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Testing and demonstration of procedures, methods and knowledge transfer for the advanced and harmonized chemical analysis of new priority HS with very low limits of detection and quantification

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Abstract

European water legislation has recently undergone substantial revision, expanding monitoring obligations for hazardous substances across drinking water, surface waters, groundwater, and wastewater systems. In response to these growing analytical demands—particularly for ultra-trace concentrations of PFAS and selected pharmaceuticals—the Interreg Danube Region Programme project Tethys implemented pilot activities aimed at advancing, harmonizing, and transferring analytical knowledge among laboratories in the Danube River Basin. These activities included two specialized workshops and two rounds of interlaboratory comparison (ILC) studies.

The first workshop (2024) highlighted limited regional readiness for PFAS monitoring, prompting a revised concept for the second workshop (2025), which emphasized hands-on laboratory training, method optimization, and expert exchange. Using a World Café facilitation approach, participants identified the main challenges in method implementation: insufficient funding, limited staff capacity, lack of communication between laboratories and authorities, and the need for better access to practical training and networks.

Two ILC rounds were subsequently organized by the Slovak National Water Reference Laboratory in accordance with ISO 17043. The first round evaluated 25 PFAS compounds and two pharmaceuticals across six laboratories, achieving a 100% success rate for pharmaceuticals but only 61% for PFAS, with long-chain PFAS showing the greatest variability. A second, expanded PFAS-focused round with 15 laboratories demonstrated clear improvement, reaching an average success rate of 77.6%. Across both rounds, the correct use of isotope-labelled internal standards was identified as the single most critical factor for reliable PFAS quantification, while laboratories lacking such standards showed consistent systematic errors and underestimated uncertainties.

Overall, the pilot actions demonstrated that harmonized ultra-trace chemical monitoring in the Danube region depends not only on technical capacity but also on strong professional networks, continuous training, and proficiency testing. The combination of hands-on workshops and interlaboratory comparisons proved highly effective in supporting method development and ensuring progress toward harmonized analytical practices for emerging hazardous substances.

Introduction

European water legislation is undergoing significant transformation. Following the adoption of the new Drinking Water Directive (EU 2020/2184), a revised Urban Wastewater Treatment Directive (EU 2024/3019) has been introduced, and further changes are underway to amend the Water Framework Directive (2000/60/EC), the Groundwater Directive (2006/118/EC), and the Priority Substances Directive (2008/105/EC). A key feature of these updates is their strong interconnection: implementation now requires cross-references and inputs from multiple directives.

This is particularly evident in the management of pollutants, such as Priority Substances. These substances are no longer assessed solely for the chemical status of surface water bodies; they are also considered in risk assessments for drinking water catchments and must be monitored in municipal wastewater—both at the inflow and outflow of treatment plants, as well as in stormwater discharges. The expanded scope of monitoring provides undeniable benefits by improving knowledge of Priority Substances across different water management contexts, thereby enhancing pollution control strategies.

However, this expansion poses major challenges. The number of Priority Substances has increased from 45 to 66, including not only individual compounds but also substance groups, and monitoring must cover diverse matrices. For example, PFAS—a group comprising 24 proposed chemicals—requires monitoring in biota (fish) for chemical status assessment, in whole water if Environmental Quality Standards are exceeded, and at wastewater treatment plants (in influent, effluent, and possibly sludge). Each matrix has distinct physicochemical properties, necessitating the development, verification, or validation of analytical methods. Furthermore, legislation mandates that these methods be accredited or performed under comparable quality management systems. Accreditation under EN ISO/IEC 17025:2017 [1] requires, among other criteria, successful participation in interlaboratory comparison tests, which provide essential insights into method performance, accuracy, and precision, and help identify weaknesses for further optimization.

Implementing new analytical methods into routine laboratory practice is a resource-intensive process, often constrained by limited financial and human capacity. In state laboratories, costs for method development and implementation are typically recognized only during or after the transposition of EU legislation into national law. Financially, new instrumentation is often required, involving budget allocation and lengthy public procurement procedures that can extend over two years. Additional delays arise from sourcing specialized chemicals, reference materials, and consumables. Staffing is equally challenging: laboratories face pressure to minimize costs and personnel, yet new methods demand hiring and training qualified staff. Analytical chemists working in ultra-trace contaminant monitoring must master complex instrumentation and possess deep understanding of the physicochemical principles behind advanced techniques.

Whenever possible, laboratories aim to adopt existing validated standard methods. However, these methods often fail to meet the full scope of legislative requirements in terms of analyte coverage and concentration ranges, necessitating method modification or even development from scratch.

The Interreg Danube Region Programme project Tethys addresses the growing challenge of hazardous pollutants in the Danube River Basin. Activity 1.2—Implementation, Development, and Harmonization of Chemical Analyses for Emerging Hazardous Substances—focuses on improving monitoring of ultra-trace concentrations of Priority Substances. Through pilot actions, we tested and demonstrated procedures and knowledge transfer for enhancing chemical analyses, with emphasis on PFAS and selected pharmaceuticals. To support knowledge dissemination, we organized two workshops and conducted two rounds of interlaboratory comparison tests to explore opportunities for method improvement and harmonization. This document describes procedures, methodological approaches used, results of activities, our findings and observations on pilot activities applied.

Workshops on analytical methods for water monitoring

As part of the pilot actions, the organization of two workshops was carried out. The first workshop was intended to focus on analytical methods in the monitoring of hazardous substances in surface waters. It was also supposed to include discussions and planning for the first round of an interlaboratory comparison (ILC) test, aimed at the analysis of PFAS compounds and pharmaceuticals in water matrices.

The preparation for the workshop began with the collection of contacts from laboratories in the Danube River Basin involved in monitoring hazardous substances. These contacts were obtained from our own sources as well as with the help of all project partners, who provided relevant contacts based on their knowledge of monitoring practices in their respective countries. To prepare a program that would be interesting to the widest possible range of potential participants, invitations were sent to the collected contacts, accompanied by a registration form and a questionnaire. The questionnaire asked potential participants about the analytical methods for hazardous substances they would like to learn more about, offered them the opportunity to present interesting methods they have implemented in their own laboratories, and inquired about their interest in participating in the interlaboratory comparison test for specific analytes. The second part of the questionnaire aimed to gather information on the current state of implementing PFAS analysis methods in water samples, including sampling methods, analytical techniques, method parameters, and other relevant factors, in preparation for the ILC.

Invitations were sent out at the end of June 2024. However, by the end of August, we had received only a few registrations. As a result, we decided to change the originally planned physical workshop format to an online event and sent out revised invitations again. The final number of registered participants was 30. Several of the contacted participants expressed interest in learning more about specific analytical methods and in presenting methods that they have implemented in their laboratories, so we included such presentations in the program. Unfortunately, none of the registered participants expressed interest in presenting their own interesting analytical methods. Eleven laboratories expressed interest in participating in the ILC. The official title of the workshop was Workshop on Analytical Methods for Water Monitoring, which took place on October 1st and 2nd, 2024.

The first day of the workshop focused on current and upcoming legislation as well as analytical methods for the analysis of various priority substances in water samples, including methods for substances on the Watch List for surface waters. The second day of the workshop focused on compounds, sampling methods, and analytical methods for PFAS substances. In addition to experts from the National Reference Laboratory (NRL), experts from TU Wien and CETI also presented monitoring methods for PFAS. The final part of the workshop was dedicated to a discussion with those interested in participating in the ILC, where topics such as ILC preparation, concentration levels, the list of substances, matrix, and sample volume were discussed. The ILC itself was prepared in accordance with the conclusions of this discussion.

Due to the relatively low interest from laboratories in the first workshop, the small number of ILC participants, and communication with potential participants, we decided to change our strategy. We decided to organize a workshop primarily for laboratories that had not yet implemented analytical methods for PFAS analysis. Therefore, we proposed a hands-on workshop with practical demonstrations in the laboratory and individual presentations focused on sharing practical experiences with methods from several experts.

For the workshop we invited speakers from TU Wien, which has many experiences in analyzing wide range of PFAS compounds in various matrices and from CETI, which has recently implemented analytical method for wide range of Priority Substances monitoring in waters including PFAS. At WRI we prepared laboratory sessions on sample preparation for both water and biota matrices. Presentations covered also details on development and optimization of instrument parameters, SPE optimization, calibration, use of internal standards and quality control.

The workshop took place on June 11 and 12, 2025 at WRI Bratislava. In total 32 participants attended the workshop from 14 different institutions (11 EU and 3 non-EU) from 8 countries (5 EU and 3 non—EU), 8 participating institutes were external and 6 were members of the Tethys project consortium. This is rather visible contrast to the first workshop which was attended by 30 experts but mainly because it was organized on-line and waste majority would not attend if travelling to Bratislava was needed.

To explore and better understand the needs of laboratories in implementing new analytical methods, we included a section using the facilitated co-creative method World Café.

Facilitated Co-creation

Facilitation methods allow for gathering opinions from a group of participants, particularly supporting the voices of quieter, more introverted participants whose views might not otherwise be expressed in a typical discussion. We chose the World Café for its organizational simplicity, and it could be completed within approximately 90 minutes, making it suitable as a standalone section of the workshop. During the World Café session, we asked participants the following questions:

1, What are the reasons behind delays in development and implementation of analytical methods for monitoring?

2, What kind of support would help laboratories involved in monitoring to develop and implement analytical methods required by legislation?

3, Regarding this workshop, what can we do better?

Facilitation began by presenting the questions to all participants and explaining the reasons behind them, as well as providing a detailed explanation of the facilitation process itself. It was important that the questions were open-ended and provided sufficient room for discussion. Participants were then divided into three groups, each assigned to a separate table with a sheet of paper for notetaking and a designated scribe (one of the workshop participants). At each table, a specific question was discussed. After settling at their tables, participants were given 3 minutes for silent reflection on the question and possible answers. Once the time was up, they were invited by the facilitator – the organizer of the process – to begin the discussion. The discussion lasted for 15 minutes, and the scribe's task was to impartially record the ideas that emerged during the discussion.

After the 15-minute discussion, the participants moved to the next table, where a new question was addressed. The process at each table followed the same pattern: silent reflection followed by discussion. The ideas generated at each new table were recorded on a new sheet of paper to ensure that the participants in the new group were not influenced by the ideas discussed at the previous table.

After completing the discussions at all three tables, all three sheets of notes were laid out on the tables, and participants were given markers. Each participant was then invited to mark the three best ideas at each table. The facilitator then presented the highest-rated ideas to all participants and led a brief discussion on them. A summary of the responses gathered during the workshop is provided in Table 1.

Based on the responses received, it can be concluded that, for more effective and timelier implementation of newly required analytical methods, securing adequate funding is essential. This includes the ability to hire new experts, acquire analytical instruments, and obtain the necessary chemicals, reference materials, and training. This finding is not new, and aside from recommending that national authorities address this need, the Tethys project cannot contribute much further in this regard.

Much more interesting, however, are the findings related to communication needs. Laboratories report that they would benefit from more communication as part of the support process. Improved communication between laboratories and the state could help clarify what the state expects from testing laboratories and, conversely, what laboratories need to fulfil those expectations. For better methods implementation, laboratories also stressed the importance of information sharing, as well as opportunities for their experts to participate in specialized training, seminars, and workshops focused on analytical instruments and methods. In some cases, laboratories would even require support in method development. Similarly, the need to organize interlaboratory comparison tests—aligned with the requirements of the WFD and its related directives—was highlighted.

Table 1.: Overview of the highest rated answers from the facilitated co-creative part of the workshop (real unedited notes directly taken from the co-creation activity).

1, What are the reasons behind delays in development and implementation of analytical methods for monitoring?	Points recieved
Workshops/trainings for "know-how".	7
Communication and lab-network.	7
Laboratory network (shared experience).	5
Communication (laboratory – government).	5
Money.	5
Limited budget (instruments, new skilled people, routine work management, maintenance).	4
2, What kind of support would help laboratories involved in monitoring to develop and implement analytical methods required by legislation?	
Sharing information between institutions.	10
Exchanging experience.	9
Training for staff for instruments, methods.	9
Governmental support (money for instruments, chemicals…).	7
PT tests.	5
Support for method developing.	4
3, Regarding this workshop, what can we do better?	
Professional networking – contact list of participants, stay in touch.	12
More frequent workshops.	9
More examples in presentations – real problems.	7
After official part, there could be an unofficial small group talk (walk around the city, dinner, drinks).	7
More lab work, practical presentations.	6
Practical problems – problems solving.	6
Hands-on experience – laboratory work.	5
More opportunities for asking questions about other WFD analysis.	4
Meeting colleagues in person.	4

Regarding suggestions for improving workshop quality, participants emphasized the importance of building professional networks and sharing contact information. Experts expressed the need for more workshops, more hands-on exercises, practical demonstrations, and troubleshooting guidance. They also highlighted the importance of supporting communication during workshops through social activities and providing more opportunities for mutual discussion and asking questions.

Overall, participants positively evaluated the workshop and confirmed through their active involvement that the approach based on practical laboratory demonstrations was well chosen. The participation of experts from several relevant institutions with experience in monitoring and analytical method development fostered constructive discussion and effective information exchange. At the request of participants, a contact list was circulated after the seminar. We are confident that this pilot action demonstrated its relevance and proposed a basis for future cooperation among Danube Region countries in the implementation and harmonization of monitoring methods and their results.

Organization of Interlaboratory Comparison Studies

Another part of the pilot action taken was organization of interlaboratory comparison studies. The Slovak National Water Reference Laboratory (SNWRL), a department of the Water Research Institute in Bratislava, is accredited to organize proficiency testing (PT) in accordance with EN ISO/IEC 17043 [2]. PT involves the use of interlaboratory comparison (ILC) for the evaluation of laboratory performance pre-established criteria. These tests consist of measurements or analyses conducted on the same or similar items by two or more laboratories under predefined conditions. PTs serve as an external quality control mechanism and provide a means to verify the analytical performance of laboratories.

