dunabogdány emerges as a hotspot of several PFAS compounds with higher concentrations than the other regions, including PFOS, PFOA, GenX, PFHpA, PFHxA, PFBS, PFHxS, PFNA and PFDA.

Districts III, XIII and XII are regions of Budapest where the summatory of PFAS detected (Total PFAS) was higher than the other regions of the capital. Districts III also show relatively higher concentrations of PFBS and PFNA. District III is notable for its significantly elevated concentrations of PFBS. District XIII is notable for the higher concentrations of ADONA, PFHxA and PFHpA.

Regions such as Százhalombatta and Ráckeve, in the south-west, consistently display lighter colors across various PFAS compounds. This indicates lower concentrations of PFAS in these areas compared with other areas, reflecting a lesser level of contamination. With an exception for PFHxS in Százhalombatta, which showed a high concentration. Biatorbágy, parts of district XVIII, and the south and south-west regions of Budapest also usually displayed a lighter color across multiple PFAS compounds, reinforcing the pattern of lower contamination levels in these regions. With exceptions for PFHxS and PFDA in Biatorbágy, the concentration was higher than the other regions.

Some compounds had a similar distribution over the map, meaning that the concentration values for the specific PFAS were similar or approximated the same for the samples analyzed, like for PFOA, GenX, PFHpA and PFNA, with some few higher or lower locations.

This work analyzes the interpolation map according to the concentration detected for each PFAS compound in each sample. The interpolation tool estimates the unknown values based on the known values, in this case, the known values are the concentration for each of PFAS compound and the estimations is the color gradient that diminishes with the distance from the sample location. That means that the sampling locations can directly interfere with the results of each other. The maps of PFNA (Figure 11) and PFDA (Figure 12) could have been influenced by this fact as these compounds were not detected in all samples.

It is important to understand PFAS and how these substances can contaminate the water resources in urban centers. The use of the software QGIS facilitates the analysis of per- and polyfluoroalkyl substances in drinking water across Budapest and neighboring municipalities in Hungary. This work helps to identify which type of PFAS has the most significant presence in each respective region.

7. Conclusion:

This work analyzed the different types of PFAS and their concentrations in 32 drinking water samples collected from Budapest and neighboring municipalities. The results were then compared between samples to determine which region contains the highest concentration for each type of PFAS detected. QGIS software was used to create images with precise georeferencing and the interpolation tool, Distance Weighting (IDW), to estimate unknown values of concentrations for near regions based on the concentration value of the sample. The result is illustrated by a gradient of color that diminishes from a darker color to a lighter color according to the distance from the sample location. The maps generated by this work show a heterogeneous distribution across Budapest and neighboring municipalities.

Districts III, XIII, XII and the neighboring regions north of Budapest, including the municipalities Dunabogdány, Kisoroszi, Pócsmegyer-Surany, and Tahitótfalu, exhibited the highest concentrations for Total PFAS, PFOS, GenX, and PFHxS. The municipality of

Dunabogdány is the region that showed the highest concentration for several PFAS compounds (PFOS, PFOA, GenX, PFHpA, PFHxA, PFBS, PFHxS, PFNA and PFDA). On the other side, regions such as Százhalombatta and Ráckeve in the south and south-west municipalities of Budapest had the lowest concentrations for the majority of PFAS compounds, with the exception being PFDA and PFOS in Halásztelek municipality.

Previous works have related PFAS contamination in drinking water with the pipeline structure and with ineffective water treatment that does not completely remove these compounds (Chen et al., 2019 Ma et al., 2019; Yu et al., 2019 Li et al., 2011; Prager, Sica, & Kohrs, 2024; Guo et al., 2022; Boiteux et al., 2017; Takagi et al., 2011; Domingo et al., 2019). It is important to know the sources of contamination, whether from pipelines or ineffective water treatment, and to determine why the northern region exhibits higher concentrations of specific PFAS. In the future, it would be valuable to investigate why certain PFAS levels are higher in the drinking water of northern Budapest municipalities and some districts. Such a study could determine if the issue is connected to pipelines or water treatment processes.

Identifying the reasons for this contamination can help to understand PFAS compounds in drinking water and it is essential to implement solutions and regulations to safeguard public health and safety. In piping materials and water treatment, common PFAS like PFOA, PFOS, PFNA, PFHxS, PFBS, and GenX chemicals are often present. However, their presence in water treatment processes can pose health risks, showing the need for careful monitoring and regulation to maintain safe drinking water standards.

8. Summary

Thesis title: Detection and mapping of per- and polyfluoroalkyl substances in the drinking water supply of Budapest.

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Course: MSc Environmental Engineering

Institute/Department: Institute of Environmental Sciences

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Institute/Department: Institute of Aquaculture and Environmental Safety/Department of Environmental Toxicology

Poly and perfluoroalkyl substances (PFAS) are a group of artificial organic chemical substances globally used in industries that have been the focus of attention for their unique chemical properties and environmental concern (Boiteux et al., 2012; Ericson et al., 2009; Hu et al., 2019). PFAS are thermodynamically stable and highly resistant to several forms of degradation, making them persistent in the environment and difficult to remediate (Boiteux et al., 2012; Kucharzyk K.H et al., 2017). These high stability and lipid and water repelling attributes make PFAS attractive for several purposes, for example: paper industry, medical devices, pesticides, metallurgical and packing, and also for the use of costumers like, cosmetics, paints, aqueous film forming foams (AFFFs) and several waterproof products (Rayne and Forest, 2009; USEPA, 2012).

