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IDENTIFICATION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN THE SURFACE WATERS OF THE DANUBE RIVER NEAR BUDAPEST USING QGIS AND LC-MS METHODS

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1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a group of complex, diverse and man-made organic compounds that have garnered significant attention in the past few years due to their widespread presence in the environment and potential adverse effects on human health and ecosystems (Starnes et al., 2022; Guelfo et al., 2021). PFAS are considered persistent organic pollutants, and they are characterized by their unique chemical properties, notably, their strong carbon-fluorine bonds that make them highly stable and extremely resistant to degradation in natural processes (Grgas et al., 2023).

In this context, the identification of possible PFAS contamination spots in surface waters represents a relevant theme of research, since surface waters, especially rivers, work as a vital resource for human consumption, agriculture, industry, and ecosystem management (Li & Wu, 2023; Tokranov et al., 2021). The presence of PFAS in rivers can pose a significant threat to water quality, as well as potentially impact human populations through drinking water sources and food chain contamination (Eschauzier et al., 2012).

The Danube River is the second biggest river in Europe, crossing multiple countries such as Hungary, Austria, Germany, Romania and Ukraine, which makes it a fundamental player in supporting the socio-economic activities and the biodiversity of the central European region (Lazar et al., 2022). Following the global tendency, concerns have been raised regarding the possible presence of PFAS in the Danube River and its tributaries. Particularly, the section of the Danube River near Budapest, Hungary, where anthropogenic activities and urbanization may contribute to PFAS contamination.

Considering this, the primary objective of this study is to investigate the presence and distribution of PFAS in the surface waters of the Danube River near Budapest, Hungary. To achieve this goal, sampling and LC-MS analysis of water from six locations along the river were performed to identify possible spots of PFAS contamination. Also, maps were generated using QGIS software (3.28.12-1 version), where an IDW interpolation was performed to visualize the estimated impact of PFAS in the surroundings, according to the samples. Through the analysis of the water samples and the assessment of potential contamination sources, this work aims to discuss some of the possible contributors to PFAS pollution in the study area, since the comprehension regarding the sources of contamination is fundamental to implement effective mitigation strategies.

The results of this work can help to provide valuable insights into the actual condition of PFAS contamination in the Danube River near Budapest and contribute to the development of strategies for mitigating the impact of PFAS pollution and safeguarding water quality in the study area, thereby contributing to the development of a sustainable approach for protecting water resources and human health.

2. OBJECTIVES

The main objective of this thesis was to conduct a preliminary investigation into the presence of PFAS in the surface waters of the Danube River near Budapest, Hungary, using maps generated by QGIS software. To achieve this objective, water sampling was performed at six points in the study area; subsequently, the samples were analyzed via LC-MS for PFAS identification. An additional objective of this study was to identify possible sources of PFAS contamination impacting the study area, such as industrial discharges.

3. LITERATURE REVIEW

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic organic substances that are characterized by the presence of fluorine atoms attached to their carbon chains. This strong carbon-fluorine bond is the main distinctive chemical characteristic that makes PFAS being known for their durability and resistance to environmental degradation (Grgas et al., 2021; Shahsavari et al., 2021). PFAS have been used for many industrial and consumer applications since the 20th century due to their specific properties, such as oil and water repellency, heat resistance, and chemical stability (Brennan et al., 2021; Jiao et al., 2022).

The historical use of PFAS can be traced back to the late 1940s and 1950s, when fluorinated compounds, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), were developed for industrial purposes (Glüge et al., 2020; Brennan et al., 2021). PFAS acquired notoriety for the use in the manufacturing of various consumer products, like non-stick cookware, stain-resistant fabrics, food packaging materials, and firefighting foams and in many industries in general, notably the aeroespacial, semiconductor, medical, automotive, construction, electronics, and aviation (Buck et al., 2011; EPA, 2016). This widespread use led to a ubiquitous presence of PFAS in the environment, with PFAS being detected in air, water, soil, wildlife, and even human tissues worldwide (Abunada, Alazaiza & Bashir., 2020; Brunn et al., 2023).

PFAS can be released to the environment through various pathways, including a direct liberation from manufacturing facilities and leaching from landfills or wastewater discharges (Meegoda et al., 2020; Sunderland et al., 2019; Hamid, Li & Grace, 2018). Since PFAS are known for having a characteristic persistence in the environment, and also a tendency to bioaccumulate in living organisms (Cousins et al., 2020), many concerns about the potential adverse effects of PFAS on environmental and human health have been raised in the past few years (NIH, 2017, assessed in March, 18; https://www.niehs.nih.gov/research/programs/pfas).

The fate of PFAS in the environment can be influenced by different factors, such as: the physicochemical properties of each type of PFAS, the conditions of the environment, and the specific transport mechanisms (Guelfo et al., 2021; Teymourian et al., 2021). Due to their carbon chains and chemical structure, PFAS have hydrophobic and oleophobic properties, which enable them to partition in different types of soil and sediments, where they can easily accumulate over time (Kurwadkar et al., 2022; Bolan et al., 2021; Aboul-Khalil et al., 2022). Additionally, PFAS have also been found to go through long-range atmospheric transport, which can lead to their widespread distribution in remote regions, even far away from the primary sources of release (Panieri et al., 2022; Faust, 2023; Paragot et al., 2020). Also, in humans, exposure to PFAS has been linked to various adverse health effects, including developmental and reproductive disorders, immune system dysfunction, and certain types of cancer (Erlich et al., 2023; Chambers, Hopkins & Richards, 2021).

Considering this, analysis to evaluate the presence of PFAS in surface waters like rivers and other aquatic environments are fundamental to identify the extent of contamination, and understand the possible implications for the environment and human health. Monitoring programs and research surveys have already detected PFAS in rivers, lakes, reservoirs, estuaries, and coastal waters, what indicates their extensive distribution in aquatic environments (EPA, 2017; Ambaye et al., 2022; Abunada, Alazaiza & Bashir., 2020; Nahar & Niven, 2023). Elevated PFAS concentrations have been reported in areas that are characterized by intense industrial activities, high urbanization, and wastewater discharges, as well as in remote regions far from primary sources (Cousins et al., 2022; Panieri et al., 2022; Wang et al., 2023; Wang et al., 2022).

High levels of PFAS have been observed all around the world in the past 10 years, especially in the United States, China and Europe (Ackerman Grunfeld et al., 2024). In February, 2024, 1245 sites contaminated with concentrations above the recommended limit in drinking water were identified in the US (EWG, 2024; available at: www.ewg.org/interactive-maps/pfas_contamination/map/ ; assessed in April, 17, 2024).

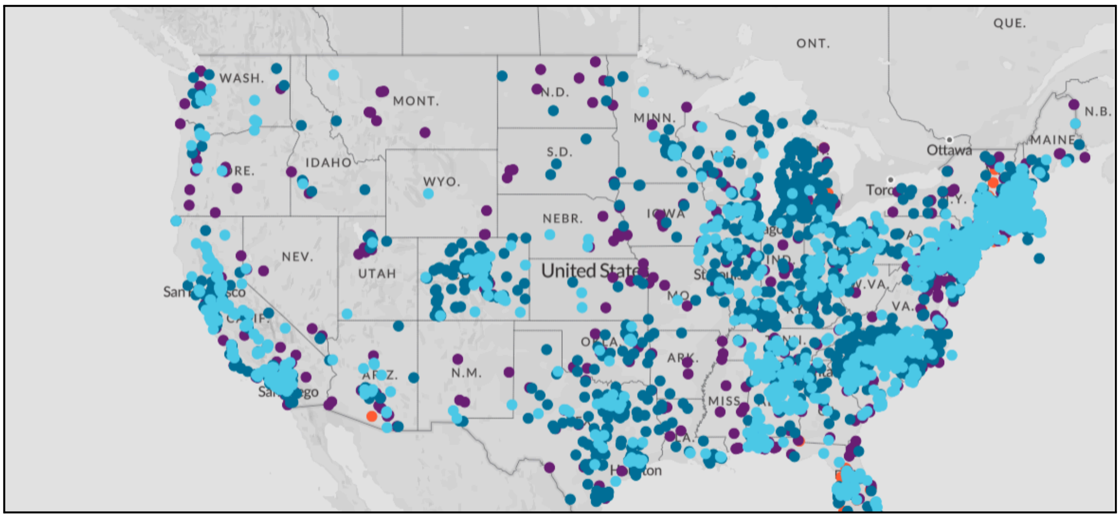


Fig.1) PFAS contamination spots identified in the United States. Light blue points represent samples above the recommendable limit, dark blue points represent samples below the recommendable limit and purple points represent military sites. (source: EWG, 2024)

Furthermore, seasonal fluctuations in PFAS concentrations have also been observed, with higher levels typically being identified during periods of increased precipitation and surface runoff, indicating that hydrological factors can influence the transport of the contaminant. This phenomenon can result in a wide PFAS distribution within water bodies, with higher concentrations typically observed in sediment-rich areas such as riverbeds, deltas, and estuarine sediments (Pulster et al., 2022; Tokranov et al., 2021).

As noted, the sources of PFAS contamination in surface waters are diverse and may include point sources such as industrial discharges, wastewater effluents, and landfill leachates, but also diffuse sources such as atmospheric deposition, urban runoff, and agricultural runoff (Ambaye et al., 2022; Wang et al., 2022). Industrial activities associated with PFAS manufacturing, processing, and product use have been identified as significant contributors to surface water contamination, particularly in regions with high industrial density (Glüge et al., 2020). Additionally, inputs from urban stormwater runoff, firefighting activities, and land application of PFAS-containing fertilizers and sludges can contribute to localized contamination of surface waters (Vogel et al., 2023; Chohan et al., 2021; Nahar, Zulkarnain & Niven, 2023).

Understanding the environmental fate of PFAS in aquatic environments is essential to assess their long-term impacts and design effective mitigation strategies. PFAS can go through various transformation processes, including sorption, partitioning, biodegradation, and photolysis, which can influence their behavior and persistence in water bodies and soil (Amen et al., 2023; Xiao et al., 2017). The fate of PFAS in surface waters and soil can be driven by different factors, such as the organic carbon content of the environment, pH, temperature, and microbial activity, which will determine the mobility, bioavailability, and fate of PFAS in aquatic ecosystems (Zhang, Sharivan & Ma, 2022; Schiavone & Portesi, 2023).

European surface waters, including the Danube River and its tributaries, have also been identified as points contaminated by PFAS. Elevated concentrations of PFAS compounds, including perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and ADONA and their precursor substances, have been detected in water samples collected from multiple locations within the Danube River basin (Atlatszo; assessed in April, 16, 2024; https://atlatszo.hu/kornyezet/2024/03/22/mar-a-dunaban-is-kimutathatoak-a-karos-es-nagyon-sokara-lebomlo-pfa-vegyuletek/). These findings suggest that PFAS contamination might not be limited to a specific region, but rather widespread through many aquatic environments across Central Europe (Obeid et al., 2023; Ng et al., 2022; Beggs et al., 2023).