The primary objective of PT is to externally assess the competence of laboratories participating in analyzing monitored parameters at the required quality level. This assessment is valuable not only for accredited laboratories but also for non-accredited ones. The results enable participants to confirm the accuracy of their analyses and to identify any deficiencies or errors. Based on these findings, laboratories can validate or enhance their existing quality systems. After implementing appropriate corrective actions, participation in PT contributes to the continuous improvement of laboratory performance.

The scope of PT-1st-round-II/2025 included the analysis of two substance groups:

- **Polyfluoroalkyl substances (PFAS)** group of **25** analytes: PFBA, PFPA (PFPeA), PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFODA, PFBS, PFPS (PFPeS), PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUnS (PFUnDS), PFDoS, PFTrDS, GenX, and ADONA.
- **Pharmaceutical substances (Pharm)**: Carbamazepine and Diclofenac.

The scope of PT-2nd-round-X/2025 included the analysis group of **27** analytes:

- **Polyfluoroalkyl substances (PFAS)**: PFBA, PFPA (PFPeA), PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA (PFUnA), PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFODA, PFBS, PFPS (PFPeS), PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUnDS (PFUnS), PFDoS, PFTrDS, HFPO-DA (GenX), 9Cl-PF3ONS, 11Cl-PF3OUdS and ADONA.

Invitation on participation in the first round of PT (PT-1st-round-II/2025) was distributed on November 26, 2025, to all laboratories which were invited to the first Workshop held in October 2025. Closing date for registration on participation was January 10, 2025. In total 6 laboratories registered for the PT. Invitation on participation in the second round of PT (PT-2nd-round-X/2025) was distributed on July 25, 2025, to all laboratories which were invited to the first or second Workshop. Closing date for registration on participation was September 5, 2025. In total 15 laboratories registered for the second round of PT.

- **In total 6 laboratories registered for the first round of PT:**

  Center for Eco-Toxicological Research Podgorica d.o.o., (Montenegro),
  Croatian Institute of Public Health, Department for Water Safety and Supply (Croatia),
  Masaryk University, Faculty of Science (Czech Republic),

State Geological Institute of Dionýz Štúr, (Slovakia),
Technical University Wien, Institute of Water Quality and Resource Management (Austria),
Water Company Inc., Bratislava (Slovakia).

- **In total 15 laboratories registered for the second round of PT:**

ALS, Inc., (Czech Republic),
Balint Analitika Kft. (Hungary),
Bavarian Environment Agency (Germany),
BAZVKH NFO, (Hungary),
Center for Eco-Toxicological Research Podgorica d.o.o., (Montenegro),
Institute for Water (Bosnia and Herzegovina),
National Laboratory of Health, Environment and Food (Slovenia),
PVKH KTHF KM, (Hungary),
Serbian Environmental Protection Agency (Serbia),
Slovak National Water Reference Laboratory (Slovakia),
State Geological Institute of Dionýz Štúr, (Slovakia),
Technical University Wien, Institute of Water Quality and Resource Management (Austria),
The Morava River Basin, s. e. (Czech Republic),
Water Company Inc., Bratislava (Slovakia),
Western Slovak Water Company Inc., (Slovakia).

Of the organizations involved in the ILC, 5 were internal to the Tethys project (4 project partners and 1 associated strategic partner) and 12 were external; 3 were from non-EU countries and 14 from EU countries

Preparation of samples

For preparation of PFAS enriched surface water samples we have tested several different sources of surface water, but we did not find any source free of PFAS contamination. Therefore, we chose water from the Lake Draždiak in Bratislava which has the lowest PFAS contamination, stable characteristics and minimal sediment—factors that could interfere with sample stability. The natural surface water used for the PFAS-enriched sample was collected a few days before sample preparation.

Commercially available certified reference materials (CRMs) were used for the preparation of both samples, the PFAS-enriched natural water samples and the model samples for pharmaceutical substances. Solutions of CRMs were prepared in analytically pure methanol. Solutions were homogenized using an ultrasonic bath and then dispensed into 2 ml glass vials.

For the first round of PT PFAS samples were prepared on February 14, 2025, and the Pharm samples on February 12, 2025, for the second round of PT PFAS samples were prepared on September 29, 2025. All samples were stored in accordance with the requirements of standard [3], refrigerated at the central sample reception facility of the SNWRL until distribution.

Participants outside Slovakia received samples by courier service. Upon receipt, PT participants were instructed to handle and analyze the samples according to the provided PT guidelines.

Pharmaceutical Substances (Pharm):

Each participant received one polyethylene (PE) bottle containing approximately 100 ml of pure laboratory water and 2 ml vial containing mixture solution of CRMs in methanol for sample spiking. Participants were instructed to prepare the 2 test samples, the first should be by spiking the received pure laboratory water and for the second sample participants were requested to spike laboratory pure water from their own laboratory. The solution was required to be diluted with pure laboratory water sent from SNWRL for (Sample A) and laboratory water from the participants own laboratory (Sample B) in a ratio of 1:1000.

Sample A: The provided 100 ml pure laboratory water sample intended for pharmaceutical analysis.

Sample B: Pure laboratory water from the participant's own laboratory (e.g., high-purity water).

Polyfluoroalkyl Substances (PFAS):

Each participant received two 1000 ml PE bottles containing surface water and the 2 ml vial with fortification solution (mixture solution of certified reference materials in methanol). The solution was required to be diluted with received surface water water in a ratio of 1:2500. The concentration of PFAS in the fortified surface water samples exceeded 10 ng/L for each compound. Samples prepared under these conditions were to be analyzed immediately after preparation. The results were not to be corrected for the volume of water added during dilution.

Instructions for PT

Instructions for sample processing and a reporting sheet for submission of PT results were included in the shipment. Participants were required to analyze samples between February 24 and 28, 2025 for the first round and between 13 and 17 October 2025 for the second round of ICL. In both rounds immediately after opening the containers, applying the standard procedures routinely applied in their laboratories.

Sample stability was tested in accordance with SNWRL's internal procedure "PSS/VŠ-ŠOP/3," based on standard [4]. Stability was monitored for all parameters, and the results confirmed that all monitored substances remained stable throughout the PT testing period.

PFAS sample stability was monitored from February 17 to March 5, 2025, while Pharm sample stability was assessed on February 25, March 3, and March 6 — within the designated testing window for the first round of PT.

PFAS sample stability was monitored from October 13 to October 22, 2025 — within the designated testing window for the second round of PT.

Whole documentation related to sample preparation, control analyses, and stability testing is archived at the SNWRL repository.

Evaluation of interlaboratory comparison tests

Statistical processing of results

Each laboratory participating in the proficiency testing (PT) at SNWRL is assigned two identifiers: a registration number and an identification code. The registration number is a permanent, unique code that remains constant for the laboratory for any PT organized. The identification code is randomly generated for each PT round to ensure anonymity during result evaluation.

The results submitted by participants were statistically processed in accordance with the standard STN ISO 5725-1 [5]. To detect extreme or outlier values, the Hampel test [6] was applied.

The results were summarized in tables and charts (results excluded from calculation of statistical characteristics according with ISO 13528 [7]).

The test statistic for the Hampel test was in the following form:

$$\hat{H}_i = \frac{|x_i - \tilde{x}|}{5{,}06\mathrm{MAD}}$$

$|x_i - \tilde{x}|$ represents the corresponding absolute median difference, while the MAD (Median Absolute Deviation) is the median of the median differences.

This test uses the median absolute deviation (MAD) to identify values that deviate significantly from the median. A test statistic greater than 1 indicates an outlier with a 95% confidence level. All statistical evaluations were conducted using a significance level of $\alpha = 0.05$. Outlier results identified by the Hampel test were excluded from the final dataset.

Tables 2A present the identification codes of participants whose results were classified as outliers for specific parameters in the first round of the PT, in the given order. Tables 2B present the identification codes of participants whose results were classified as outliers for specific parameters in the second round of the PT. For parameters with four or fewer reporting participants, outlier analysis was not performed in the first round PT. The results from the PT organizer were also included in the evaluation.

Table 2A: ID code of participant with outliers results by Hampel test “H” and capability index coefficient “ks” for the 1st PT round.

Parameters	ID of Participant outlier by “H”	ID of Participant outlier by “ks”
PFBA	2	2
PFBS	2 ,5	2, 5
PFDA	_	2, 5
PFDoDA	_	2
PFDoS	_	2, 4
PFDS	_	2
PFHpA	2	2
PFHpS	_	2
PFHxA	2	2
PFHxS	_	2
PFNA	2	2
PFNS	_	2
PFOA	2	2
PFODA	_	4
PFOS	_	2, 5
PFPA	_	2, 5
PFPS	_	2
PFTrDA	_	2
PFTrDS	_	4
PFUnDA	_	2
PFUnDS	_	2, 4

Table 2B: ID code of participant with outliers results by Hampel test "H" and capability index coefficient "ks" for the 1st PT round.

Parameters	ID of Participant outlier by "H"	ID of Participant outlier by "ks"
ADONA	14	14
PFBA	_	8
PFBS	1, 8, 11	1, 8, 11
PFDA	8, 14	8, 11, 14
PFDoDA	14	8, 10, 14
PFDoS	_	2, 6, 7, 8, 15
PFDS	8	2, 8
PFHpA	8	8
PFHpS	8	8, 10
PFHxA	8, 10	8, 10
PFHxDA	_	3
PFHxS	8, 14	7, 8, 11, 14
PFNA	_	8, 14
PFNS	8	8
PFOA	8	8
PFODA	3	3
PFOS	8	8
PFPA	_	2
PFPS	8	8
PFTrDA	_	8, 10
PFTrDS	_	3, 4, 9
PFUnDA	14	8, 14
PFUnDS	_	5, 6, 7, 8, 10, 15

An overview of the dataset—both before and after the elimination of outliers — for the first round of PT is provided in Table 4A and Table 4B, for the second round in the Table 4C are included both datasets. These Tables include the lower and upper limits of acceptable results, which define the interval for satisfactory performance.

The graphical outputs from the second PT round are presented in a different format compared to the first round due to the use of the new R.OBUSTAT program, which was implemented in June 2025 for evaluating data obtained in proficiency tests organized by SNWRL.

The performance of each laboratory for individual parameters for 1st round PT is visually represented in z-score charts in Figures 1 to 5 for the first round and in Figures 8 to 34 for the second round.

The z-score charts illustrate each laboratory's performance relative to the reference value and other participants. The z-score is calculated using the formula:

$$z = \frac{x_i - X}{\sigma}$$

Where:
x_i is the participant's measured value,
X is the reference value,
σ is the standard deviation derived from the interlaboratory comparison.
The standard deviation σ is calculated using the capability index coefficient *ks* and the reference value X:

$$\sigma = 0.5 * ks * X$$

According to standards [5] and [7], z-scores are interpreted as follows:

Satisfactory: $|z| \leq 2{,}0$

Questionable: $2{,}0 < |z| < 3{,}0$

Unsatisfactory: $|z| \geq 3$

Reference value criteria and Uncertainty Estimation

For the pharmaceutical (Pharm) samples, the reference values were based on the certified values of the reference materials (CRMs) used. For the PFAS samples, due to the presence of background contamination in the enriched natural surface water, the reference values were determined as the average concentrations measured during the stability testing phase. The uncertainty of the robust average (U) was calculated in accordance with ISO 13528 [7].

The assigned reference values for PFAS for first round PT are summarized in Table 3A. Table 3B presented the assigned reference values for PFAS for second round of PT. These include spiked concentrations, background levels, and the final average concentrations used as reference values.

The capability index (ks) used in the PT ranged from 0.3 to 0.5 of the reference value. The expanded uncertainties of the reference values (X) were calculated by combining the uncertainty of the CRMs with uncertainties arising from sample preparation processes (e.g., weighing, dilution).

The assessment criteria for each group of substances were defined as follows:

- Pharm: ±30% of the reference value (based on expert estimation)
- PFAS: ±40% of the reference value the 1st PT round and ±50% of the reference value the the 2nd PT round (based on chapter 16, DIN 38407-42:2011-03 [8]).

These criteria are consistent with commonly accepted standards for PT in the field of organic trace analysis.

Table 3A: Determination of assigned reference values for the 1st PT round.

PFAS parameters	Concentration ng/L		
	Spike	Background	"X" Reference value
PFBA	60	4,43	61,4
PFPA, (PFPeA)	60	<1,00	57,2
PFHxA	60	1,11	57,6
PFHpA	60	<1,00	57,5
PFOA	60	6,90	58,2
PFNA	60	<1,00	53,1
PFDA	60	<1,00	54,7
PFUnDA	60	<1,00	58,2
PFDoDA	60	<1,00	55,8
PFTrDA	60	<1,00	61,5
PFTeDA	60	<1,00	60,4
PFHxDA	80	<1,00	83,8
PFODA	80	<1,00	81,5
PFBS	53	2,52	57,2
PFPS, (PFPeS)	84,6	<1,00	90,1
PFHxS	57	<1,00	61,8
PFHpS	57	<1,00	56,1
PFOS	58	<1,00	58,8
PFNS	67,34	<1,00	66,9
PFDS	55	<1,00	58,1
PFUnS, (PFUnDS)	72,6	<1,00	77,2
PFDoS	48,5	<1,00	47,9
PFTrDS	48,6	<1,00	47,8
GenX	80	2,37	64,4
ADONA	37,84	<1,00	29,1

Table 3B: Determination of assigned reference values for the 2nd PT round.