The wide use of PFAS make them an emergent contaminant in the environment. PFAS has the capacity to bioaccumulate in organisms, and many types of PFAS are considered toxic, and can lead to multiple types of negative health impacts (Cousins et al., 2017; European Environmental Agency, 2019). It is important to understand these substances better and also to detect them in water supplies.

In this study, thirty-two samples of drinking water were collected from various locations in Budapest and applied to the guideline of USA EPA Method nr. 537.1 for PFAS detection. Using this method the result the PFAS identified were visualized using an interpolated map utilizing the QGIS software to estimate the PFAS values of the surroundings of the samples. The results showed varied PFAS distribution, with higher concentrations in northern regions, suggesting potential contamination sources from pipelines or water treatment processes, necessitating further investigation for safeguarding public health.

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In this journey that began with the dream of studying and living abroad becoming a reality, I reach the end of the MSc Environmental Engineering course with the submission of this thesis, and just as the beginning of this dream, I have many to thank for their direct and indirect support for my personal, professional, and emotional development. Firstly, I thank the unconditional love of my entire family, especially my mother, Mariléa, my father, Gérson, my grandmother, Dirceléa, and my sister, Carolina, who have always supported me in my dreams, even with the great distance, never failing to provide support in every aspect. I dedicate this thesis to them, my beloved family, and to my deceased grandparents, Adalberto, Sidney, and Marly.

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11. Appendices

Appendix 1: Table of PFAS concentration.

	PFAS concentration (ng/L)										
Sample location	**PFBS**	**PFHxA**	**HFPO-DA (GenX)**	**PFHpA**	**ADONA**	**PFHxS**	**PFOA**	**PFNA**	**PFOS**	**PFDA**	**Total PFAS**
District. XIV- Budapest	1.29	1.65	1.73	1.32	4.21	0.87	2.74	0.28	2.59		16.68
District X - Budapest	1.27	1.93	1.85	1.34	4.21	0.83	2.55	0.22	2.59		16.79
District XVIII - Budapest	1.57	1.21	1.26	0.87	2.15	1.03	2.17	0.25	3.23		13.74
District XVIII – Budapest	1.31	1.25	1.29	1	2.29	0.96	2.15	0.21	3.55		14.01
Biatorbágy	1.17	1.27	1.43	1.01	2.52	0.9	1.72	0.22	2.38		12.62
Budakeszi	1.06	2.26	1.12	1.32	3.98	0.44	2.84	0.3	3.05	0.26	16.63
Budaörs	0.96	2.12	1.24	1.3	4.14	0.53	2.94	0.24	3.16	0.3	16.93
District XXII – Budapest	0.92	1.21	0.67	0.76	1.63	0.51	1.99	0.23	2.87	0.23	11.02
Százhalombatta	0.9	0.65	0.51	0.46	0.96	0.49	1.65	0.24	1.79	0.24	7.89
Százhalombatta	0.94	0.65	0.54	0.43	0.87	0.67	1.85	0.23	2.07	0.24	8.49
District XXI - Budapest	1	1.03	0.6	0.65	1.15	0.59	2.1	0.26	4.12	0.26	11.76
District XXI - Budapest	0.73	1.08	0.73	0.81	1.92	0.26	2.12	0.29	2.88	0.2	11.02
Halásztelek	0.89	0.98	0.58	0.68	1.18	0.42	2.07	0.22	3.1	0.24	10.36
Szigetszentmiklós	1	1.05	0.75	0.7	1.48	0.48	2.34	0.34	4.75	0.27	13.16
Tököl	0.82	1.39	0.73	0.88	1.9	0.43	1.78	0.27	2.86	0.25	11.31
Ráckeve	0.79	1.29	0.76	0.88	2.12	0.39	1.95	0.3	3.12	0.25	11.85
District IV - Budapest	0.89	1.9	1.71	1.19	4.93	0.38	3.38		2.5		16.88
District IV - Budapest	0.81	1.69	1.54	1.03	4.6	0.39	3.27		2.3		15.63
District IV - Budapest	0.99	1.93	1.7	1.18	4.94	0.42	3.38		2.64		17.18
District XIII - Budapest	1.31	3.1	2.02	1.71	6.68	0.52	3.86		1.81		21.01
District III - Budapest	0.99	2.21	1.65	1.22	5.4	0.55	3.57		2.69		18.28
District XII - Budapest	0.98	2.25	1.8	1.34	5.49	0.55	3.71		2.82		18.94
District I - Budapest	1.13	2.29	1.58	1.37	5.4	0.48	3.66		2.76		18.67
District III - Budapest	8.95	1.48	0.56	1	2.94	0.66	3.26	0.23	2.25	0.24	21.57
Dunabogdány	1	0.96	0.56	0.83	1.99	0.41	2.68	0.36	2.17	0.3	11.26
Dunabogdány	1.67	2.99	3.48	1.93	4.37	1.33	7.38	0.29	6.5	0.16	30.1
Kisoroszi	1.28	1.75	1.82	1.24	5.12	0.77	3.08	0.32	3.24	0.07	18.69
Kisoroszi	1.27	1.72	1.75	1.15	4.97	0.83	2.99	0.35	3.63	0.12	18.78
Tahitótfalu	1.26	1.52	1.68	1.13	4.78	0.81	2.88	0.25	3.89	0.14	18.34
Pócsmegyer-Surány	0.98	1.72	1.39	1.17	3.44	0.62	4.13	0.38	5.13	0.26	19.22
Pócsmegyer-Surány	0.95	1.73	1.32	1.06	3.36	0.54	4	0.25	4.84	0.27	18.32
Szigetmonostor	0.93	1.64	0.92	1.12	3.4	0.47	2.85	0.34	3.44	0.32	15.43

DECLARATION

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