The primary point sources of PFAS contamination in European surface waters, including the Danube River basin, are usually related to industrial activities, specifically chemical manufacturing, textile processing, and metal platings, that can all potentially contribute to localized contamination of water bodies (Clara et al., 2009; Saxena et al., 2023). Additionally, inputs from urban runoff and wastewater effluents, also represent important non-point sources of PFAS contamination in surface waters, particularly in densely populated and urbanized areas such Budapest, Hungary.

Since PFAS present a bioaccumulative potential in aquatic organisms, such as fish, invertebrates, and algae, leading to biomagnification through the food chain, this whole process can lead to elevated concentrations of PFAS in higher trophic level organisms, increasing the risk of exposure to humans through consumption of contaminated seafood (Serena, Baker & Baker, 2023; Boisvert et al., 2019). Moreover, PFAS contamination in

European surface waters may also pose risks to human health through exposure via drinking water sources and recreational activities. Contaminated surface waters can serve as sources of drinking water for downstream communities, potentially leading to human exposure to PFAS compounds, and recreational activities such as swimming, boating, and fishing may result in dermal contact or ingestion of PFAS-contaminated water (Burkhard, 2020; Brunn et al., 2023).

Epidemiological studies have reported associations between PFAS exposure and adverse health outcomes in communities living near contaminated water sources, highlighting the importance of addressing PFAS contamination to protect public health. Additionally, regulatory agencies, such as the European Commission have established drinking water quality standards and guidelines for PFAS compounds, aiming to minimize human exposure and mitigate potential health risks. For example, in Europe, the limit threshold for PFAS in drinking water varies between 0.1 µg/L (100 ng/L). (European Commission, 2020; Fabelova et al., 2023; Papadopoulou et al., 2021; Richterova et al., 2021), and elevated concentrations of PFAS compounds, including the perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) already have have been found in water samples collected along the Danube River (Lindim, Cousins & VanGils, 2015; Pistochi & Loos, 2009).

Additionally, there is a need to establish standard monitoring protocols and analytical methods for PFAS analysis in the Danube River basin to ensure consistency and comparability of data across different studies and regions. Harmonized monitoring efforts would facilitate the assessment of temporal and spatial trends in PFAS contamination and support informed decision-making for water quality management and protection of ecosystem and human health.

While there are thousands of PFAS compounds, certain types have received particular attention due to specific characteristics, such their prevalence, persistence, and potential health and environmental impacts.

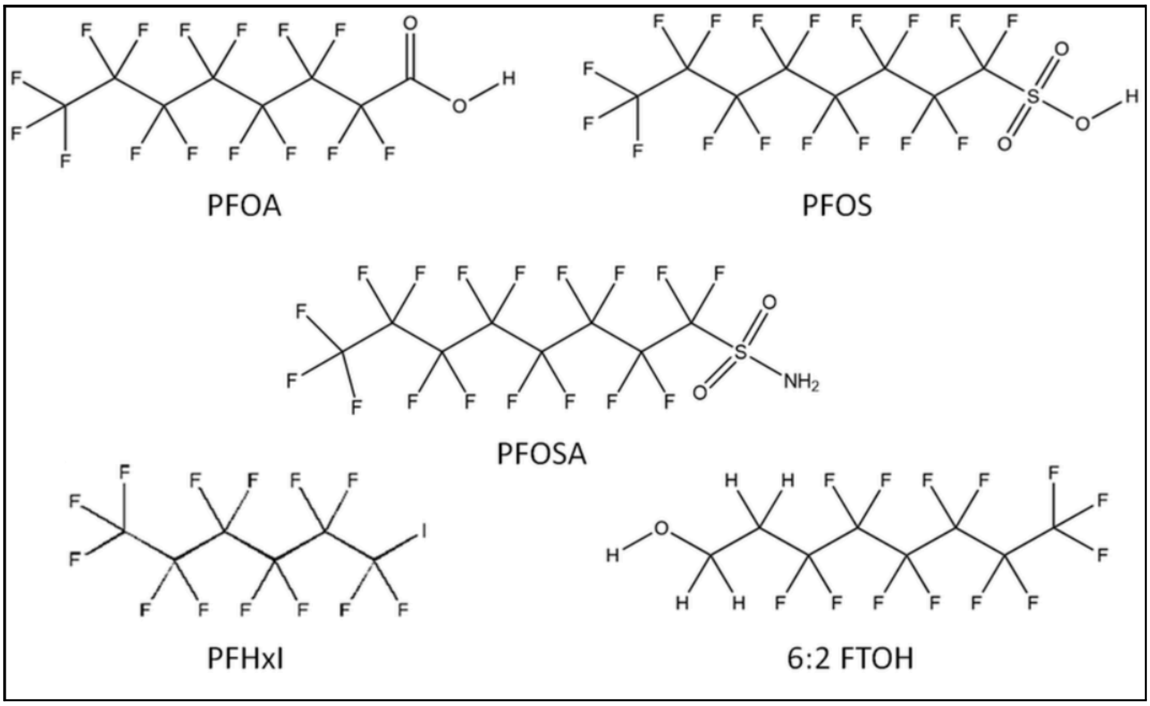


Fig.2) Example of the chemical structures of some PFAS (source: Ramirez Carnero et al., 2021)

Among the most important types of PFAS, it is possible to highlight some, such as: a) the Perfluorooctanoic Acid (PFOA), that is a widely studied PFAS compound that has been used in the manufacturing of fluoropolymers and non-stick coatings, among other applications (Zaraitelabad et al., 2013), and it has raised concerns due to its persistence in the environment, bioaccumulation in living organisms, and potential adverse health effects, including developmental and reproductive disorders (Steenland, Fletcher & Savitz, 2010); b) Perfluorooctane Sulfonate (PFOS), that is another extensively studied PFAS compound that has been used in a variety of industrial and consumer products, including firefighting foams, surface treatments, and textiles, and is known for its widespread occurrence in the environment and bioaccumulative potential (Fragki et al., 2021); c) Perfluorohexane Sulfonate (PFHxS), that is a shorter-chain PFAS compound that has been used in similar applications as PFOS, including firefighting foams and industrial processes. While PFHxS has been detected in environmental samples, its toxicity and environmental behavior are still being studied (Schulz, Silva & Klapner, 2020; Kreychman et al., 2024); d) Perfluorobutanesulfonic Acid (PFBS), that is a shorter-chain PFAS compound that has been used as a replacement for longer-chain compounds in some applications. While PFBS is less bioaccumulative than longer-chain PFAS compounds, it has still been detected in environmental samples and is of interest due to its potential for environmental persistence and human exposure (Ivantsova, Lu & Martinyuk, 2024; Chen et al., 2018).

However, these are just a few examples of the many PFAS compounds that have been identified and studied. It is important to highlight that PFAS can vary in their chemical properties, uses, and environmental behavior, and additional research is needed to fully understand the risks associated with each different type of PFAS (Fenton et al., 2021), but with a deep focus on the most important PFAS compounds and their characteristics, it is possible to prioritize efforts to assess and mitigate the environmental and human health impacts of PFAS contamination.

In order to remediate environments contaminated by PFAS, some techniques can be considered: such as: activated carbon, ion exchange resins, bioremediation and thermal treatment. The activated carbon adsorption is a widely used remediation technique for PFAS-contaminated water and soil. Activated carbon has high affinity for PFAS compounds, which allows PFAS removal through adsorption onto the surface of carbon particles. However, challenges such as saturation and regeneration of the activated carbon, as well as the disposal of spent carbon, must still be addressed for successful implementation of this technique (Cantoni et al., 2021; Pauleto & Bandosz., 2022).

The ion exchange resins offer another promising method for PFAS removal from water. Ion exchange resins function by exchanging PFAS ions in solution with other ions immobilized on the resin matrix. This process results in the removal of PFAS from the water phase, with the contaminants retained on the resin (Dixit et al., 2021). While ion exchange resins can achieve high removal efficiencies for PFAS, challenges such as resin saturation and disposal of spent resin still require careful management (Karbassiyazdi et al., 2023);

Bioremediation techniques can be defined by the use of metabolic activity of microorganisms to degrade PFAS compounds. The main goal with the bioremediation is to use biological processes, such as microbial degradation and phytoremediation, to break down PFAS molecules into less toxic or non-toxic byproducts (Lafond et al., 2023; Marchetto et al., 2021)

Lastly, thermal treatment techniques, such as incineration and thermal desorption, involve the application of heat to degrade PFAS compounds in contaminated media (Kumar et al., 2023). Incineration can destroy PFAS molecules at high temperatures, while thermal desorption can volatilize PFAS for subsequent capture and treatment. However, there are still concerns to be addressed such as energy consumption, air emissions, and potential formation of hazardous byproducts (Longendyke, Katel & Wang, 2022).

The accurate detection and quantification of PFAS in water samples require robust methodologies for sampling, extraction, and analysis. Different techniques have been developed and employed for this purpose, each having their own strengths and limitations. The most common methodologies include liquid chromatography/mass spectrometry (LC-MS), gas chromatography-mass spectrometry (GC-MS), and solid-phase extraction (Al-Amin et al., 2020; Jia et al., 2022).

Liquid chromatography/mass spectrometry (LC-MS) is one of the most used analytical techniques for PFAS analysis due to its high sensitivity, selectivity, and versatility (Mulin et al., 2019). LC-MS allows for the separation of PFAS compounds based on their chemical properties using chromatographic columns, followed by detection and quantification using mass spectrometry. LC-MS methods can achieve low detection limits and high resolution, making them suitable for the analysis of complex environmental samples such as water. However, LC-MS methods may also require extensive sample preparation steps, including extraction and cleanup procedures, which can be time-consuming and labor-intensive (Forster et al., 2024; Frigerio et al., 2022).

Gas chromatography-mass spectrometry (GC-MS) is another analytical technique that can be used for PFAS analysis. GC-MS relies on the separation of PFAS compounds by their vapor pressures using a gas chromatograph, followed by detection and quantification using mass spectrometry. Gas chromatography methods offer high sensitivity and selectivity for certain PFAS compounds, but they can have limited applicability, being used mostly for non-volatile and thermally stable analytes (Al Amin et al., 2020). Additionally, derivatization may be required for some PFAS compounds to improve their volatility and chromatographic performance, adding complexity to the analysis (Li et al., 2020).

Solid-phase extraction is a sample preparation technique commonly used for the extraction and preconcentration of PFAS from water samples prior to analysis. This method involves passing water samples through a solid-phase sorbent, such as a reversed-phase cartridge, which can selectively retain PFAS compounds (Tanyasu et al., 2022). SPE methods can achieve high extraction efficiencies and reduce matrix effects, thereby improving the accuracy and precision of PFAS analysis. However, SPE procedures may require large volumes of solvents and specialized equipment, and they can be susceptible to variability and contamination issues (Lockwood et al., 2019).