PFAS parameters	Concentration ng/L		
	Spike	Background	"X" Reference value
PFBA	24	4,95	28,95
PFPA, (PFPeA)	24	<1,00	24,00
PFHxA	24	<1,00	24,00
PFHpA	24	<1,00	24,00
PFOA	24	7,92	31,92
PFNA	24	<1,00	24,00
PFDA	24	<1,00	24,00
PFUnDA	24	<1,00	24,00
PFDoDA	24	<1,00	24,00
PFTrDA	24	<1,00	24,00
PFBS	28,32	2,69	31,01
PFPS, (PFPeS)	37,6	<1,00	37,60
PFHxS	30,4	<1,00	30,40
PFHpS	49,64	<1,00	49,64
PFOS	30,72	<1,00	30,72
PFNS	33,67	<1,00	33,67
PFDS	30,88	<1,00	30,88
PFUnS, (PFUnDS)	43,56	<1,00	43,56
PFDoS	29,1	<1,00	29,10
PFTrDS	38,88	<1,00	38,88
PFTeDA	24	<1,00	24,00
PFHxDA	30	<1,00	30,00
PFODA	35	<1,00	35,00
HFPO-DA	64	<1,00	64,00
9Cl-PF3ONS	24	<1,00	24,00
11Cl-PF3OUdS	24	<1,00	24,00
ADONA	41,6	<1,00	41,60

Table 4A provides an overview of success rates and recovery percentages for each evaluated parameter for the first round of the PT. Table 4B presents the results after excluding outliers identified using by the Hampel test for first round PT. Table 4C summarizes success rates and recovery percentages for each evaluated parameter in the second round of the PT, including values after excluding outliers identified by the Hampel test.

The individual laboratory results, including measured values, reference values, z-scores, and recovery rates, are detailed in the annexes of this report.

Table 4A: Statistical parameters of file and limits of satisfactory values for the 1st PT round.

Parameters	n	X [ng/L]	U_X [ng/L]	x_p [ng/ L]	s_R [ng/L]	LL [ng/L]	UL [ng/L]	R [%]	S [%]
Pharm									
Carbamazepine A	3	205	0,70	229	30,7	144	267	112	100
Carbamazepine B	3	205	0,70	233	24,8	144	267	114	100
Diclofenac A	3	260	0,78	265	10,1	182	338	102	100
Diclofenac B	3	260	0,78	269	8,2	182	338	103	100
PFAS									
PFBA	4	61,4	3,07	36,7	22,5	36,8	85,9	60	75
PFPA, (PFPeA)	5	57,2	2,86	35,5	23,3	34,3	80,0	62	60
PFHxA	4	57,6	2,88	42,8	21,4	34,5	80,6	74	75
PFHpA	4	57,5	2,88	42,4	18,8	34,5	80,6	74	75
PFOA	4	58,2	2,91	46,3	19,7	34,9	81,5	80	75
PFNA	4	53,1	2,66	48,7	20,6	31,9	74,4	92	75
PFDA	5	54,7	2,74	40,2	26,4	32,8	76,6	73	60
PFUnDA	4	58,2	2,91	52,3	23,3	34,9	81,5	90	75
PFDoDA	4	56,4	2,82	53,1	31,2	33,9	79,0	94	50
PFTrDA	3	61,5	3,08	38,8	22,4	36,9	86,1	63	33
PFTeDA	3	60,4	3,02	52,2	13,0	36,3	84,6	86	100
PFHxDA	1	83,8	4,19	111	-	50,3	117	132	100
PFODA	1	81,5	4,08	192	-	48,9	114	236	0
PFBS	5	57,2	2,86	44,9	21,2	34,3	80,1	78	60
PFPS, (PFPeS)	3	90,1	4,51	67,8	40,9	54,0	126	75	67
PFHxS	5	61,8	3,09	53,3	22,0	37,1	86,5	86	80
PFHpS	4	56,1	2,81	50,8	22,6	33,6	78,5	91	75
PFOS	5	58,8	2,94	44,6	19,7	35,3	82,3	76	60
PFNS	2	66,9	3,35	39,1	18,8	40,1	93,6	58	50
PFDS	3	58,1	2,91	47,7	30,0	34,9	81,4	82	67
PFUnS, (PFUnDS)	2	77,2	3,86	25,4	13,9	46,3	108	33	0
PFDoS	2	47,9	2,40	15,9	5,7	28,8	67,1	33	0
PFTrDS	1	48,4	2,42	24,1	-	29,0	67,7	50	0
GenX	1	65,4	3,27	72,9	-	39,3	91,6	111	100
ADONA	1	29,7	1,49	33,0	-	17,8	41,6	111	100

n - number of laboratories, X - reference value, U_X - combined relative standard uncertainty of reference value (k=2), x_p - average value, s_R - standard deviation of reproducibility, LL - lower limit of satisfactory results, UL - upper limit of satisfactory results, R – recovery, S - rate of success (according to the ks)

Table 4B: Statistical parameters of file and limits of satisfactory values without outlier results for the 1st PT round.

Parameters	n	X [ng/l]	U_X [ng/l]	x_p [ng/l	s_R [ng/l]	LL [ng/l]	UL [ng/l]	R [%]
PFAS								
PFBA	3	61,4	3,07	48,0	1,98	36,8	85,9	75
PFHxA	3	57,6	2,88	53,4	3,48	34,5	80,6	93
PFHpA	3	57,5	2,88	51,4	6,44	34,5	80,6	89
PFOA	3	58,2	2,91	55,7	6,97	34,9	81,5	96
PFNA	3	53,1	2,66	58,3	8,96	31,9	74,4	110
PFBS	3	57,2	2,86	59,9	4,14	34,3	80,1	105

n = number of laboratories without outliers, x_p = average value without outliers, s_R = standard deviation of reproducibility, LL = lower limit of satisfactory results, UL = upper limit of satisfactory results, X = reference value, U_X = combined relative standard uncertainty of reference value (k=2) R = recovery without outliers

Table 4C: Statistical parameters of file and limits of satisfactory values for the 2nd PT round.

Parameters	n	x_p [ng/ L]	min [ng/ L]	max [ng/ L]	n*	x_{p^*} [ng/ L]	s_R [ng/L]	X [ng/L]	U_X [ng/L]	LL [ng/L]	UL [ng/L]	R [%]	S [%]
11Cl-PF3OUdS	5	18,12	12,80	26,00	5	18,12	5,38	24,00	1,20	12,00	36,00	75,5	100
9Cl-PF3ONS	5	22,27	17,30	29,00	5	22,27	4,22	24,00	1,20	12,00	36,00	92,8	100
ADONA	8	36,29	14,00	52,00	7	37,43	10,70	41,60	2,09	20,80	62,40	89,97	87,5
HFPO-DA	6	60,28	43,80	78,00	6	60,28	11,64	64,00	3,21	32,00	96,00	94,2	100
PFBA	12	31,44	15,00	51,70	12	31,42	7,62	28,95	1,45	14,47	43,42	109	91,7
PFBS	14	32,66	9,46	85,50	11	32,34	14,13	31,01	1,55	15,51	46,52	104	78,6
PFDA	13	27,59	10,00	60,70	11	25,46	12,97	24,00	1,20	12,00	36,00	106	76,9
PFDoDA	13	30,24	15,10	62,00	12	28,53	13,16	24,00	1,20	12,00	36,00	119	76,9
PFDoS	10	38,73	9,00	78,10	10	38,62	20,63	29,10	1,46	14,55	43,65	133	50,0
PFDS	12	32,50	10,00	78,00	11	30,61	17,34	30,88	1,55	15,44	46,32	99,1	83,3
PFHpA	12	26,84	18,20	66,80	11	25,07	9,94	24,00	1,20	12,00	36,00	105	91,7
PFHpS	12	54,94	37,40	95,00	11	52,62	15,88	49,64	2,48	24,82	74,46	106	83,3
PFHxA	12	28,39	19,50	60,50	10	26,57	9,32	24,00	1,20	12,00	36,00	111	83,3
PFHxDA	6	27,83	15,60	48,00	6	27,43	11,47	30,00	1,51	15,00	45,00	91,4	83,3
PFHxS	15	42,20	26,60	91,20	13	39,19	15,67	30,40	1,52	15,20	45,60	129	73,3
PFNA	12	29,11	19,20	65,60	12	26,63	11,79	24,00	1,20	12,00	36,00	111	83,3
PFNS	11	30,56	17,00	80,40	10	27,77	15,49	33,67	1,69	16,84	50,51	82,5	90,9
PFOA	13	34,14	23,90	65,20	12	33,14	9,02	31,92	1,60	15,96	47,88	104	92,3
PFODA	5	41,86	23,40	93,00	4	41,86	27,68	35,00	1,76	17,50	52,50	120	80,0
PFOS	15	33,09	18,49	90,40	14	31,04	13,55	30,72	1,54	15,36	46,08	101	93,3
PFPA	12	25,11	11,00	36,40	12	25,59	6,25	24,00	1,20	12,00	36,00	107	91,7
PFPS	12	37,92	28,00	81,60	11	36,05	10,83	37,60	1,89	18,80	56,40	95,9	91,7
PFTeDA	8	22,94	17,70	33,00	8	22,73	5,23	24,00	1,20	12,00	36,00	94,7	100
PFTrDA	11	28,14	14,93	63,60	11	27,06	11,74	24,00	1,20	12,00	36,00	113	81,8
PFTrDS	10	30,27	12,90	62,40	10	30,01	15,57	38,88	1,96	19,44	58,32	77,2	70,0
PFUnDA	13	30,88	14,80	84,00	12	26,98	17,41	24,00	1,20	12,00	36,00	112	84,6
PFUnDS	10	60,27	17,60	102,0	10	60,27	28,85	43,56	2,19	21,78	65,34	138	40,0

n- number of participants; xp - average measured value; min – minimal value of data set; max - maximum value of data set; n*- number of participants - outliers removed; xp* - robust estimate of the participants mean; sR - standard deviation of reproducibility; X - reference value; UX - expanded uncertainty; LL - lower limit of acceptable results; UL - upper limit of acceptable results; R - recovery as a percentage of the reference value; S - Success rate based on the assessment criterion (ks)

Extended uncertainties of measurements for Pharm were reported by 2 out of 3 participating laboratories, and extended uncertainties for PFAS were reported by 4 out of 5 laboratories for the 1st PT round. One laboratory submitted uncertainty in "%", while the other laboratories expressed uncertainty in the required units in "ng/l". In the annex of this report, there is Figures 6 (Pharm) and Figures 7 (PFAS) of extended uncertainties reported (average, minimum and maximum values) for individual parameter for the 1st PT round.

Extended uncertainties of measurements for PFAS were reported by 13 out of 15 laboratories for the 2nd PT round is overview. Four laboratory submitted uncertainty in "%", while the other laboratories expressed uncertainty in the required units in "ng/l". In the appendix of this report, there is a chart overview of the range of uncertainties reported (average, minimum and maximum values) for individual parameters in Figure 35.

Analytical methods

Overview of existing standard methods and methods used by participating laboratories in the 1st PT round is presented in Table 5A. Overview of existing standard methods and methods used by participating laboratories in the 2nd PT round is presented in Table 5B. Methods are presents as their description was reported by participating laboratories.

Table 5A: List of analytical methods for the 1st PT round.

Code number for used analytical method	Number of participants utilizing the method per group of substances	
	PFAS	Pharm
50 - DIN 38407-42:2011-03 German standard methods for the examination of water, wastewater and sludge - Jointly determinable substances (group F) - Part 42: Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42) [8]	1	0
20 - EN 17892:2024 Water quality — Determination of selected per- and polyfluoroalkyl substances in drinking water — Method using liquid chromatography/tandem-mass spectrometry (LC-MS/MS) [9]	1	0
60 - other method	3	3

Overview of other (different methodologies) analytical methods applied by participants for the 1st PT round:

ID 1: 60 - other method (PFAS, Pharm)
For preparation of water samples for analysis of PFAS and pharmaceutical substances is used Biotage Horizon 5000 Automated Disk Extraction System. Disk-based solid-phase extraction, utilizes a porous disk medium-HLB disk to capture analytes as water flows through it. For conditioning of SPE disk and extraction of analytes is used methanol and ethyl acetate. For analysis, isotope-labelled internal standards are used. Chromatographic separation and detection was done by LCMS/MS 6475, Agilent.

ID 3: 60 - other method (PFAS, Pharm)
Extraction

Water samples (1x100 mL of synthetic and lab water; 3x200 ml of natural water) were spiked with IS (MPFAC-MXA, Diclofenac d4, Carbamazepin13C6), and extracted using the SPE cartridges StrataX-AW, Phenomenex (200 mg, 6ml, 33pm polymeric weak anion) preconditioned by basic methanol, methanol and water. The dried cartridges were eluted by methanol (3 ml) and basic methanol (3 ml). The dried eluates (6 ml by nitrogen) were reconstituted in 200 pL of methanol and ammonium acetate (1:1).

LC/MS Pharm

For detection, we used UPLC Acquity (Waters, Milford, MA, USA) coupled with Xevo TQ-S (Waters, Milford, MA, USA). Analytes were separated on Acquity BEH C18 column (100 x 2.1 mm, 1.7 mm) with mobile phase contained 0.01 % formic acid, and ImM ammonium acetate in both methanol (B) and water (A). Recovery (tap water, SPE) for Diclofenac (100 ng/L; 98±7%; N=14) and Carbamazepine (100 ng/L; 96±9%; N=14).

LC/MS PFAS

For detection, we used UPLC Agilent 1290 series (Agilent Technologies, Waldbronn, Germany) coupled with AB Sciex Qtrap 5500+ (AB Sciex, Concord, ON, Canada). Analytes were separated on Luna Omega C18 column (100 x 2.1 mm, 1.6 mm). The mobile phase consisted of Methanol: 5Mm ammonium fluoride in ratio 55:45 (A) and Methanol (B).

ID 4: 60 - other method (PFAS)
According to EPA 1633: manually SPE 100-200 mL, isotope-labelled internal standards EIS-NIS, direct injection, external calibration, chromatographic separation and detection by LCMS.

Table 5B: List of analytical methods for the 2nd PT round.

Code number for used analytical method	Number of participants utilizing the method per group of substances
10 - ISO 21675:2019 Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [10]	3
20 - EN 17892:2024 Water quality — Determination of selected per- and polyfluoroalkyl substances in drinking water — Method using liquid chromatography/tandem-mass spectrometry (LC-MS/MS) [9]	4
30 - ISO 25101:2009 Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry [11]	3
40 - ASTM D7979-20 Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) [12]	0

50 - DIN 38407-42:2011-03 German standard methods for the examination of water, wastewater and sludge - Jointly determinable substances (group F) - Part 42: Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42) [8]	0
60 – other method	5

Overview of analytical methods applied by participants for the 2nd PT round:

Participant ID 3

We use a modified EPA 1633 method. Briefly, we analyzed 50 and 100 mL from spiked water samples provided and prepared according to instructions. EIS was added to all samples before SPE (Phenomenex Strata-X-AW 33 µm). After cartridge loading, we did a cartridge washing step with 1 mL 25 mM NH4Ac. Cartridges were centrifuged and PFAS were eluted using 2 mL 1% NH4-Methanol solution. 1 mL from each eluate were transferred to vials, and NIS was then added to all of them. Samples were analyzed in an LC-MS using Methanol and 20 mM NH4Ac as mobile phase.

Participant ID 5

LCMSMS, SPE, 100 ml of water is extracted into 1 ml methanol

Literature: EPA Method 533, EPA Method 537.1

Participant ID 6

Principle, reagents: Per- and polyfluoroalkyl substances (PFAS) are extracted from the water sample using solid-phase extraction (SPE) on Strata-X-AW (200 mg, weak anion-exchange) cartridges. After elution with 1 % NH_4OH in methanol, the eluate is evaporated under N_2 at 50 °C to dryness and reconstituted in MeOH:H_2O (1:1). The analysis is performed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in negative ESI mode, using dynamic MRM detection. Quantification is based on isotope-labelled internal standards (ISTD) added prior to extraction. Chromatographic separation and detection: C18 analytical column (Agilent ZORBAX Eclipse Plus C18, 150 × 3 mm, 3 µm); mobile phases: A = 5 mM ammonium acetate in water, B = methanol; flow = 0.5 mL min^{-1}; gradient elution from 5 % B → 100 % B in 7 min; injection volume = 50 µL; column temperature = 40 °C. Detection: Agilent 6420 LC-MS/MS, dMRM, 2 transitions per analyte (quantifier + qualifier), negative ESI, 3000 V capillary voltage, 80 °C gas temp, 13 L/min gas flow. Detection: Agilent 6420 LC-MS/MS, dMRM, 2 transitions per analyte (quantifier + qualifier), negative ESI, 3000 V capillary voltage, 80 °C gas temp, 13 L/min gas flow. Matrix calibration: external calibration with 6 points (0.9–150 ng L^{-1}) using ISTD spiking; weighted (1/x) regression. Pre-treatment & clean-up: sample spiked with ISTD, extracted by SPE as described above. Sample volume: 500 mL. Internal standards: mixture of isotope-labelled PFAS analogues (e.g. $^{13}C_4$-PFBA, $^{13}C_5$-PFPeA, $^{13}C_8$-PFOA, $^{13}C_8$-PFOS, etc.).

Literature:

– DIN EN 17892:2023 Determination of PFAS in drinking water by LC-MS;

– Agilent Application Note “Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Samples per EPA Draft Method 1633”.

Participant ID 10
IS-labelled; HPLC-MS/MS

Literature: EPA 537:2009

Participant ID 13
Extraction: Water samples intended for PFAS determination were processed using the Biotage Horizon 5000 Automated Disk Extraction System. The method is based on disk-based solid-phase extraction (SPE), employing hydrophilic-lipophilic balanced (HLB) extraction disks designed to retain PFAS compounds as the sample passes through a porous polymeric sorbent medium. Prior to extraction, SPE disks were conditioned with methanol and ethyl acetate, followed by equilibration with ultrapure water to ensure optimal analyte retention. After sample loading, the disks were dried and analytes were eluted using methanol and ethyl acetate. The obtained eluates were subsequently concentrated under a gentle nitrogen stream and reconstituted in an appropriate solvent prior to instrumental analysis.

Internal Standards: Isotope-labelled internal standards were added to each sample prior to extraction, to correct for potential matrix effects, recovery variability and ionization suppression/enhancement during LC-MS/MS detection.

Chromatographic separation and detection of PFAS compounds were performed using an LC-MS/MS system (Agilent 6475). The method is based on reversed-phase LC separation followed by MS/MS detection in ESI- mode, applying MRM for selective identification and quantification of target analytes.

Evaluation of Laboratory Results and Overall Performance

The individual results submitted by each laboratory for the analyzed parameters are documented in the annex for **1st round PT** Table A-ID1 to Table A-ID5 and Table B-ID1 to Table B-ID15.

These personalized summary from 1st round PT by identification code of laboratory include the average laboratory’s measured value “xi”, assessment criterion “ks”, the defined criteria for acceptable performance lower limits of acceptable results “LL” and upper limits of acceptable results “UL”, “z-scores” and deviation from the assigned (reference) value “D”.

In the 1st round of PT, laboratories demonstrated varying levels of success:

Pharmaceutical Substances (Pharm): A **100%** success rate was achieved across all reported parameters.

Polyfluoroalkyl Substances (PFAS) 25 analytes: The average success rate was **61%**. The lower success rate in this group is partly attributed to the lower performance of participants for this group of substances and to low number of participants for certain parameters, where only 1–2 laboratories participated.

Notable observations:

Participant ID 1 - Success rate: PFAS 100% (22 reported parameters – all acceptable); Pharm 100% (2 reported parameters – all acceptable).

Participant ID 2 - Success rate: PFAS 0% (19 reported parameters – all unacceptable).
Reported z-scores below −3 for all submitted PFAS parameters, indicating significant issues with the applied analytical method. The consistent nature of these deviations suggests a systematic error, potentially related to sample preparation, calibration, or analytical execution.

Participant ID 3 - Success rate: PFAS 100% (16 reported parameters – all acceptable); Pharm 100% (2 reported parameters – all acceptable).
Achieved successful results for all reported parameters, covering both pharmaceutical substances and 16 PFAS compounds.

Participant ID 4 - Success rate: PFAS 80% (25 reported parameters – 20 acceptable / 4 questionable / 1 unacceptable); Pharm 100% (2 reported parameters – all acceptable).
Showed deviations in results for PFHxDA and PFODA. These long-chain carboxylic acids (C16 and C18) exhibit different behavior compared to shorter-chain homologues due to their molecular structure, which includes both polar and non-polar regions. We assume that selection of more suitable internal standards could improve performance for these substances.

Participant ID 5 - Success rate: PFAS 33% (6 reported parameters – 2 acceptable / 2 questionable / 2 unacceptable).
Reported deviated results for PFPA and PFDA.

Figures 6 and 7 present charts illustrating the range and average values of extended uncertainties reported by participants. A significant variation in reported uncertainty values was observed. For PFAS, minimum extended uncertainties were typically in the range of 1 ng/L to 3 ng/L, which is relatively low considering the spiked concentrations (60–80) ng/L. Similarly, for Pharm, some reported uncertainties appear low for ultra-trace environmental analysis.

These personalized summary from 2nd round PT by identification code of laboratory include the average laboratory's measured value "xi", uncertainty of participant "u", code number for used analytical "Method", "z-scores", deviation from the assigned (reference) value "D", the defined criteria for acceptable performance lower limits of acceptable results "LL" and upper limits of acceptable results and defined the Performance.

In the 2nd round of PT, laboratories demonstrated varying levels of success:

Polyfluoroalkyl Substances (PFAS) 27 analytes: The average success rate was 77,6%. Compared to the first PT round, a higher success rate was observed for these compounds. The lower success rate among participants with less than 50% correctly determined results is primary attributed to analytical methods lacking internal standards.

The individual results submitted by each laboratory for the analyzed parameters are documented in the annex. These include the laboratory's measured values, the corresponding reference values, deviations from the reference, z-scores, robust standard deviations, and the defined criteria for acceptable performance (lower and upper limits).

In this round of PT, laboratories demonstrated varying levels of success:

The lowest success rate was achieved by laboratories that used methods of determination without internal standards.

The lowest success rate 40% were achieved by parameters PFUnDS. Of the 10 reported results 4 were acceptable, 3 questionable and 3 unacceptable.

The success rate of 50% was achieved by parameter PFDoS. Of the 10 reported results were 5 acceptable, 3 questionable and 2 unacceptable

The success rate of 70% was achieved by parameter PFTrDS. Of the 10 reported results there were 7 acceptable and 3 questionable.

All parameters are from the group of perfluoroalkyl sulfonic acids with long chain C11, C12 and C13. Since there is no internal standard for perfluoroalkyl sulfonic acids with long chains most of the participants used for quantification MPFOS (C8). Due to the different polarity and behavior of perfluoroalkyl sulfonic acids with long chain it will be reasonable to change the internal standards used for quantification of those substances, for example: MPFDoDA for PFUnDS and PFDoS, M2PFTeDA for PFTrDS.

The success rate of perfluoroalkyl acids with long chain C11- C16 and C18, are higher than success rate of perfluoroalkyl sulfonic acids with long chain C11, C12 and C13. For the long chain perfluoroalkyl acids there are suitable internal standards and laboratories use them. The variability of the internal standards used for the quantification of perfluoroalkyl sulfonic acids reported by laboratories is also wider than of the internal standards used for the quantification of perfluoroalkyl acids. The greatest variability in the use of internal standards was reported for these parameters: ADONA (M4PFHpA, MPFNA, MPFHxS, MPFOA/MPFOS,M2ADONA), PFPS (M3PFBS, MPFHxS, MPFOS, M4PFHpA, MPFHxA), PFDoDS (MPFOS, MPFDoA, Perfluorotridecanoic acid 13C2 (1,2-13C2), M2PFTeDA) and PFTrDA (M2PFTeDA, MPFDoA, M2PFDA, Perfluorotridecanoic acid 13C2 (1,2-13C2)).

The highest success rate of 100% was achieved by parameters 9Cl-PF3ONS, 11Cl-PF3OUdS, HFPO-DA and PFTeDA. These parameters are not included in Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption and are analyzed by laboratories experienced in determining PFAS. All reporting laboratories analyzing those parameters achieved success rates higher than 88%. Most of these laboratories reported results for 22 or more parameters.

Notable observations:

Participant ID 1

Success rate 80% (5 reported parameters – 4 acceptable / 1 questionable).
The laboratory reported MPFOS as an internal standard for the determination of PFBS. MPFOS elutes far from PFBS so it would be appropriate to include another internal standard, for example MPFHxS. Reported results have 4 decimal places, usually results are reported to three significant figures.

Participant ID 2

Success rate 85% (20 reported parameters – 17 acceptable / 3 questionable).
The laboratory reported MPFOS as an internal standard for the determination of PFBS. MPFOS elutes far from PFBS so it would be appropriate to include another internal standard, for example MPFHxS.

Participant ID 3

Success rate 88,89% (27 reported parameters – 24 acceptable / 2 questionable/ 1 unacceptable).
The laboratory reported use of extracted internal standards EIS and non-extracted internal standard NIS. The appropriate combination of both internal standards used for quantification also plays an important role. The reported values of uncertainties are low, possibly underestimated, for organic trace analysis, values of 20–40% are common.

Participant ID 4

Success rate 96,3% (27 reported parameters – 26 acceptable / 1 questionable).
Laboratory reported deviated results for PFTrDS.

Participant ID 5

Success rate 96% (25 reported parameters – 24 acceptable / 1 questionable).
Laboratory reported deviated results for PFUnDS. Another internal standard for the quantification of PFUnDS, for example MPFDoDA, can improve the method of analysis.

Participant ID 6

Success rate 90% (20 reported parameters – 18 acceptable / 1 questionable/ 1 unacceptable).
The laboratory reported MPFOS as an internal standard for the determination of PFDoDS and PFUdS. Another internal standard for the quantification of those compounds, for example MPFDoDA, can improve the method of analysis. Reported results have 3 decimal places, usually results are reported to three significant figures.

Participant ID 7

Success rate 88% (25 reported parameters – 22 acceptable / 3 questionable).
Laboratory reported deviated results for PFDoDS, PFHxS and PFTrDS.

Participant ID 8

Success rate 10% (20 reported parameters – 2 acceptable / 2 questionable/ 16 unacceptable).
Laboratory reported uses a method of determination without internal standards, what can be crucial. The laboratory also demonstrated the largest difference between the 1st result and the 2nd result.

Participant ID 9

Success rate 96,3% (27 reported parameters – 26 acceptable / 1 questionable).
Laboratory reported deviated results for PFTrDS. Another internal standard for the quantification of PFTrDS, for example M2PFTeDA, can improve the method of analysis.

Participant ID 10

Success rate 68,75% (16 reported parameters – 11 acceptable / 3 questionable/ 2 unacceptable).
Laboratory reported deviated results for PFDoDA, PFHpS, PFHxA, PFTrDA and PFUnDS. Another internal standard for quantification, for example MPFUnDA for PFDoDA, MPFHxS for PFHpS, MPFDA for PFUnDS, can improve the method of analysis. The reported date of analysis was out of testing period. Reported uncertainties have more decimal places than results, both should by expressed with same number of decimal places. The uncertainties were expressed as double of standard deviation of the 1st result and the 2nd result.

Participant ID 11

Success rate 40% (5 reported parameters – 2 acceptable / 3 questionable).
Laboratory reported uses a method of determination without internal standards, what can be crucial. Reported uncertainties have more decimal places than results, both should by expressed with same number of decimal places.

Participant ID 12

Success rate 100% (20 reported parameters – 20 acceptable).
Reported uncertainties have more decimal places than results, both should by expressed with same number of decimal places.

Participant ID 13

Success rate 100% (19 reported parameters – 19 acceptable).

Participant ID 14

Success rate 33,33% (9 reported parameters – 3 acceptable / 1 questionable/ 5 unacceptable).
Laboratory reported uses a method of determination without internal standards, what can be crucial.

Participant ID 15

Success rate 90,91% (22 reported parameters – 20 acceptable / 1 questionable/ 1 unacceptable).
Laboratory reported deviated results for PFUnDS and PFDoDS. Another internal standard for the quantification, for example MPFDoDA, can improve the method of analysis.