Thus, the choice of the technique and method to be used for PFAS analysis in water samples depends on different factors such as the target analytes, sample matrix, detection limits, and available resources, but in general, a LC-MS is often preferred for its versatility and sensitivity, especially for non-volatile and polar PFAS compounds (Mulin et al., 2019; Stramenga et al., 2021).

Regulatory frameworks and guidelines at European and international levels play a crucial role in addressing PFAS contamination in surface waters. In Hungary and Europe, efforts have been made to establish regulatory measures to manage PFAS pollution and protect water quality.

In Hungary, the management of PFAS contamination in surface waters is governed by national legislation and regulations, as well as European Union (EU) directives and guidelines. The Hungarian Water Act (Act XVII of 1995) sets a legal framework for the protection and management of surface waters, including provisions for the prevention and control of water pollution, in which PFAS contamination is set. Additionally, Hungary is subject to EU regulations and directives related to water quality, such as the EU Water Framework Directive (WFD) and the Groundwater Directive, which aim to achieve good ecological and chemical status of surface waters and groundwater.

At the European level, the European Chemicals Agency (ECHA) regulates the manufacture, use, and marketing of chemicals, including PFAS compounds, under the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) Regulation. REACH requires companies to register and submit data on the properties and uses of chemicals, including PFAS, and to comply with restrictions on their use to protect human health and the environment (ECHA, 2024). Additionally, according to the European Commission, the limit value for total PFAS is in the range of 0.5 µ/L (500ng/L).

In terms of regulatory limits for PFAS in surface waters, Hungary itself has not yet established a specific numeric standard or maximum allowable concentrations for PFAS compounds. However, the EU Environmental Quality Standards Directive sets the environmental quality standard (EQS) for 20 individual PFAS to 0.1 µg/l, including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These values can be used as reference concentrations to guide management actions in order to address PFAS contamination.

Monitoring requirements for PFAS in surface waters vary across European countries and may include routine monitoring programs, targeted surveys, and investigative studies to assess PFAS contamination levels and trends. In Hungary, monitoring of PFAS contamination in surface waters may be conducted as part of national water quality monitoring programs, research projects, or regulatory compliance assessments. As seen before, analytical methods for PFAS analysis in water samples typically involve high-performance liquid chromatography-mass spectrometry (LC-MS), which provide high sensitivity and selectivity for PFAS compounds.

Risk assessment methodologies for PFAS in water quality management involve evaluating the potential risks to human health and the environment posed by PFAS contamination in surface waters. This may include assessing exposure pathways, estimating exposure levels, and characterizing the toxicity and hazards of PFAS compounds (Bil et al., 2023). Risk assessments can be conducted at the national or regional level by regulatory agencies or scientific advisory bodies to inform decision-making and management strategies for addressing PFAS pollution.

Considering this, while specific regulatory limits for PFAS in surface waters may vary, efforts are being made to establish monitoring programs, assess risks, and implement management measures to protect water quality and public health from PFAS contamination both in Hungary and Europe.

One relevant tool that can be used to visualize the impact of possible focus of environmental contamination, such as PFAS, is the QGIS software. QGIS is a powerful open-source geographic information system (GIS) that offers valuable tools and capabilities for identifying potential pollutants in a given area through spatial analysis and mapping (Flenniken, Stuglik & Iannone, 2020). By integrating spatial data layers, including environmental parameters, land use, and potential pollution sources, QGIS enables users to visualize and analyze spatial patterns of pollution and assess potential risks to human health and the environment.

One approach to identify a potential pollutant in a given area using QGIS involves overlaying spatial data layers representing known pollution sources, such as industrial facilities, hazardous waste sites, and urban areas, with environmental and land use data layers. By visually inspecting the spatial distribution of pollution sources relative to sensitive receptors, such as water bodies, residential areas, and ecological habitats, users can identify areas at heightened risk of contamination and prioritize further investigation and monitoring efforts.

QGIS also offers advanced spatial analysis tools, such as interpolation techniques that can be used to estimate pollutant concentrations at unsampled locations based on available data. In particular, inverse distance weighting (IDW) interpolation is a commonly used method for spatially interpolating pollutant concentrations from point data measurements to create continuous surfaces or maps of pollution levels across a study area (Khouni, Louhichi & Ghrabi, 2021).

IDW interpolation is particularly important in identifying the impact of a pollutant in a given area, as it allows for the estimation of pollutant concentrations at locations where direct measurements are not available. This is especially relevant in environmental monitoring and risk assessment where spatial coverage of monitoring stations may be limited, and it is impractical or cost-prohibitive to collect data at every location of interest (Qiao et al., 2019).

IDW interpolation works by assigning weights to measured data points based on their distance from the location being interpolated, with closer points receiving higher weights than more distant points. This approach assumes that pollutant concentrations decrease with distance from known sources, reflecting the spatial patterns of pollution dispersion and transport. The interpolated surface generated provides a continuous representation of pollutant levels, allowing users to visualize spatial gradients and identify areas of elevated contamination (Li, 2021).

In the context of QGIS, IDW interpolation can be applied to pollutant concentration data collected from monitoring stations or sampling points distributed across a study area. By interpolating these data using IDW, users can generate maps or surfaces depicting predicted pollutant concentrations, providing valuable insights into spatial patterns of pollution and identifying hotspots or areas of concern for further investigation and management.

4. MATERIALS AND METHODS

4.1) Sampling and Sample Preparation

The water samples used in this work were gathered from sites managed by the Budapest Water Works. Briefly, these samples were collected in 250 mL narrow-mouth polypropylene bottles. The samples were kept in a freezer at a constant temperature of -18°C until they were ready for examination, within 90 days after they were collected.

To concentrate and extract PFAS from the drinking water samples, weak anion exchange solid-phase extraction tubes (Strata X-AW 33µm, Polymeric phase, 500mg/6ml) were used. To prevent any potential cross-contamination, all extraction tools passed through a proper washing with a solution of 5% NH4OH in MeOH before the analysis. Before extraction, the samples were acidified to 0.1% using acetic acid to facilitate ionization on the weak anion exchange SPE cartridge. Also, 10µl of SUR standard solution was introduced into the samples to monitor recovery through the analysis process. 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. After that, the samples were loaded onto the cartridges, which were then rinsed with 4 mL of 25mM acetate buffer (pH=4) and 2 mL of 0.1% acetic acid in H2O-MeOH (1:1, v/v). After complete drying, the analytes were eluted using 4 ml of 5 v/v % NH4OH solution in MeOH. The solvents were evaporated under nitrogen gas, and the residuals were reconstituted with 495 µL MeOH (containing 4% H2O) and 5 µL of IS standard solution.

4.2) Instrumental Analysis

For the LC-MS/MS studies, an Agilent 1290 Infinity II HPLC system fitted with an Ultivo triple quadrupole and an ESI ion source was used. A Zorbax Eclips RRHD column (50 mm x 3.2 mm, 1.8 µm) was used for chromatographic separation, and gradient elution was used to run the column at 40°C. Mobile phases consisted of 4 mM ammonium-hydrogen-carbonate and 0.01% acetic acid (A) and methanol (B). The initial eluent composition was 10% B eluent, which reached 100% in 25 minutes followed by a re-equilibration in 5 minutes. Before injecting the sample into the UHPLC system, the needle was washed in the flush port with acetonitrile/water (50:50, v/v) for 3 s. The total time of one run was 30 min, and 3 µL of the sample was injected on the column with a flow rate of 0.4 mL/min. In the mass spectrometer, nitrogen was used for the collision as well as nebulizing gas (with >99.9999 purity grade, provided by means of a Whatman, Austria, Model 75-72 nitrogen generator). The mass spectrometer was used in dynamic multiple reaction monitoring mode (dMRM), filtering one precursor and two ions of each PFAS. The PFAS were measured in negative ion mode.

4.3) Identification, Quantification, and Quality Assurance

For identification purposes, the ion ratio of the secondary mass transition to the primary mass transition and retention time were recorded for each compound. Criteria of +-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, an internal standard calibration was used. Calibration curves covering concentrations from 0 to 20 ng/ml with 6 points were constructed, with a regression coefficient (r2) greater than 0.99 for all curves. Quality control involved calculating the recoveries of four SUR species in each measured sample.

4.4) Map Construction using QGIS

The maps in this work were generated using QGIS software (3.28.12-1 version), where an IDW interpolation was performed to visualize the estimated impact of PFAS in the surroundings according to each sample. The coordinates of the sampling sites proceeded to be shown using the Google Maps and the Google Roads map services as backgrounds. After that, the interpolation tool, Distance Weighting (IDW), was used. For the IDW Interpolation, the following settings were used: Interpolation: Discrete; Mode: Equal Interval; Classes: 7. These settings were used for all types of PFAS.

5. RESULTS AND DISCUSSION

The maps created in the QGIS software to show the potential contamination spots by PFAS near the Danube River in Budapest can be seen in this section. The table containing the PFAS values used for plotting each of the maps can be found in the appendix of this thesis. First, it is important to visualize the point locations in which the sampling was done. The map containing the sample locations can be seen below:

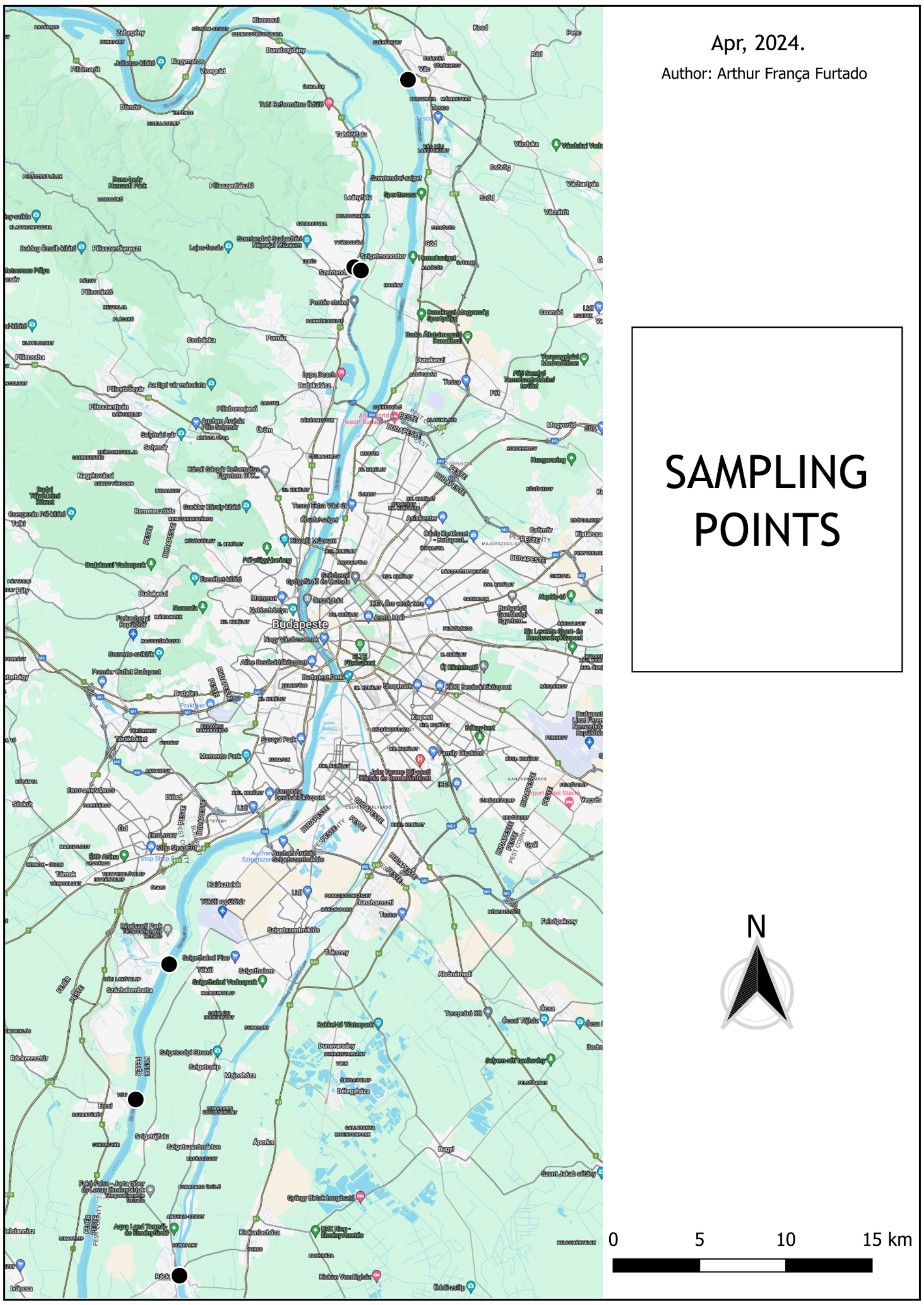


FIG.3) Map containing the location of the sampling points in the Danube river near Budapest. The samples can be visualized as the black circles distributed along the river.

The sample locations visualized in the map above are, respectively from the top down: Danube river region under the direct influence of the center of Vác; Danube river region under the direct influence of the center of Szentendre (2 sampling points); Danube river region under the direct influence of the center of Tököl; Danube river region under the direct influence of the center of Ercsi and the Danube river region under the influence of the center of Ráckeve.

After visualizing the sample locations, it is possible to check the state of every point regarding contamination by PFAS. The PFAS analyzed in this work are, in order: PFBS, PFHxA, HFPO-DA, PFHpA, ADONA, PFHxS, PFOA, PFOS and PFDA. Also, a map containing the distribution of Total PFAS was created in order to visualize the distribution of all of the PFAS.

The IDW Interpolation method was used to identify the range of the impact by contamination from each given sample point according to its concentration value in comparison to the concentration of the other samples measured. In the maps containing the IDW Interpolation, a gradual color gradient was used for better visualization, having discrete characteristics, with seven classes distributed in equal intervals. Basically, the darker the area is, the higher the concentration represented in relation to the other samples. In the same way, the lighter the area is, the lower the concentration represented in relation to the other samples. If a map presents the same color pattern along different sampling points, it means that the concentration of these sample points are similar to each other. The IDW interpolation is relevant here to identify the potential impact of PFAS contamination in a given area where direct measurements were not made, as it allows for the estimation of pollutant concentrations at locations where direct measurements are not available.

Figure 3 contains the first map with IDW Interpolation for PFAS, specifically Perfluorobutane Sulfonic Acid (PFBS) a type of PFAS that has been recognized as a substance of very high concern (SVHC) by the European Chemicals Agency (Health and Environmental Alliance, 2019).

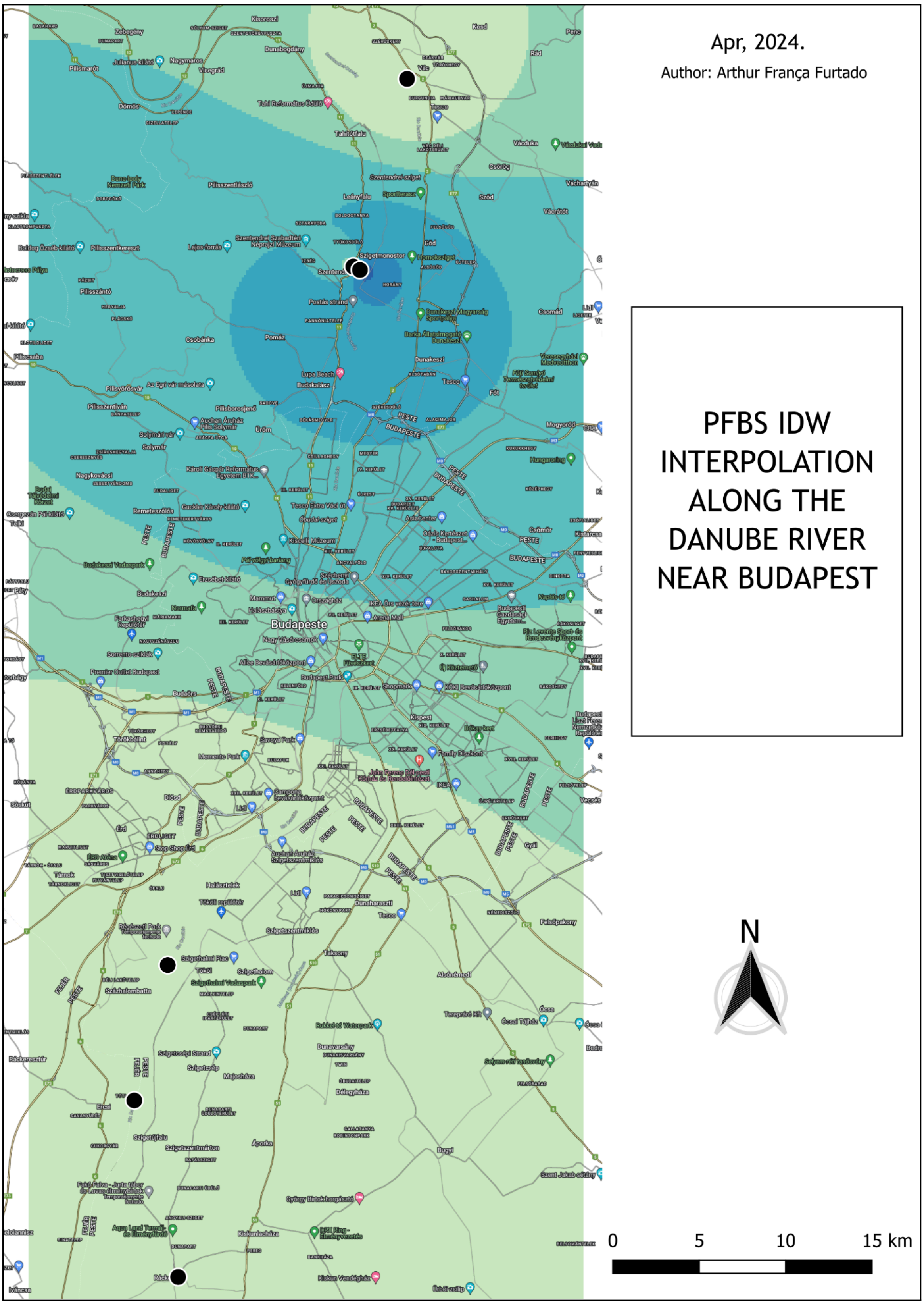


FIG.4) Map containing the IDW Interpolation of PFBS values along the Danube river near Budapest.

As seen in figure 3, the points with higher concentration in the map were located near the center of Szentendre, with the point located more to the east having a bigger effect in the area than the point located on the west. In general, the points located near the center of Vác, Tököl, Ercsi and Ráckeve had similar results, all lower than the values identified in Szentendre, since the color distribution along their points is similar, getting a green lighter tone in comparison to the blue distribution of Szentendre.

Figure 4 shows the IDW Interpolation for Perfluorohexanoic Acid (PFHxA), another type of PFAS that has been recognized as a SVHC by the European Chemicals Agency. PFHxA can also be considered a breakdown product of other PFAS, and it is used as a substitute for longer chain perfluoroalkyl carboxylic acids (PFCAs) in consumer products (Alam et al., 2023; Grgas et al., 2023; Anderson et al., 2019). The distribution in the map shows that the highest values of PFHxA were identified in the southern part of the map, specifically near the center of Ercsi, followed by the points located in Ráckeve and then the points located in Tököl and Vác, all of them having an evident blue color. As opposed to figure 3, the points located near the city of Szentendre had lower values in comparison to the remaining points. The main factors guiding this difference between types of PFAS found in the same location are: a potential different source of contamination, since PFBS and PFHxA may have been originated by different industrial activities or influenced by physico-chemical processes such as volatilization and binding to nearby particles. Also, it is important to consider that some PFAS can degrade into other PFAS, exactly what happens with PFHxA.

Figure 5 shows the IDW Interpolation for Hexafluoropropylene Oxide Dimer Acid (HFPO-DA) also known as GEN-X, another type of PFAS that has been recognized as a SVHC by the European Chemicals Agency. The HFPO-DA can be used as a processing aid for producing fluoro-polymers with many applications, such as fluoropolymer resins, wire cables, and coatings (Mullin et al., 2019; Yang et al., 2022). Figure 5 shows that the biggest concentrations of HFPO-DA were found near the center of Szentendre, just like it was observed with the PFBS interpolation, but this time, both samples contributed almost equally to maintain a strong blue as the main color of the area. Also, the point near Ercsi presented a slightly more intense blue color than the point located near Vác, indicating that the concentration of HFPO-DA was a little bit higher in the first location. The points located near Tököl and Ráckeve presented the lightest colors of the map, indicating that they also presented the lowest concentration of HFPO-DA.

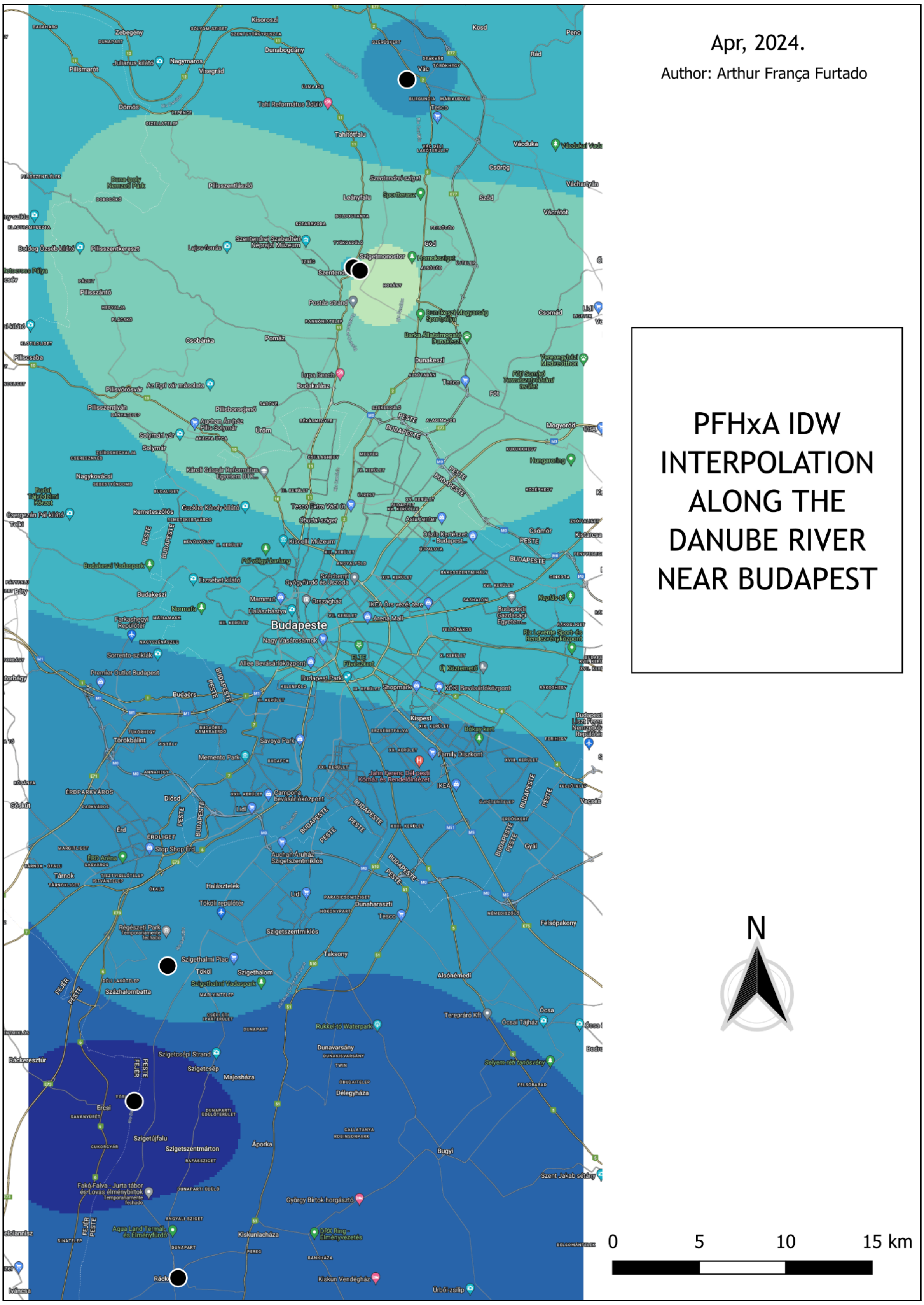
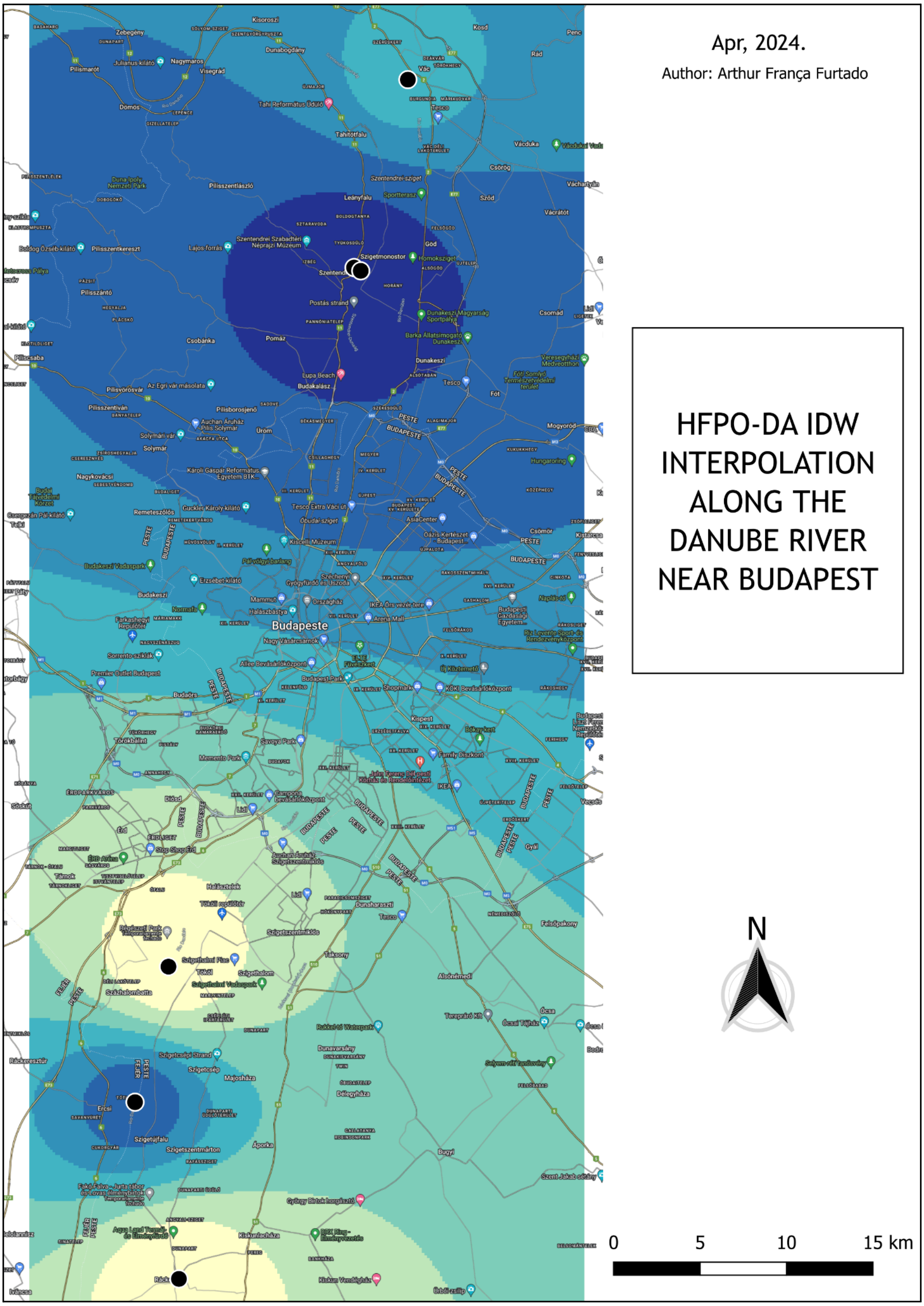


FIG.5) Map containing the IDW Interpolation of PFHxA values along the Danube river near Budapest.



Apr, 2024.

Author: Arthur França Furtado

HFPO-DA IDW INTERPOLATION ALONG THE DANUBE RIVER NEAR BUDAPEST

FIG.6) Map containing the IDW Interpolation of HFPO-DA values along the Danube river near Budapest.

Figure 6 shows the IDW Interpolation for Perfluoroheptanoic Acid (PFHpA) another type of PFAS that has been recognized as a SVHC by the European Chemicals Agency. PFHpA is a byproduct of minor degradation of several long-chain PFAS that have been detected in rain, soil, streams, air, wildlife, and humans worldwide, including in Europe (ECHA, 2022; Weatherly et al., 2023). Figure 6 shows that there was a relatively uniform value between almost all samples, with the only exception being Szentendre, which presented a slightly lower value in the point located in the east, while the point located in the west presented a slightly higher value than all other ones.

Figure 7 shows the IDW Interpolation for dodecafluoro-3H-4,8-dioxanonanoate (ADONA) a type of PFAS that was developed to work as a replacement for PFOA (BVNA, 2018). Figure 7 shows that the point near Vác presented the highest concentration in comparison to the other samples, even though the points near Ercsi and Ráckeve also presented slightly blue colors. The points near Szentendre had a similar behavior, with the exception being the point on the West being slightly blue in color, in comparison to the point in the east, that had a light green color, indicating a lower concentration. The lowest concentration of all points was found near Tököl, whose point had the lightest color in the whole map.

Figure 8 shows the IDW Interpolation for Perfluorohexanesulfonic acid (PFHxS), a fluorinated organic compound with a sulfonic acid functional group and a six-carbon fluorinated chain. It has been used in various industrial applications, including as a surfactant, stain repellent, and fire-fighting foam additive (Zhong et al., 2022). Figure 8 shows that the points near Szentendre presented the highest concentrations, since they had the darkest colors of the map, with the point on the East having a bigger concentration than the point on the West. All the other four points presented a similar scheme of light color, indicating that their concentrations were similar and lower than the concentration values found in the points located in Szentendre.

Figure 9 shows the IDW Interpolation for PFOA, an eight-carbon fluorinated chain with a carboxylic acid functional group. Along with PFOS, PFOA is one of the most detected PFAS in many environments (Wee & Aris, 2023). Figure 9 shows that most of the points had a similar strong blue color. This represents that five (Vác, both of Szentendre, Ercsi and Ráckeve) out of six points had similar concentrations that were higher than the last point (Tököl).