Recommendation

Given the relatively low success rate in PFAS determination during the first round PT, a second round PT focused specifically on PFAS was scheduled for autumn 2025. The second round PT aimed to provide laboratories with an opportunity to reassess and improve their performance.

In the first-round participants were requested to review their methods for estimating expanded uncertainty. In several cases, the reported values may underestimate the actual uncertainty associated with analyses at ultra-trace pollutants levels.

The results obtained from laboratories employing analytical methods without internal standards indicate significant problems in determination of correct values of PFAS. Significant deviations of the reported results from the reference value indicate the presence of systematic errors that may originate from different steps of the analytical process. These errors may be related to sample preparation, calibration as well as the analytical procedure itself.

In several cases, the reported values may be underestimated by the uncertainty associated with analyses at the ultra-trace level. Analytical work should be performed according to an appropriate quality system, including validated analytical methods, proficiency testing, internal laboratory quality control and external assessment where necessary. Validation procedures should include deviation checks using CRM. Laboratories performing chemical analysis should report uncertainties with the results of analyses. Reporting information on values below the LOD will lead to an underestimation of uncertainty.

The numerical values of the result and its uncertainty should not be reported with an excessive number of digits. Regardless of whether expanded uncertainty or a standard uncertainty is provided, in most cases it is sufficient to state no more than two significant digits for the uncertainty. The reported results should be rounded to ensure consistency with the stated uncertainty.

Laboratories' measurements often underestimate uncertainty due to the failure to account for systematic errors (bias).

An excessively low uncertainty may lead to an underestimation of the true value, primarily because it can indicate the presence of unaccounted systematic errors or an inaccurate representation of measurement variability.

Suitable tools for calculating the uncertainty of analytical procedures is literature [13] and [14].

Each participant will receive this final report together with the identification number under which his results were evaluated.

One participant, following recommendations from the first PT round, incorporated internal standards in his method, which significantly increased his success rate.

We recommend that participants in the second round of PT reconsider their methods for determining expanded uncertainty based on the statistical outputs of the analytical data evaluation.

Summary: In conclusion, the 2nd round of PT for analysis of PFAS was successful, the scheme remains a useful and relevant tool within the qualitative framework for comparing analytical methods suitable for evaluating new pollutants monitored in the water of the Danube region.

Conclusions and lessons learned

As a pilot action to test and demonstrate procedures for knowledge transfer aimed at improving the implementation, development, and harmonization of analytical methods for monitoring emerging hazardous substances, two workshops and two rounds of interlaboratory comparison (ILC) studies were carried out.

The first workshop on analytical methods for monitoring water and related matrices attracted limited interest among invited laboratories, leading to its organization in an online format. A revised approach—focusing on PFAS monitoring and targeting laboratories with limited or no experience in PFAS analysis—proved significantly more successfully. The most valued components were hands-on sessions, where experts demonstrated sample preparation techniques for water and biota matrices in small groups.

To explore effective ways of supporting laboratories in method development and implementation, the workshop applied the facilitated co-creative method *World Café.* Beyond obvious needs such as funding, equipment, and staffing, participants identified key priorities:

- Information sharing among experts
- Creation of a professional network
- Education through workshops and training
- Organization of interlaboratory comparison studies (proficiency testing)

The first ILC focused on PFAS (25 compounds) and two pharmaceuticals (Diclofenac and Carbamazepine), with five laboratories submitting results. For PFAS, the average success rate was 61%, though performance varied widely across compounds (0–100%). Longer-chain PFAS were most problematic, likely due to inadequate use of internal standards. Pharmaceutical analysis was successful with all participants.

The second ILC round focused exclusively on PFAS, expanding the target list to 27 compounds and attracting 15 laboratories. The average success rate improved to 77.6%. Analysis of reported methods confirmed that the correct application of internal standards remains the most critical factor for achieving reliable results.

Higher participation in the second ILC round was likely driven by increased awareness of the Tethys project through workshops and the first ILC. This confirms workshop findings: improving implementation and analytical quality requires **networking opportunities, a strong expert community, and continuous training activities among financial and staff capacity resources.**

References

[1] EN ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories

[2] EN ISO/IEC 17043:2023 Conformity assessment - General requirements for the competence of proficiency testing providers

[3] EN ISO 5667-3:2024 Water quality - Sampling - Part 3: Preservation and handling of water samples

[4] PSS/VŠ-ŠOP/3" Hodnotenie homogenity a stability vzoriek" (Internal SOP on Assessment of homogenity and stability of samples).

[5] ISO 5725-1:2023 Accuracy (trueness and precision) of measurement methods and results

[6] REICHENBÄCHER, M. - EINAX, J. W. 2011. Challenges in Analytical Quality Assurance. New York: Springer, 2011. 356 s. ISBN 978-3-642-16594-8

[7] ISO 13528:2022 Statistical methods for use in proficiency testing by interlaboratory comparisons

[8] DIN 38407-42:2011-03 German standard methods for the examination of water, waste water and sludge - Jointly determinable substances (group F) - Part 42: Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42)

[9] EN 17892:2024 Water quality — Determination of selected per - and polyfluoroalkyl substances in drinking water — Method using liquid chromatography/tandem-mass spectrometry (LC-MS/MS)

[10] ISO 21675:2019 Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)

[11] ISO 25101:2009 Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry

[12] ASTM D7979-20 Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

[13] ISO 11352:2012 Water quality – Estimation of measurement uncertainty based on validation and quality control data

[14] Setting and Using Target Uncertainty in Chemical MeasurementEurachem/Citac Guide, 2015

Annex

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Table A ID 1 - results of participant 1st PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFAS								
PFPA, (PFPeA)	58,3	7,7	60	0,10	1,98	34,3	80,0	Acceptable
PFHxA	57,2	10,6	60	-0,04	-0,72	34,5	80,6	Acceptable
PFHpA	57,1	7,4	60	-0,04	-0,86	34,5	80,6	Acceptable
PFOA	63,8	7,8	60	0,48	9,55	34,9	81,5	Acceptable
PFNA	57,4	7,9	60	0,40	8,05	31,9	74,4	Acceptable
PFDA	57,4	6,4	60	0,24	4,88	32,8	76,6	Acceptable
PFUnDA	69,3	8,1	60	0,95	19,08	34,9	81,5	Acceptable
PFDoDA	82,2	17,2	60	2,28	45,69	33,9	79,0	Questionable
PFTeDA	64,5	12,3	60	0,33	6,63	36,3	84,6	Acceptable
PFBS	64,6	8,2	60	0,65	12,96	34,3	80,1	Acceptable
PFPS, (PFPeS)	90,1	14,6	60	0,00	0,00	54,0	126,1	Acceptable
PFHxS	65,4	8,7	60	0,29	5,73	37,1	86,5	Acceptable
PFHpS	60,1	11,1	60	0,36	7,11	33,6	78,5	Acceptable
PFOS	64,1	7,4	60	0,45	8,91	35,3	82,3	Acceptable
Pharm								
diclofenac_A	255	_	60	-0,13	-1,9	182	338	Acceptable
diclofenac_B	260	_	60	0	0	182	338	Acceptable
carbamazepine_A	195	_	60	-0,33	-4,9	144	267	Acceptable
carbamazepine_B	205	_	60	0	0	144	267	Acceptable

Table A ID 2 - results of participant 1st PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFAS								
PFBA	3,0	_	50	-4,76	-95,1	36,8	85,9	Unacceptable
PFPA, (PFPeA)	12,4	_	50	-3,92	-78,3	34,3	80,0	Unacceptable
PFHxA	11,1	_	50	-4,04	-80,8	34,5	80,6	Unacceptable
PFHpA	15,3	_	50	-3,67	-73,5	34,5	80,6	Unacceptable
PFOA	18,1	_	50	-3,44	-68,9	34,9	81,5	Unacceptable
PFNA	19,8	_	50	-3,14	-62,7	31,9	74,4	Unacceptable
PFDA	17,7	_	50	-3,38	-67,7	32,8	76,6	Unacceptable
PFUnDA	21,0	_	50	-3,20	-64,0	34,9	81,5	Unacceptable
PFDoDA	14,5	_	50	-3,71	-74,3	33,9	79,0	Unacceptable
PFTrDA	18,4	_	50	-3,50	-70,1	36,9	86,1	Unacceptable
PFBS	16,5	_	50	-3,56	-71,1	34,3	80,1	Unacceptable
PFPS, (PFPeS)	20,7	_	50	-3,85	-77,1	54,0	126,1	Unacceptable
PFHxS	18,3	_	50	-3,52	-70,5	37,1	86,5	Unacceptable
PFHpS	22,0	_	50	-3,04	-60,8	33,6	78,5	Unacceptable
PFOS	19,7	_	50	-3,33	-66,6	35,3	82,3	Unacceptable
PFNS	25,8	_	50	-3,07	-61,4	40,1	93,6	Unacceptable
PFDS	16,7	_	50	-3,56	-71,3	34,9	81,4	Unacceptable
PFUnS, (PFUnDS)	15,6	_	50	-3,99	-79,8	46,3	108,0	Unacceptable
PFDoS	11,9	_	50	-3,76	-75,2	28,8	67,1	Unacceptable

Table A ID 3 - results of participant 1st PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFAS								
PFBA	50,2	8,0	60	-0,91	-18,2	36,8	85,9	Acceptable
PFPA, (PFPeA)	50,0	13,0	60	-0,63	-12,5	34,3	80,0	Acceptable
PFHxA	50,3	5,5	60	-0,63	-12,6	34,5	80,6	Acceptable
PFHpA	44,4	10,7	60	-1,14	-22,8	34,5	80,6	Acceptable
PFOA	52,5	5,8	60	-0,49	-9,79	34,9	81,5	Acceptable
PFNA	67,7	10,2	60	1,37	27,4	31,9	74,4	Acceptable
PFDA	71,0	14,2	60	1,49	29,7	32,8	76,6	Acceptable
PFUnDA	70,7	21,2	60	1,07	21,5	34,9	81,5	Acceptable
PFDoDA	74,4	15,6	60	1,59	31,9	33,9	79,0	Acceptable
PFTrDA	62,8	18,2	60	0,10	2,07	36,9	86,1	Acceptable
PFTeDA	53,6	17,7	60	-0,57	-11,3	36,3	84,6	Acceptable
PFBS	56,7	6,2	60	-0,04	-0,86	34,3	80,1	Acceptable
PFHxS	57,9	9,8	60	-0,32	-6,32	37,1	86,5	Acceptable
PFHpS	75,3	16,6	60	1,72	34,3	33,6	78,5	Acceptable
PFOS	60,6	9,7	60	0,15	3,05	35,3	82,3	Acceptable
PFDS	76,6	25,3	60	1,59	31,8	34,9	81,4	Acceptable
Pharm								
diclofenac_A	264	40	60	0,09	1,42	182	338	Acceptable
diclofenac_B	275	41	60	0,38	5,73	182	338	Acceptable
carbamazepine_A	238	43	60	1,09	16,3	144	267	Acceptable
carbamazepine_B	244	44	60	1,26	18,9	144	267	Acceptable

Table A ID 4 - results of participant 1st PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFAS								
PFBA	47,2	1,67	60	-1,16	-23,1	36,8	85,9	Acceptable
PFPA, (PFPeA)	48,7	1,95	60	-0,74	-14,8	34,3	80,0	Acceptable
PFHxA	52,7	1,98	60	-0,42	-8,45	34,5	80,6	Acceptable
PFHpA	52,8	1,99	60	-0,41	-8,25	34,5	80,6	Acceptable
PFOA	51,0	2,66	60	-0,62	-12,4	34,9	81,5	Acceptable
PFNA	49,9	1,86	60	-0,31	-6,16	31,9	74,4	Acceptable
PFDA	46,3	2,31	60	-0,77	-15,4	32,8	76,6	Acceptable
PFUnDA	48,2	2,56	60	-0,86	-17,1	34,9	81,5	Acceptable
PFDoDA	41,5	1,93	60	-1,32	-26,5	33,9	79,0	Acceptable
PFTrDA	35,3	1,63	60	-2,13	-42,7	36,9	86,1	Questionable
PFTeDA	38,5	1,46	60	-1,82	-36,3	36,3	84,6	Acceptable
PFHxDA	110,9	4,27	60	1,62	32,4	50,3	117,3	Acceptable
PFODA	192,2	8,92	60	6,79	135,8	48,9	114,2	Unacceptable
PFBS	58,5	3,45	60	0,12	2,34	34,3	80,1	Acceptable
PFPS, (PFPeS)	92,7	2,59	60	0,15	2,93	54,0	126,1	Acceptable
PFHxS	48,8	2,14	60	-1,05	-21,0	37,1	86,5	Acceptable
PFHpS	46,0	2,30	60	-0,90	-18,0	33,6	78,5	Acceptable
PFOS	50,4	2,40	60	-0,71	-14,2	35,3	82,3	Acceptable
PFNS	52,3	2,92	60	-1,09	-21,7	40,1	93,6	Acceptable
PFDS	49,9	2,22	60	-0,71	-14,2	34,9	81,4	Acceptable
PFUnS, (PFUnDS)	35,3	1,87	60	-2,71	-54,3	46,3	108,0	Questionable
PFDoS	20,0	1,60	60	-2,92	-58,3	28,8	67,1	Questionable
PFTrDS	24,1	1,23	60	-2,51	-50,2	29,0	67,7	Questionable
GenX	72,9	2,52	60	0,57	11,4	39,3	91,6	Acceptable
ADONA	33,0	1,41	60	0,56	11,2	17,8	41,6	Acceptable
Pharm								
diclofenac_A	275,2	1,59	_	0,39	5,85	182	338	Acceptable
diclofenac_B	273,3	1,59	_	0,34	5,12	182	338	Acceptable
carbamazepine_A	254,2	0,98	_	1,60	24,0	144	267	Acceptable
carbamazepine_B	251,1	0,98	_	1,50	22,5	144	267	Acceptable