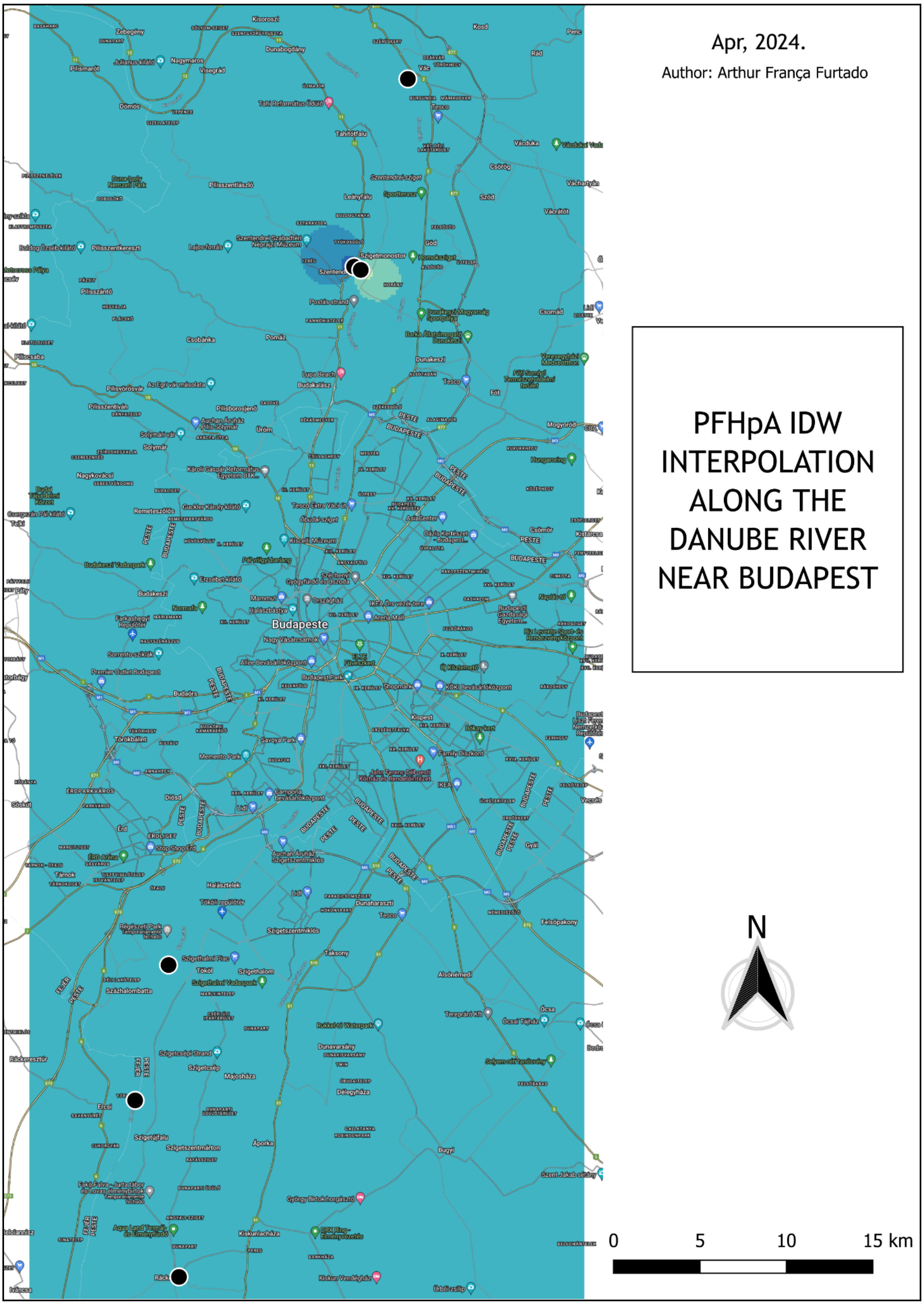


FIG.7) Map containing the IDW Interpolation of PFHpA values along the Danube river near Budapest.

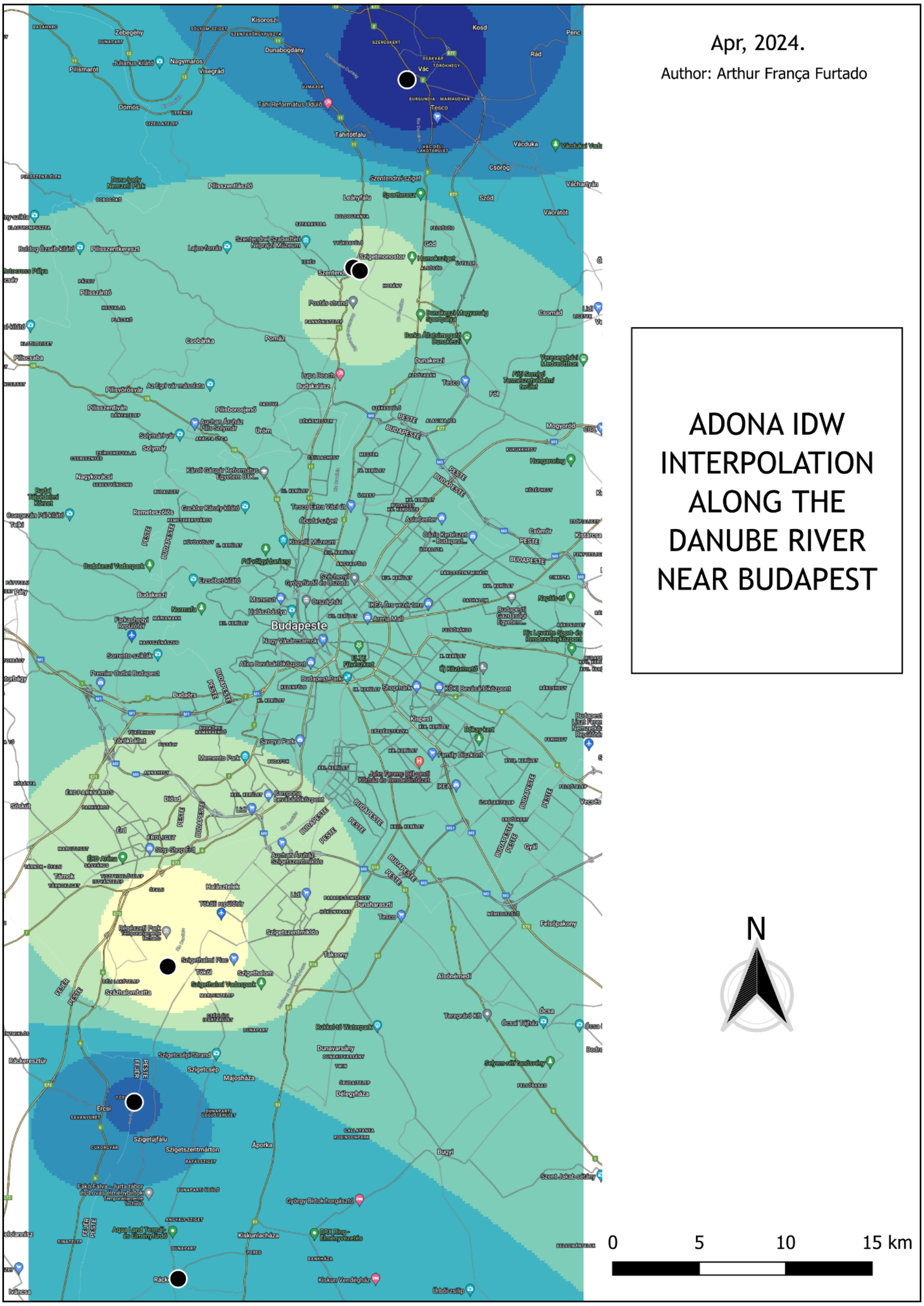


FIG.8) Map containing the IDW Interpolation of ADONA values along the Danube river near Budapest.

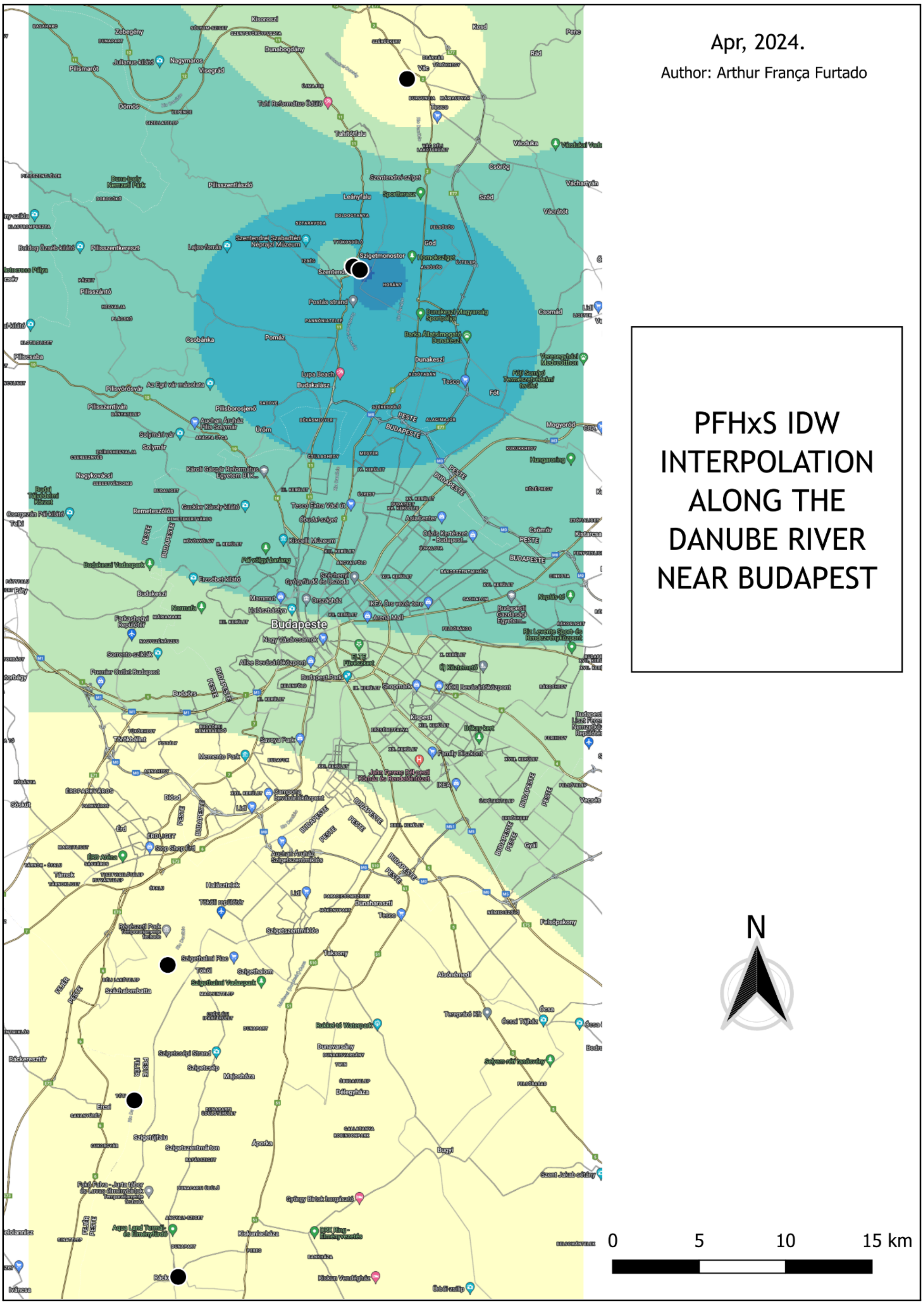


FIG.9) Map containing the IDW Interpolation of PFHxS values along the Danube river near Budapest.

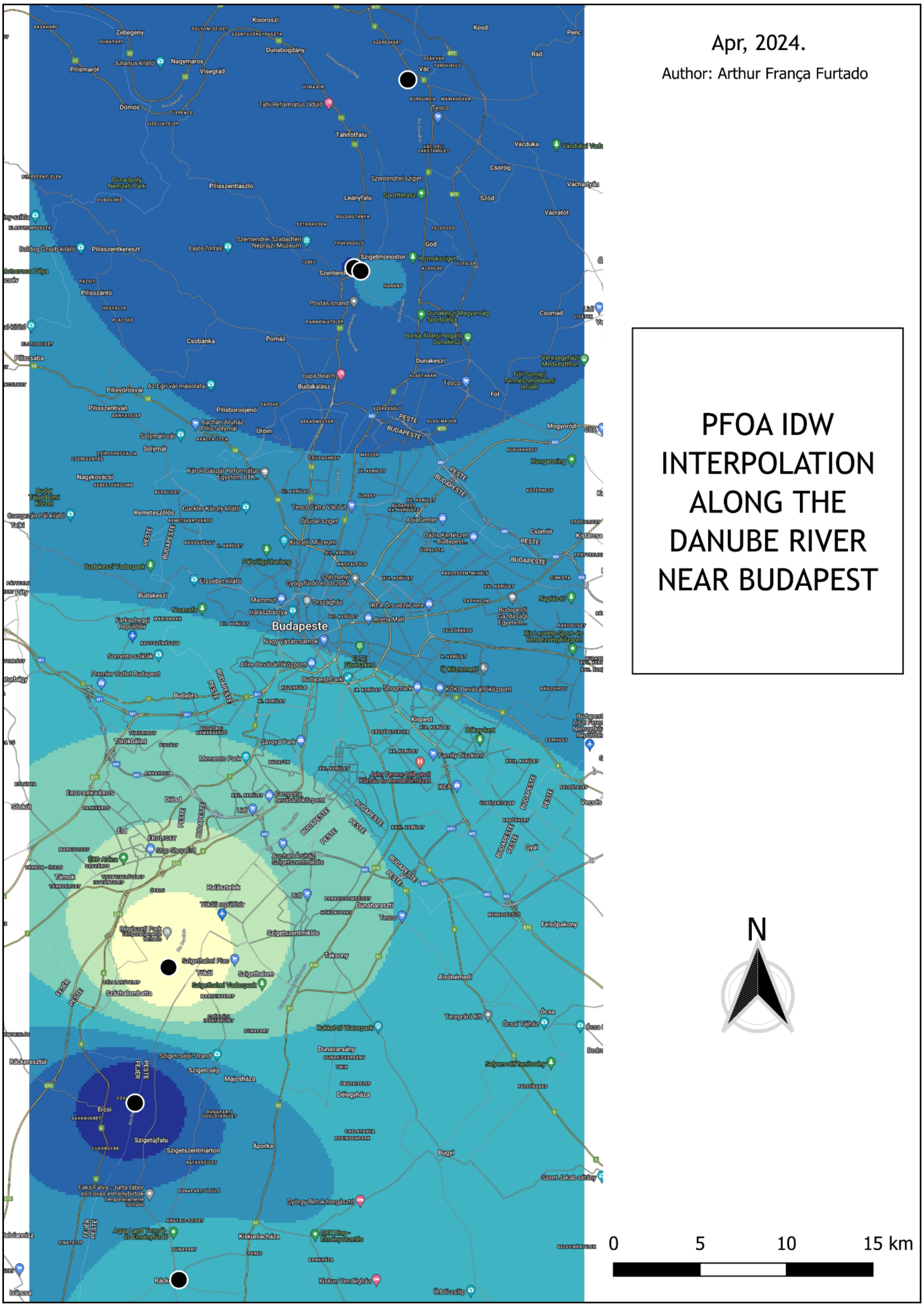


FIG.10) Map containing the IDW Interpolation of PFOA values along the Danube river near Budapest.

Figure 10 shows the IDW Interpolation for PFOS, an eight-carbon fluorinated chain with a sulfonic acid functional group. Figure 10 shows that most of the points had a similar pale light color. This represents that four (Vác, Ercsi, Ráckeve and Tököl) out of six points had similar concentrations that were considerably lower (in this case, zero) than the one found in the points located near Szentendre, specifically the point located on the East.

Figure 11 shows the IDW Interpolation for Perfluorodecanoic acid (PFDA), a molecule with a long carbon chain and a carboxylic acid functional group. Figure 11 shows that the points located in the north (Vác and Szentendre), represented as a blue color, indicating that they had the highest concentrations in comparison with all the other points.

Finally, figure 12 shows the IDW Interpolation for all PFAS sampled and analyzed in this work. Using this figure as a reference, it is possible to identify that the points located in Szentendre had the biggest influence in the map, indicating that the highest concentration between the points were found there. Also, it is possible to see that almost all of the points located in the south (Ercsi, Ráckeve and Tököl) had similar values, with relatively lower concentration than the ones found in Szentendre.

There are some factors that can be responsible for this pattern found in the map, with the higher concentrations of PFAS between the 5 sampling locations being found mainly up to the North of Budapest, near Szentendre. Since Szentendre is the closest point to Budapest, which is a major commercial and industrial center in Hungary, and usually the highest PFAS concentrations are located down-stream of populous cities in the Danube river, such as Budapest (Beggs et al., 2023), the businesses and industries located near Budapest might act as point sources for PFAS contamination. Specifically, some of the industrial zones and parks are located on the outskirts of the city. Key industries in Budapest and nearby regions that could potentially contribute to PFAS contamination are: the automotive industry, the electronics and IT industry, the chemical industry, the manufacturing industry and the logistics industry, since it is possible to find companies such as Audi, IBM, GE, MOL, eXcellence, Industry-Tech Kft and Prologis. Notably, the logistics and industrial sector is experiencing a fast growth in Budapest, with high demands and low vacancy since 2022 (source: BBJ.hu ; assessed on 16 April 2024).

Other than the industrial activity, landfills and waste disposal facilities can often contribute directly to the release of PFAS in the environment. The most common PFAS found in landfills and waste disposal facilities include PFOA and PFOS, along with their precursor compounds (Meegoda et al., 2020). Discarded products that are thrown away, like food packaging, carpet, clothing, and bedding, can leak PFAS into landfills, where rainfall might carry it along with other chemicals, resulting in a concentrated toxic waste that can seep into the ground and surrounding water sources. Since Budapest is a major urban center, there are several waste disposal facilities nearby, managed by Fővárosi Közterület Fenntartó (FKF), the city's public waste management company.

Moreover, wastewater treatment plants/facilities can play an important role in the spread of PFAS into the environment. Just like in the landfills and waste disposal facilities, the most common PFAS found in wastewater treatment plants are PFOS and PFOA (Leenka et al., 2021). These substances can enter wastewater treatment plants through domestic wastewater from households or industrial wastewater from facilities that use PFAS-containing materials in their processes, and even though wastewater treatment plants are designed to treat and remove contaminants, PFAS compounds might be resistant to traditional treatment methods and may pass through the treatment process, leading to their discharge into surface water bodies (Barisci & Suri, 2021).

Secondarily, military bases and the Ferenc Liszt Airport might also be active contributors to PFAS contamination, mostly from training and testing exercises that can employ firefighting foams that often contain PFAS (Pozo et al., 2022).

Lastly, historical pollution, such as past industrial activities, improper waste disposal practices, or accidents may have led to the accumulation of PFAS in the soil and groundwater, which can continue to leach into the surface waters of the Danube river. It is important to note that these are just hypotheses for the potential sources of the PFAS contamination found in this thesis, and the actual sources can be different. Thus, future investigations and studies should be conducted in order to continue the monitoring of PFAS in the environment to protect the water resources and human health and to determine the precise sources of PFAS contamination.

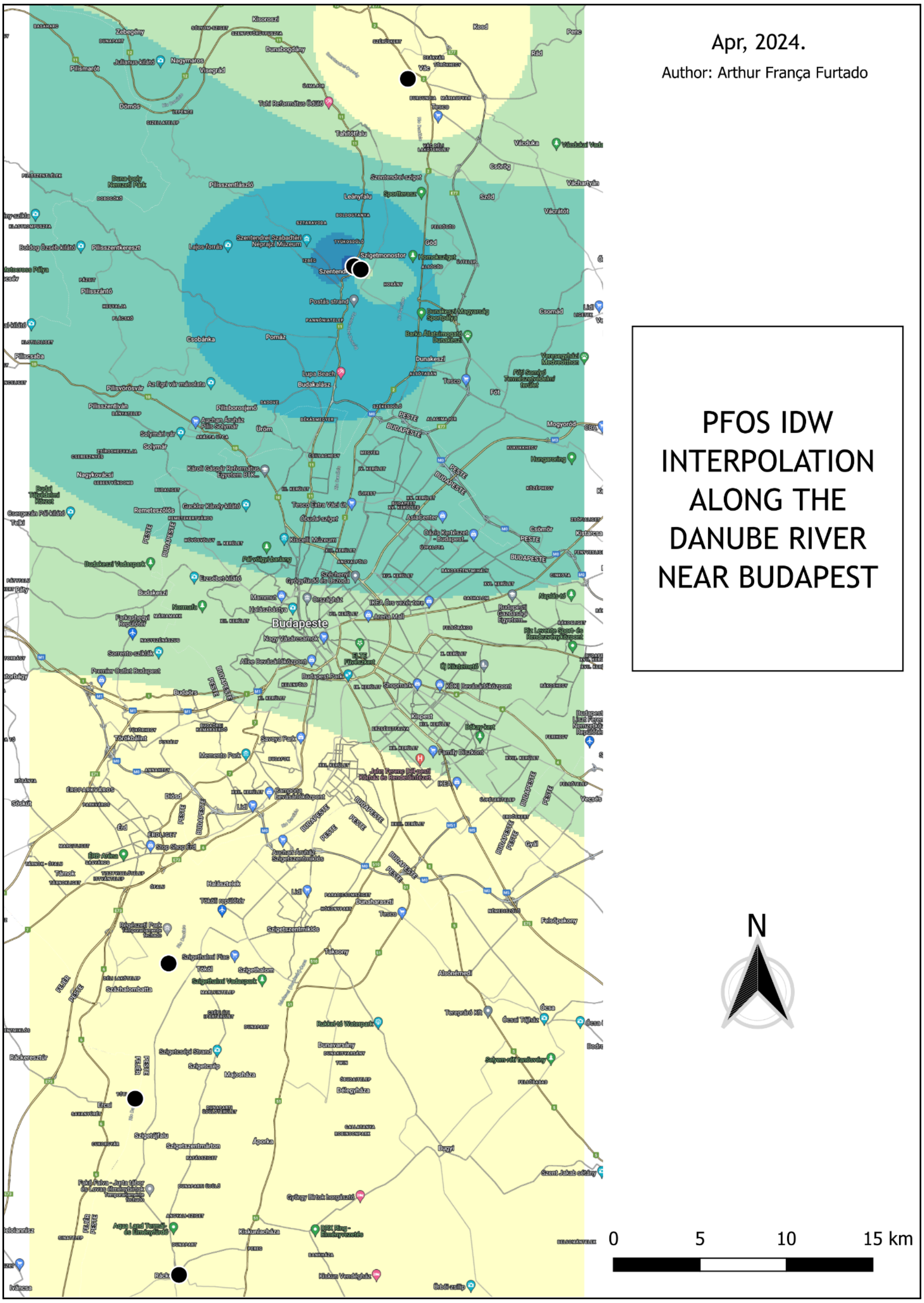


FIG.11) Map containing the IDW Interpolation of PFOS values along the Danube river near Budapest.