Table A ID 5 - results of participant 1st PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFAS								
PFBA	46,5	15,0	20	-1,21	-24,2	36,8	85,9	Acceptable
PFPA, (PFPeA)	8,3	3,0	20	-4,27	-85,5	34,3	80,0	Unacceptable
PFDA	8,5	3,0	20	-4,22	-84,5	32,8	76,6	Unacceptable
PFBS	28,0	10,0	20	-2,55	-51,0	34,3	80,1	Questionable
PFHxS	76,0	24,0	20	1,15	23,0	37,1	86,5	Acceptable
PFOS	28,5	9,0	20	-2,58	-51,5	35,3	82,3	Questionable

Table B ID 1 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
ADONA	31,27	3,14	30	-0,99	-24,83	20,80	62,40	Acceptable
PFBS	10,56	2,74	30	-2,64	-65,94	15,51	46,52	Questionable
PFHxS	37,27	6,68	30	0,90	22,61	15,20	45,60	Acceptable
PFOA	36,84	2,11	30	0,62	15,41	15,96	47,88	Acceptable
PFOS	18,81	0,98	30	-1,55	-38,78	15,36	46,08	Acceptable

Table B ID 2 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFBA	31,00	15,50	30	0,28	7,09	14,47	43,42	Acceptable
PFBS	27,50	13,75	30	-0,45	-11,33	15,51	46,52	Acceptable
PFDA	24,50	12,25	30	0,08	2,08	12,00	36,00	Acceptable
PFDoDA	28,00	14,00	30	0,67	16,67	12,00	36,00	Acceptable
PFDoS	10,00	5,00	30	-2,63	-65,64	14,55	43,65	Questionable
PFDS	10,50	5,25	30	-2,64	-66,00	15,44	46,32	Questionable
PFHpA	22,50	11,25	30	-0,25	-6,25	12,00	36,00	Acceptable
PFHpS	48,50	24,25	30	-0,09	-2,30	24,82	74,46	Acceptable
PFHxA	24,50	12,25	30	0,08	2,08	12,00	36,00	Acceptable
PFHxS	34,00	17,00	30	0,47	11,84	15,20	45,60	Acceptable
PFNA	26,00	13,00	30	0,33	8,33	12,00	36,00	Acceptable
PFNS	19,00	9,50	30	-1,74	-43,57	16,84	50,51	Acceptable
PFOA	31,50	15,75	30	-0,05	-1,32	15,96	47,88	Acceptable
PFOS	31,00	15,50	30	0,04	0,91	15,36	46,08	Acceptable
PFPA	11,50	5,75	30	-2,08	-52,08	12,00	36,00	Questionable
PFPS	36,00	18,00	30	-0,17	-4,26	18,80	56,40	Acceptable
PFTrDA	23,50	11,75	30	-0,08	-2,08	12,00	36,00	Acceptable
PFTrDS	29,50	14,75	30	-0,97	-24,13	19,44	58,32	Acceptable
PFUnDA	28,50	14,25	30	0,75	18,75	12,00	36,00	Acceptable
PFUnDS	36,50	18,25	30	-0,65	-16,21	21,78	65,34	Acceptable

Table B ID 3 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
11Cl-PF3OUdS	13,35	0,90	60	-1,78	-44,38	12,00	36,00	Acceptable
9Cl-PF3ONS	18,00	1,00	60	-1,00	-25,00	12,00	36,00	Acceptable
ADONA	35,50	1,70	60	-0,59	-14,66	20,80	62,40	Acceptable
HFPO-DA	44,45	1,80	60	-1,22	-30,55	32,00	96,00	Acceptable
PFBA	28,15	2,90	60	-0,11	-2,76	14,47	43,42	Acceptable
PFBS	32,50	1,70	60	0,19	4,80	15,51	46,52	Acceptable
PFDA	20,60	1,30	60	-0,57	-14,17	12,00	36,00	Acceptable
PFDoDA	23,20	2,30	60	-0,13	-3,33	12,00	36,00	Acceptable
PFDoS	17,75	1,20	60	-1,56	-39,00	14,55	43,65	Acceptable
PFDS	22,10	1,90	60	-1,14	-28,43	15,44	46,32	Acceptable
PFHpA	18,45	0,80	60	-0,93	-23,13	12,00	36,00	Acceptable
PFHpS	37,45	1,90	60	-0,98	-24,56	24,82	74,46	Acceptable
PFHxA	19,50	0,70	60	-0,75	-18,75	12,00	36,00	Acceptable
PFHxDA	47,80	6,80	60	2,37	59,33	15,00	45,00	Questionable
PFHxS	26,65	1,40	60	-0,49	-12,34	15,20	45,60	Acceptable
PFNA	20,05	1,00	60	-0,66	-16,46	12,00	36,00	Acceptable
PFNS	22,95	1,30	60	-1,27	-31,84	16,84	50,51	Acceptable
PFOA	24,85	1,00	60	-0,89	-22,15	15,96	47,88	Acceptable
PFODA	88,80	14,70	60	6,15	153,71	17,50	52,50	Unacceptable
PFOS	26,50	1,30	60	-0,55	-13,74	15,36	46,08	Acceptable
PFPA	18,20	0,90	60	-0,97	-24,17	12,00	36,00	Acceptable
PFPS	28,50	1,60	60	-0,97	-24,20	18,80	56,40	Acceptable
PFTeDA	18,60	1,80	60	-0,90	-22,50	12,00	36,00	Acceptable
PFTrDA	20,50	2,30	60	-0,58	-14,58	12,00	36,00	Acceptable
PFTrDS	13,90	1,30	60	-2,57	-64,25	19,44	58,32	Questionable
PFUnDA	22,40	2,00	60	-0,27	-6,67	12,00	36,00	Acceptable
PFUnDS	32,40	2,50	60	-1,02	-25,62	21,78	65,34	Acceptable

Table B ID 4 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
11Cl-PF3OUdS	12,85	5,14	20	-1,86	-46,46	12,00	36,00	Acceptable
9Cl-PF3ONS	18,30	7,32	20	-0,95	-23,75	12,00	36,00	Acceptable
ADONA	40,00	16,00	20	-0,15	-3,85	20,80	62,40	Acceptable
HFPO-DA	63,75	25,50	20	-0,02	-0,39	32,00	96,00	Acceptable
PFBA	31,70	12,68	20	0,38	9,51	14,47	43,42	Acceptable
PFBS	33,85	13,54	20	0,37	9,15	15,51	46,52	Acceptable
PFDA	19,50	7,80	20	-0,75	-18,75	12,00	36,00	Acceptable
PFDoDA	15,30	6,12	20	-1,45	-36,25	12,00	36,00	Acceptable
PFDoS	21,65	8,66	20	-1,02	-25,60	14,55	43,65	Acceptable
PFDS	15,65	6,26	20	-1,97	-49,32	15,44	46,32	Acceptable
PFHpA	24,85	9,94	20	0,14	3,54	12,00	36,00	Acceptable
PFHpS	51,95	20,78	20	0,19	4,65	24,82	74,46	Acceptable
PFHxA	25,40	10,16	20	0,23	5,83	12,00	36,00	Acceptable
PFHxDA	22,60	9,04	20	-0,99	-24,67	15,00	45,00	Acceptable
PFHxS	35,55	14,22	20	0,68	16,94	15,20	45,60	Acceptable
PFNA	21,70	8,68	20	-0,38	-9,58	12,00	36,00	Acceptable
PFNS	18,15	7,26	20	-1,84	-46,09	16,84	50,51	Acceptable
PFOA	32,25	12,90	20	0,04	1,03	15,96	47,88	Acceptable
PFODA	24,60	9,84	20	-1,19	-29,71	17,50	52,50	Acceptable
PFOS	26,05	10,42	20	-0,61	-15,20	15,36	46,08	Acceptable
PFPA	25,15	10,06	20	0,19	4,79	12,00	36,00	Acceptable
PFPS	34,00	13,60	20	-0,38	-9,57	18,80	56,40	Acceptable
PFTeDA	17,95	7,18	20	-1,01	-25,21	12,00	36,00	Acceptable
PFTrDA	16,80	6,72	20	-1,20	-30,00	12,00	36,00	Acceptable
PFTrDS	15,05	6,02	20	-2,45	-61,29	19,44	58,32	Questionable
PFUnDA	15,00	6,00	20	-1,50	-37,50	12,00	36,00	Acceptable
PFUnDS	36,90	14,76	20	-0,61	-15,29	21,78	65,34	Acceptable

Table B ID 5 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
ADONA	35,50	12,40	60	-0,59	-14,66	20,80	62,40	Acceptable
HFPO-DA	50,15	17,50	60	-0,87	-21,64	32,00	96,00	Acceptable
PFBA	24,50	8,60	60	-0,61	-15,37	14,47	43,42	Acceptable
PFBS	31,45	11,00	60	0,06	1,41	15,51	46,52	Acceptable
PFDA	20,40	7,10	60	-0,60	-15,00	12,00	36,00	Acceptable
PFDoDA	20,25	7,10	60	-0,63	-15,63	12,00	36,00	Acceptable
PFDoS	33,60	11,80	60	0,62	15,46	14,55	43,65	Acceptable
PFDS	30,50	10,70	60	-0,05	-1,23	15,44	46,32	Acceptable
PFHpA	21,35	7,50	60	-0,44	-11,04	12,00	36,00	Acceptable
PFHpS	41,75	14,60	60	-0,64	-15,89	24,82	74,46	Acceptable
PFHxA	22,15	7,70	60	-0,31	-7,71	12,00	36,00	Acceptable
PFHxDA	20,50	7,20	60	-1,27	-31,67	15,00	45,00	Acceptable
PFHxS	36,65	12,80	60	0,82	20,56	15,20	45,60	Acceptable
PFNA	20,35	7,10	60	-0,61	-15,21	12,00	36,00	Acceptable
PFNS	24,10	8,40	60	-1,14	-28,42	16,84	50,51	Acceptable
PFOA	26,85	9,40	60	-0,64	-15,89	15,96	47,88	Acceptable
PFODA	23,80	8,30	60	-1,28	-32,00	17,50	52,50	Acceptable
PFOS	29,60	10,40	60	-0,15	-3,65	15,36	46,08	Acceptable
PFPA	21,10	7,40	60	-0,48	-12,08	12,00	36,00	Acceptable
PFPS	30,15	10,50	60	-0,79	-19,81	18,80	56,40	Acceptable
PFTeDA	19,60	6,90	60	-0,73	-18,33	12,00	36,00	Acceptable
PFTrDA	20,25	7,10	60	-0,63	-15,63	12,00	36,00	Acceptable
PFTrDS	19,70	6,90	60	-1,97	-49,33	19,44	58,32	Acceptable
PFUnDA	19,95	7,00	60	-0,68	-16,88	12,00	36,00	Acceptable
PFUnDS	18,35	6,40	60	-2,31	-57,87	21,78	65,34	Questionable

Table B ID 6 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFBA	30,64	_	60	0,23	5,83	14,47	43,42	Acceptable
PFBS	28,61	_	60	-0,31	-7,75	15,51	46,52	Acceptable
PFDA	22,06	_	60	-0,32	-8,07	12,00	36,00	Acceptable
PFDoDA	21,79	_	60	-0,37	-9,20	12,00	36,00	Acceptable
PFDoS	63,60	_	60	4,74	118,55	14,55	43,65	Unacceptable
PFDS	29,55	_	60	-0,17	-4,30	15,44	46,32	Acceptable
PFHpA	22,26	_	60	-0,29	-7,27	12,00	36,00	Acceptable
PFHpS	50,79	_	60	0,09	2,31	24,82	74,46	Acceptable
PFHxA	24,18	_	60	0,03	0,74	12,00	36,00	Acceptable
PFHxS	30,42	_	60	0,00	0,08	15,20	45,60	Acceptable
PFNA	24,19	_	60	0,03	0,78	12,00	36,00	Acceptable
PFNS	28,52	_	60	-0,61	-15,29	16,84	50,51	Acceptable
PFOA	28,90	_	60	-0,38	-9,47	15,96	47,88	Acceptable
PFOS	27,68	_	60	-0,40	-9,91	15,36	46,08	Acceptable
PFPA	26,10	_	60	0,35	8,74	12,00	36,00	Acceptable
PFPS	39,30	_	60	0,18	4,51	18,80	56,40	Acceptable
PFTrDA	15,08	_	60	-1,49	-37,17	12,00	36,00	Acceptable
PFTrDS	54,18	_	60	1,57	39,34	19,44	58,32	Acceptable
PFUnDA	23,89	_	60	-0,02	-0,47	12,00	36,00	Acceptable
PFUnDS	70,33	_	60	2,46	61,45	21,78	65,34	Questionable

Table B ID 7 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
11Cl-PF3OUdS	25,50	13,12	20	0,25	6,25	12,00	36,00	Acceptable
9Cl-PF3ONS	27,50	9,32	20	0,58	14,58	12,00	36,00	Acceptable
ADONA	51,00	14,65	20	0,90	22,60	20,80	62,40	Acceptable
HFPO-DA	76,50	22,60	20	0,78	19,53	32,00	96,00	Acceptable
PFBA	36,50	10,63	20	1,04	26,09	14,47	43,42	Acceptable
PFBS	39,00	13,92	20	1,03	25,75	15,51	46,52	Acceptable
PFDA	29,50	8,79	20	0,92	22,92	12,00	36,00	Acceptable
PFDoDA	31,50	14,62	20	1,25	31,25	12,00	36,00	Acceptable
PFDoS	47,00	18,86	20	2,46	61,51	14,55	43,65	Questionable
PFDS	39,00	17,92	20	1,05	26,30	15,44	46,32	Acceptable
PFHpA	30,50	8,53	20	1,08	27,08	12,00	36,00	Acceptable
PFHpS	60,00	21,31	20	0,83	20,87	24,82	74,46	Acceptable
PFHxA	30,50	8,29	20	1,08	27,08	12,00	36,00	Acceptable
PFHxS	47,50	16,01	20	2,25	56,25	15,20	45,60	Questionable
PFNA	32,00	8,49	20	1,33	33,33	12,00	36,00	Acceptable
PFNS	35,50	14,40	20	0,22	5,44	16,84	50,51	Acceptable
PFOA	39,50	13,84	20	0,95	23,74	15,96	47,88	Acceptable
PFOS	39,50	16,92	20	1,14	28,58	15,36	46,08	Acceptable
PFPA	30,50	9,18	20	1,08	27,08	12,00	36,00	Acceptable
PFPS	36,50	12,11	20	-0,12	-2,93	18,80	56,40	Acceptable
PFTeDA	32,50	15,28	20	1,42	35,42	12,00	36,00	Acceptable
PFTrDA	32,50	21,66	20	1,42	35,42	12,00	36,00	Acceptable
PFTrDS	30,00	10,14	20	-0,91	-22,84	19,44	58,32	Acceptable
PFUnDA	29,50	12,09	20	0,92	22,92	12,00	36,00	Acceptable
PFUnDS	74,50	32,64	20	2,84	71,03	21,78	65,34	Questionable

Table B ID 8 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFBA	43,55	_	20	2,02	50,44	14,47	43,42	Questionable
PFBS	68,40	_	20	4,82	120,55	15,51	46,52	Unacceptable
PFDA	50,40	_	20	4,40	110,00	12,00	36,00	Unacceptable
PFDoDA	41,30	_	20	2,88	72,08	12,00	36,00	Questionable
PFDoS	74,15	_	20	6,19	154,81	14,55	43,65	Unacceptable
PFDS	75,20	_	20	5,74	143,52	15,44	46,32	Unacceptable
PFHpA	53,40	_	20	4,90	122,50	12,00	36,00	Unacceptable
PFHpS	94,30	_	20	3,60	89,97	24,82	74,46	Unacceptable
PFHxA	49,40	_	20	4,23	105,83	12,00	36,00	Unacceptable
PFHxS	73,10	_	20	5,62	140,46	15,20	45,60	Unacceptable
PFNA	53,55	_	20	4,93	123,13	12,00	36,00	Unacceptable
PFNS	72,00	_	20	4,55	113,84	16,84	50,51	Unacceptable
PFOA	56,75	_	20	3,11	77,78	15,96	47,88	Unacceptable
PFOS	74,00	_	20	5,64	140,89	15,36	46,08	Unacceptable
PFPA	30,05	_	20	1,01	25,21	12,00	36,00	Acceptable
PFPS	66,40	_	20	3,06	76,60	18,80	56,40	Unacceptable
PFTrDA	54,05	_	20	5,01	125,21	12,00	36,00	Unacceptable
PFTrDS	57,75	_	20	1,94	48,53	19,44	58,32	Acceptable
PFUnDA	45,90	_	20	3,65	91,25	12,00	36,00	Unacceptable
PFUnDS	99,85	_	20	5,17	129,22	21,78	65,34	Unacceptable

Table B ID 9 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
11Cl-PF3OUdS	20,45	6,12	10	-0,59	-14,79	12,00	36,00	Acceptable
9Cl-PF3ONS	22,80	6,83	10	-0,20	-5,00	12,00	36,00	Acceptable
ADONA	43,00	12,90	10	0,13	3,37	20,80	62,40	Acceptable
HFPO-DA	66,30	19,88	10	0,14	3,59	32,00	96,00	Acceptable
PFBA	32,65	9,80	10	0,51	12,79	14,47	43,42	Acceptable
PFBS	35,40	10,63	10	0,57	14,15	15,51	46,52	Acceptable
PFDA	26,80	8,04	10	0,47	11,67	12,00	36,00	Acceptable
PFDoDA	27,35	8,21	10	0,56	13,96	12,00	36,00	Acceptable
PFDoS	28,90	8,67	10	-0,03	-0,69	14,55	43,65	Acceptable
PFDS	29,65	8,89	10	-0,16	-3,98	15,44	46,32	Acceptable
PFHpA	28,35	8,51	10	0,73	18,13	12,00	36,00	Acceptable
PFHpS	58,20	17,45	10	0,69	17,24	24,82	74,46	Acceptable
PFHxA	28,25	8,47	10	0,71	17,71	12,00	36,00	Acceptable
PFHxDA	27,10	8,12	10	-0,39	-9,67	15,00	45,00	Acceptable
PFHxS	36,50	10,95	10	0,80	20,07	15,20	45,60	Acceptable
PFNA	26,40	7,92	10	0,40	10,00	12,00	36,00	Acceptable
PFNS	29,40	8,81	10	-0,51	-12,68	16,84	50,51	Acceptable
PFOA	38,20	11,46	10	0,79	19,67	15,96	47,88	Acceptable
PFODA	27,30	8,19	10	-0,88	-22,00	17,50	52,50	Acceptable
PFOS	37,30	11,18	10	0,86	21,42	15,36	46,08	Acceptable
PFPA	28,40	8,51	10	0,73	18,33	12,00	36,00	Acceptable
PFPS	35,60	10,67	10	-0,21	-5,32	18,80	56,40	Acceptable
PFTeDA	28,20	8,46	10	0,70	17,50	12,00	36,00	Acceptable
PFTrDA	27,15	8,15	10	0,53	13,13	12,00	36,00	Acceptable
PFTrDS	18,05	5,40	10	-2,14	-53,58	19,44	58,32	Questionable
PFUnDA	29,35	8,81	10	0,89	22,29	12,00	36,00	Acceptable
PFUnDS	53,40	16,02	10	0,90	22,59	21,78	65,34	Acceptable

Table B ID 10 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFBS	39,45	0,14	60	1,09	27,21	15,51	46,52	Acceptable
PFDoDA	49,80	0,28	60	4,30	107,50	12,00	36,00	Unacceptable
PFDoS	39,70	11,03	60	1,46	36,43	14,55	43,65	Acceptable
PFDS	45,25	4,95	60	1,86	46,53	15,44	46,32	Acceptable
PFHpA	24,40	8,49	60	0,07	1,67	12,00	36,00	Acceptable
PFHpS	74,70	1,13	60	2,02	50,48	24,82	74,46	Questionable
PFHxA	41,85	6,08	60	2,98	74,38	12,00	36,00	Questionable
PFHxS	40,45	1,84	60	1,32	33,06	15,20	45,60	Acceptable
PFNS	39,75	3,82	60	0,72	18,06	16,84	50,51	Acceptable
PFOA	27,40	8,77	60	-0,57	-14,17	15,96	47,88	Acceptable
PFOS	39,75	1,56	60	1,18	29,39	15,36	46,08	Acceptable
PFPS	42,10	5,09	60	0,48	11,97	18,80	56,40	Acceptable
PFTrDA	39,95	9,19	60	2,66	66,46	12,00	36,00	Questionable
PFTrDS	31,50	10,18	60	-0,76	-18,98	19,44	58,32	Acceptable
PFUnDA	27,10	8,20	60	0,52	12,92	12,00	36,00	Acceptable
PFUnDS	84,20	0,00	60	3,73	93,30	21,78	65,34	Unacceptable

Table B ID 11 - results of participant 2nd PT round

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFBA	20,50	6,15	20	-1,17	-29,18	14,47	43,42	Acceptable
PFBS	12,50	3,75	20	-2,39	-59,69	15,51	46,52	Questionable
PFDA	11,50	3,45	20	-2,08	-52,08	12,00	36,00	Questionable
PFHxS	50,00	15,00	20	2,58	64,47	15,20	45,60	Questionable
PFOS	24,50	7,35	20	-0,81	-20,25	15,36	46,08	Acceptable

Table B ID 12 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
ADONA	39,56	4,99	30	-0,20	-4,92	20,80	62,40	Acceptable
PFBA	34,24	5,66	30	0,73	18,26	14,47	43,42	Acceptable
PFBS	34,41	3,09	30	0,44	10,94	15,51	46,52	Acceptable
PFDA	33,99	5,24	30	1,66	41,60	12,00	36,00	Acceptable
PFDoDA	26,75	6,12	30	0,46	11,46	12,00	36,00	Acceptable
PFDS	46,28	13,43	30	1,99	49,85	15,44	46,32	Acceptable
PFHpA	29,44	5,32	30	0,91	22,65	12,00	36,00	Acceptable
PFHpS	51,95	3,85	30	0,19	4,65	24,82	74,46	Acceptable
PFHxA	27,67	2,29	30	0,61	15,27	12,00	36,00	Acceptable
PFHxDA	33,05	9,00	30	0,41	10,15	15,00	45,00	Acceptable
PFHxS	40,16	3,10	30	1,28	32,11	15,20	45,60	Acceptable
PFNA	29,86	1,90	30	0,98	24,42	12,00	36,00	Acceptable
PFOA	42,03	5,97	30	1,27	31,65	15,96	47,88	Acceptable
PFODA	44,79	6,12	30	1,12	27,97	17,50	52,50	Acceptable
PFOS	37,47	9,22	30	0,88	21,96	15,36	46,08	Acceptable
PFPA	30,33	6,17	30	1,05	26,35	12,00	36,00	Acceptable
PFPS	39,71	4,35	30	0,22	5,60	18,80	56,40	Acceptable
PFTeDA	19,40	6,59	30	-0,77	-19,17	12,00	36,00	Acceptable
PFTrDA	30,52	4,54	30	1,09	27,15	12,00	36,00	Acceptable
PFUnDA	32,35	4,10	30	1,39	34,77	12,00	36,00	Acceptable

Table B ID 13 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
11Cl-PF3OUdS	18,45	4,93	60	-0,93	-23,13	12,00	36,00	Acceptable
9Cl-PF3ONS	24,75	6,01	60	0,13	3,13	12,00	36,00	Acceptable
HFPO-DA	60,55	17,50	60	-0,22	-5,39	32,00	96,00	Acceptable
PFBS	32,70	2,68	60	0,22	5,44	15,51	46,52	Acceptable
PFDA	22,90	2,56	60	-0,18	-4,58	12,00	36,00	Acceptable
PFDoDA	23,05	4,82	60	-0,16	-3,96	12,00	36,00	Acceptable
PFDS	22,45	7,34	60	-1,09	-27,30	15,44	46,32	Acceptable
PFHpA	24,45	2,32	60	0,07	1,88	12,00	36,00	Acceptable
PFHpS	46,40	9,88	60	-0,26	-6,53	24,82	74,46	Acceptable
PFHxA	24,45	4,55	60	0,08	1,88	12,00	36,00	Acceptable
PFHxS	31,80	2,89	60	0,18	4,61	15,20	45,60	Acceptable
PFNA	24,05	2,04	60	0,01	0,21	12,00	36,00	Acceptable
PFNS	23,40	6,79	60	-1,22	-30,50	16,84	50,51	Acceptable
PFOA	30,65	2,85	60	-0,16	-3,99	15,96	47,88	Acceptable
PFOS	31,10	7,50	60	0,05	1,24	15,36	46,08	Acceptable
PFPA	25,35	4,36	60	0,23	5,63	12,00	36,00	Acceptable
PFPS	34,80	5,64	60	-0,30	-7,45	18,80	56,40	Acceptable
PFTeDA	23,90	4,52	60	-0,02	-0,42	12,00	36,00	Acceptable
PFUnDA	23,80	2,76	60	-0,03	-0,83	12,00	36,00	Acceptable

Table B ID 14 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
ADONA	14,50	3,60	10	-2,61	-65,14	20,80	62,40	Questionable
PFBA	41,50	15,50	10	1,73	43,36	14,47	43,42	Acceptable
PFDA	56,00	13,80	10	5,33	133,33	12,00	36,00	Unacceptable
PFDoDA	61,50	19,70	10	6,25	156,25	12,00	36,00	Unacceptable
PFHxS	78,50	19,70	10	6,33	158,22	15,20	45,60	Unacceptable
PFNA	50,00	18,70	10	4,33	108,33	12,00	36,00	Unacceptable
PFOS	25,00	9,90	10	-0,74	-18,62	15,36	46,08	Acceptable
PFPA	31,50	10,20	10	1,25	31,25	12,00	36,00	Acceptable
PFUnDA	83,00	22,50	10	9,83	245,83	12,00	36,00	Unacceptable

Table B ID 15 - results of participant 2nd PT round.