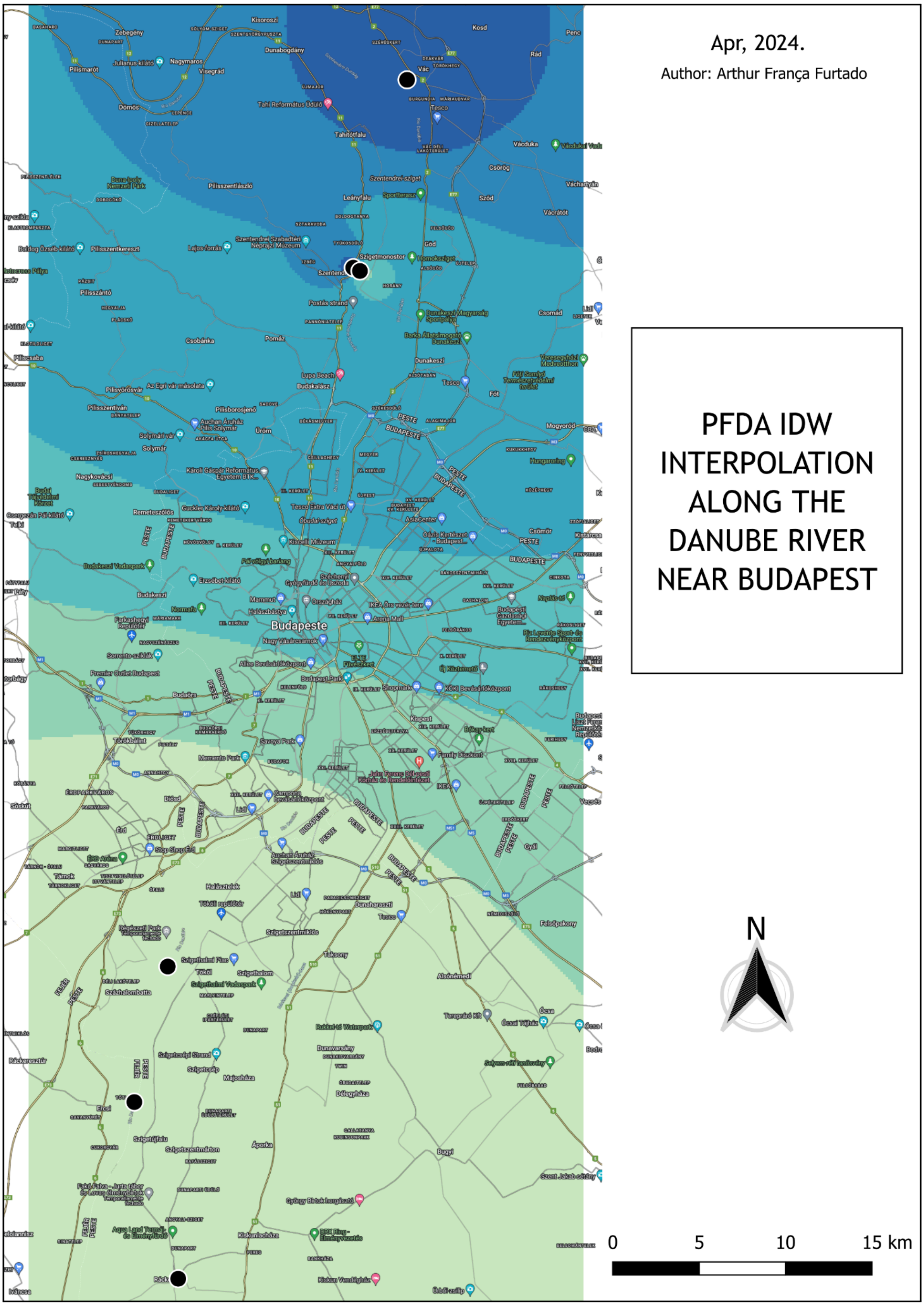


FIG.12) Map containing the IDW Interpolation of PFDA values along the Danube river near Budapest.

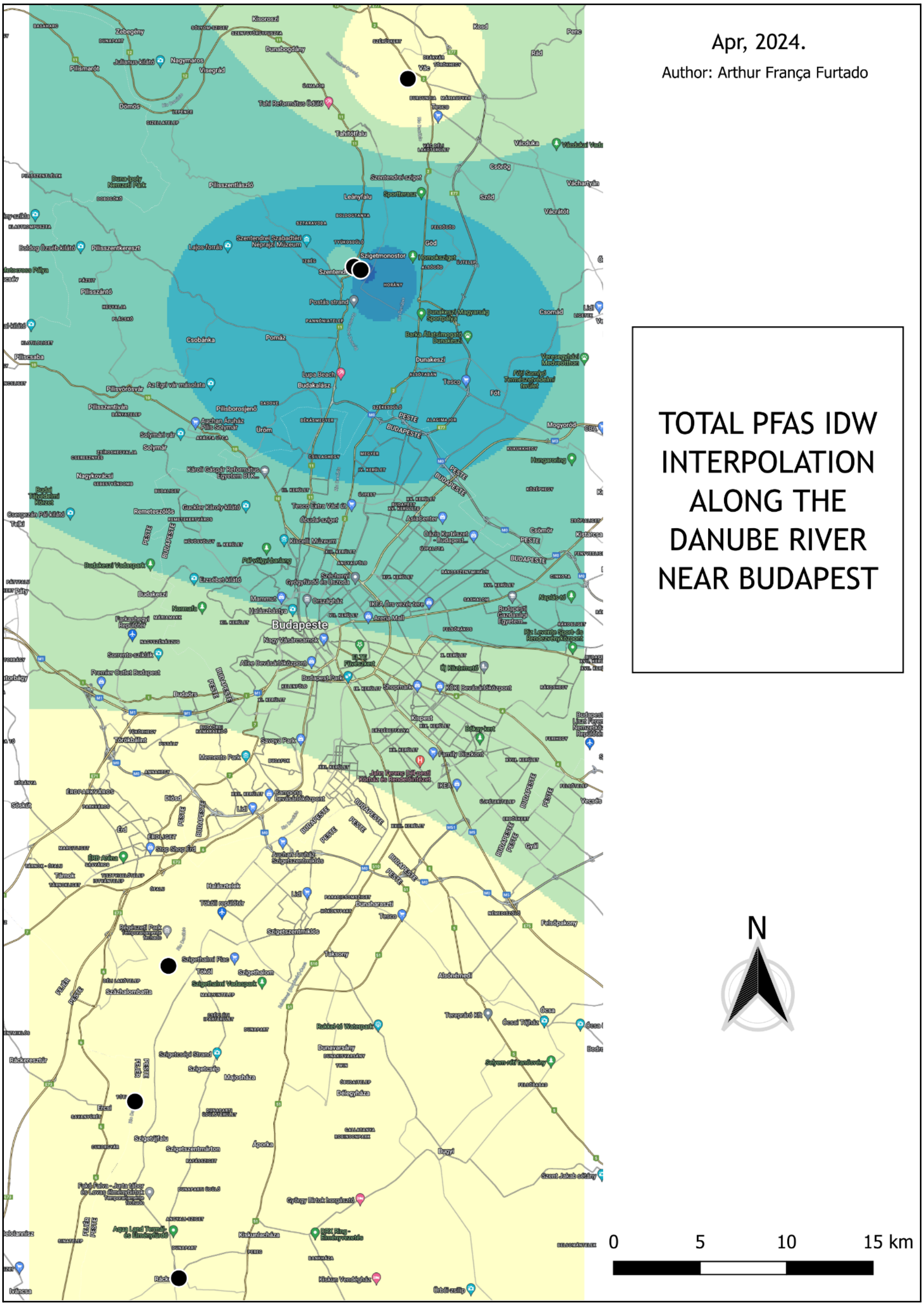


FIG.13) Map containing the IDW Interpolation of Total PFAS values along the Danube river near Budapest.

6. CONCLUSIONS

The present work identified possible contamination spots of PFAS in the surface waters of the Danube River near Budapest, Hungary using maps generated by QGIS software to visualize which locations had the highest concentrations of PFAS in comparison with the data obtained through the instrumental analysis obtained by LC-MS methods. An IDW Interpolation was used inside the QGIS platform to estimate possible values of PFAS concentrations in the areas near the sampling points, generating a map that had a gradient of colors that could represent the biggest to the smallest concentrations in a color scale, from darker to lighter color, respectively.

Through analysis of the content of the maps, it was possible to identify that the points located near Szentendre had the highest concentrations for PFAS in general, while the points located in the South, such as Ercsi, Ráckeve and Tököl had the lowest.

Thus, the results of this work provide an easy way to visualize the actual state of PFAS contamination in the Danube River near Budapest, in order to supply and contribute to the development of strategies for mitigating the impact of PFAS pollution in the area, with the future goal of preserving the water quality in the Danube and contributing to the development of a sustainable approach for protecting water resources and human health.

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8. APPENDIX

Region (Sampling) / PFAS concentration (ng/L)	PFBS	PFHxA	HFPO-DA	PFHpA	ADONA	PFHxS	PFOA	PFOS	PFDA	TOTAL PFAS
Ráckeve	0.18	0.38	0.20	0.17	0.93	0.10	0.49	0	0	2.45
Tökol	0.21	0.37	0.20	0.17	0.84	0	0.47	0	0	2.26
Ercsi	0.19	0.39	0.25	0.17	0.99	0.08	0.51	0	0	2.58
Szentendre (West)	4.66	0.34	0.25	0.16	0.86	1.13	0.49	0	0	7.89
Szentendre (East)	0.16	0.37	0.26	0.18	0.92	0.05	0.51	0.15	0.06	2.66
Vác	0.16	0.37	0.23	0.17	1.04	0.07	0.50	0	0.05	2.59

Table with PFAS concentrations in ng/l, which were used to create the maps and do the IDW Interpolation in the QGIS Software

DECLARATION

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Year of publication: 2024

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