Parameter	xi [ng/L]	u [ng/L]	Method	z-score	D [%]	LL [ng/L]	UL [ng/L]	Performance
PFBA	22,35	5,80	10	-0,91	-22,79	14,47	43,42	Acceptable
PFBS	30,95	7,50	10	-0,01	-0,20	15,51	46,52	Acceptable
PFDA	20,50	5,30	10	-0,58	-14,58	12,00	36,00	Acceptable
PFDoDA	23,30	6,20	10	-0,12	-2,92	12,00	36,00	Acceptable
PFDoS	50,90	13,80	10	3,00	74,91	14,55	43,65	Questionable
PFDS	23,90	6,10	10	-0,90	-22,60	15,44	46,32	Acceptable
PFHpA	22,15	8,60	10	-0,31	-7,71	12,00	36,00	Acceptable
PFHpS	43,25	11,50	10	-0,51	-12,87	24,82	74,46	Acceptable
PFHxA	22,85	6,40	10	-0,19	-4,79	12,00	36,00	Acceptable
PFHxDA	15,95	4,40	10	-1,87	-46,83	15,00	45,00	Acceptable
PFHxS	34,50	9,30	10	0,54	13,49	15,20	45,60	Acceptable
PFNA	21,20	5,90	10	-0,47	-11,67	12,00	36,00	Acceptable
PFNS	23,35	6,40	10	-1,23	-30,65	16,84	50,51	Acceptable
PFOA	28,10	7,60	10	-0,48	-11,97	15,96	47,88	Acceptable
PFOS	28,10	8,00	10	-0,34	-8,53	15,36	46,08	Acceptable
PFPA	23,10	6,90	10	-0,15	-3,75	12,00	36,00	Acceptable
PFPS	32,00	9,00	10	-0,60	-14,89	18,80	56,40	Acceptable
PFTeDA	23,40	6,40	10	-0,10	-2,50	12,00	36,00	Acceptable
PFTrDA	29,20	8,50	10	0,87	21,67	12,00	36,00	Acceptable
PFTrDS	33,10	10,00	10	-0,59	-14,87	19,44	58,32	Acceptable
PFUnDA	20,75	6,30	10	-0,54	-13,54	12,00	36,00	Acceptable
PFUnDS	96,25	28,70	10	4,84	120,96	21,78	65,34	Unacceptable

Fig. 1. Chart of z-score pharmaceuticals

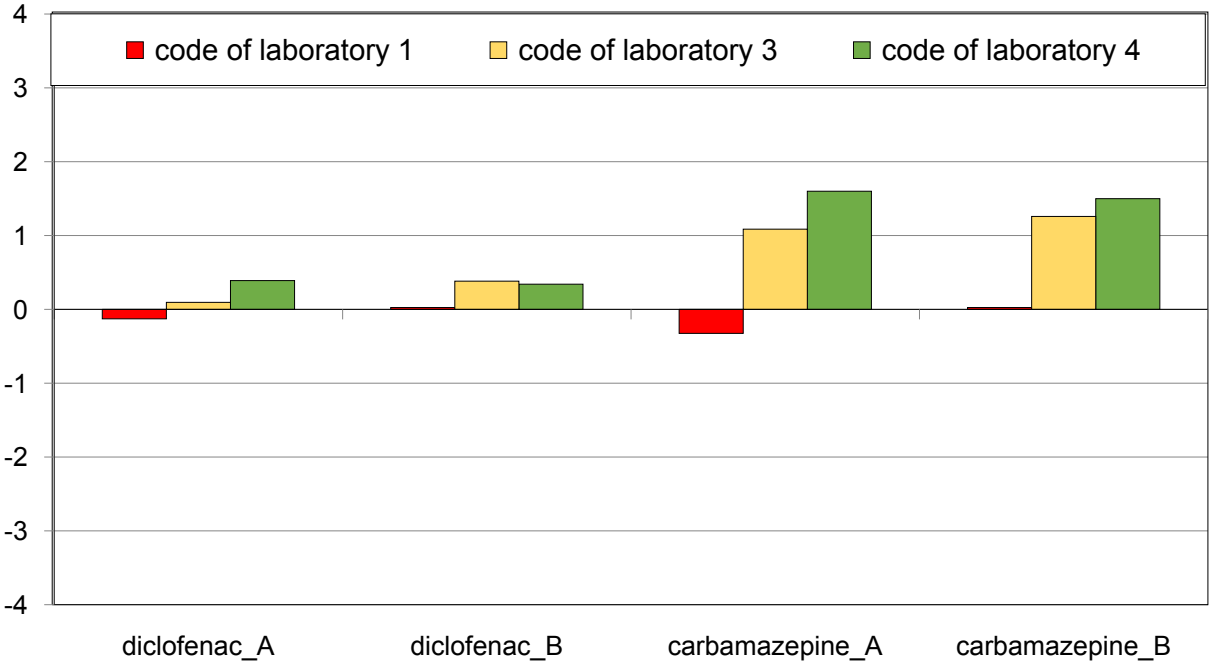


Fig. 2. Chart of z-score PFAS_1

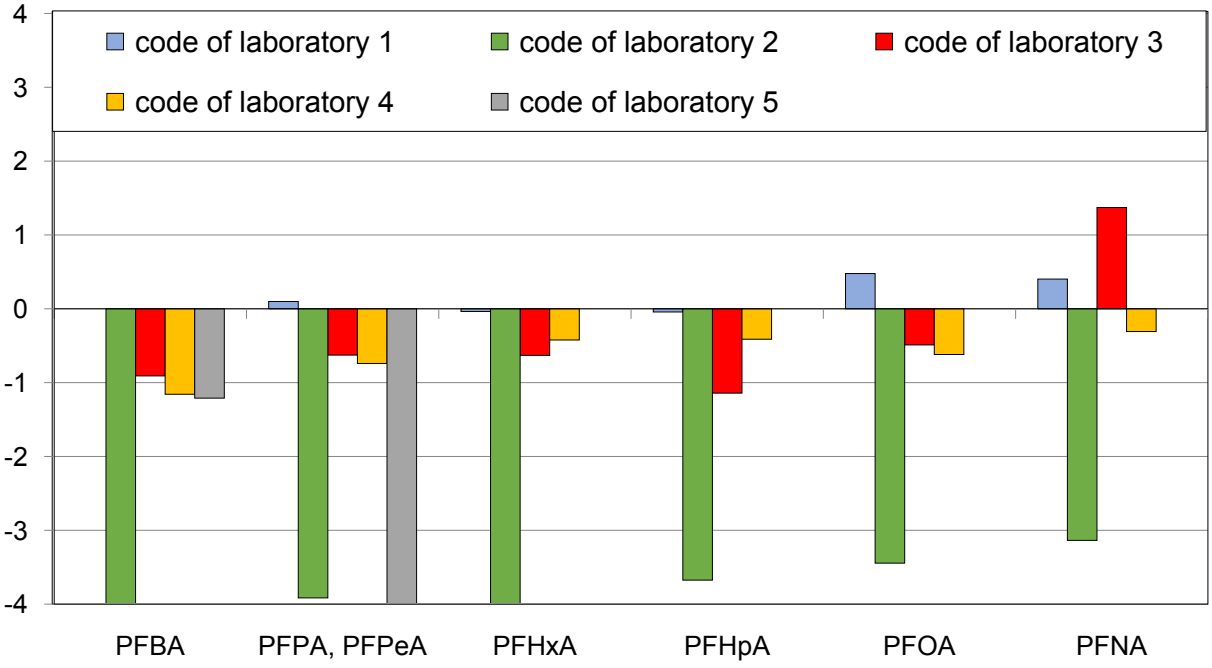


Fig. 3. Chart of z-score PFAS_2

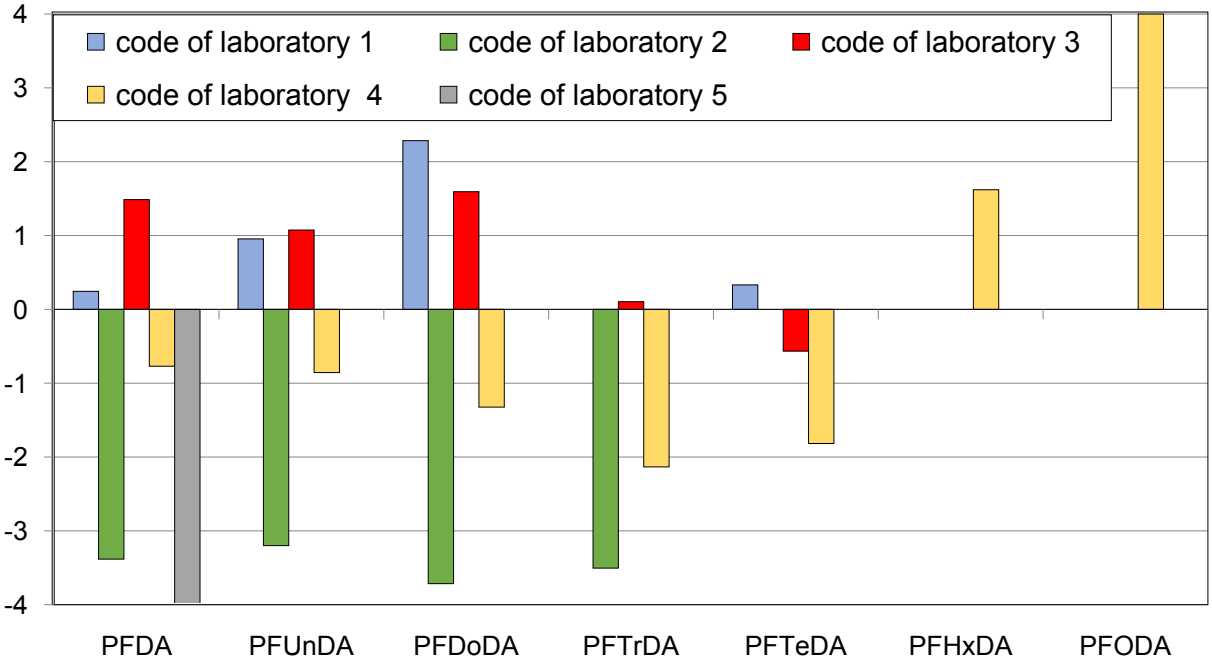


Fig. 4. Chart of z-score PFAS_3

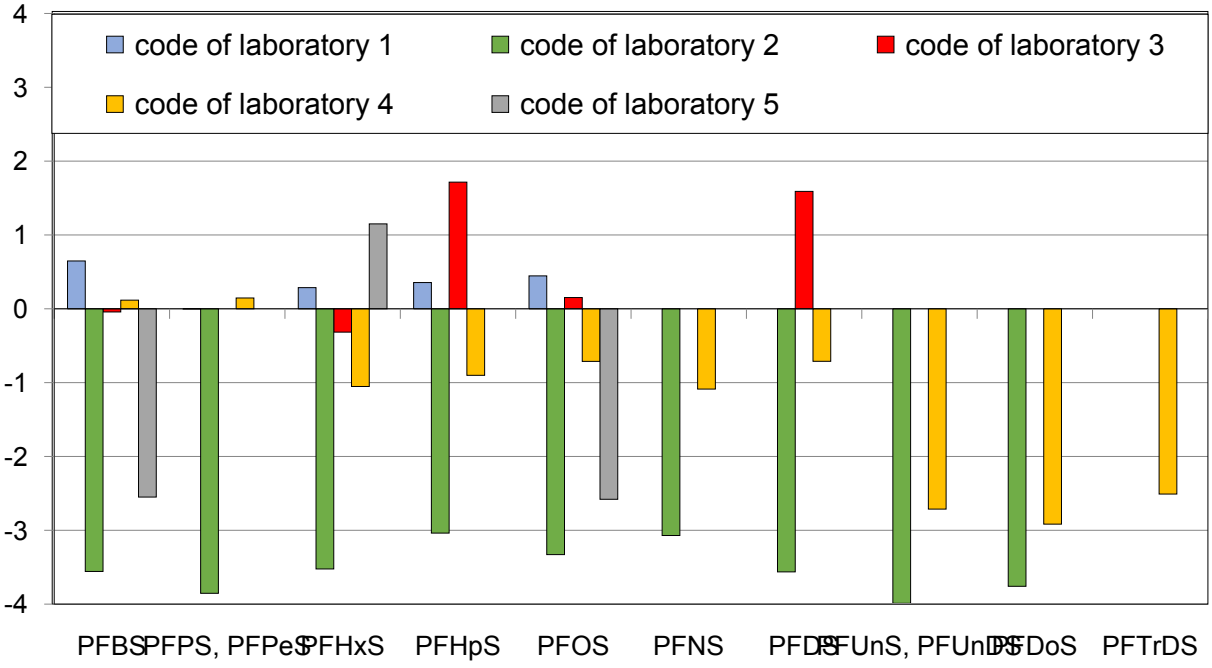


Fig. 5. Chart of z-score PFAS_4

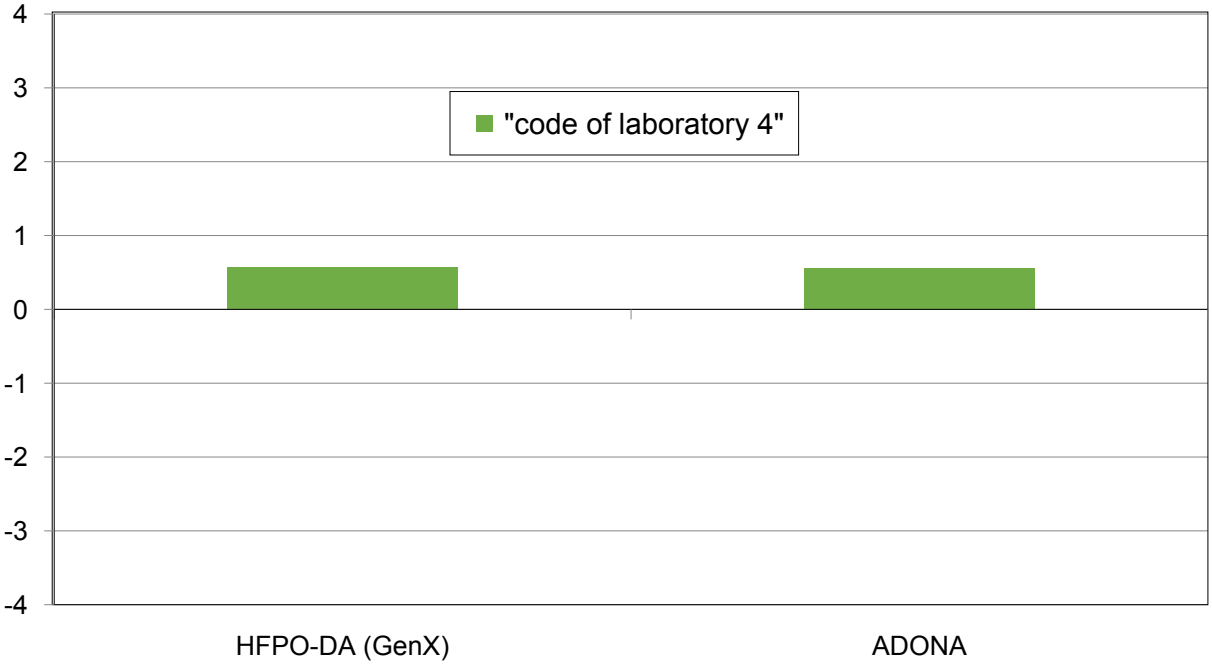


Fig. 6. Range of Extended Uncertainty (Pharm)

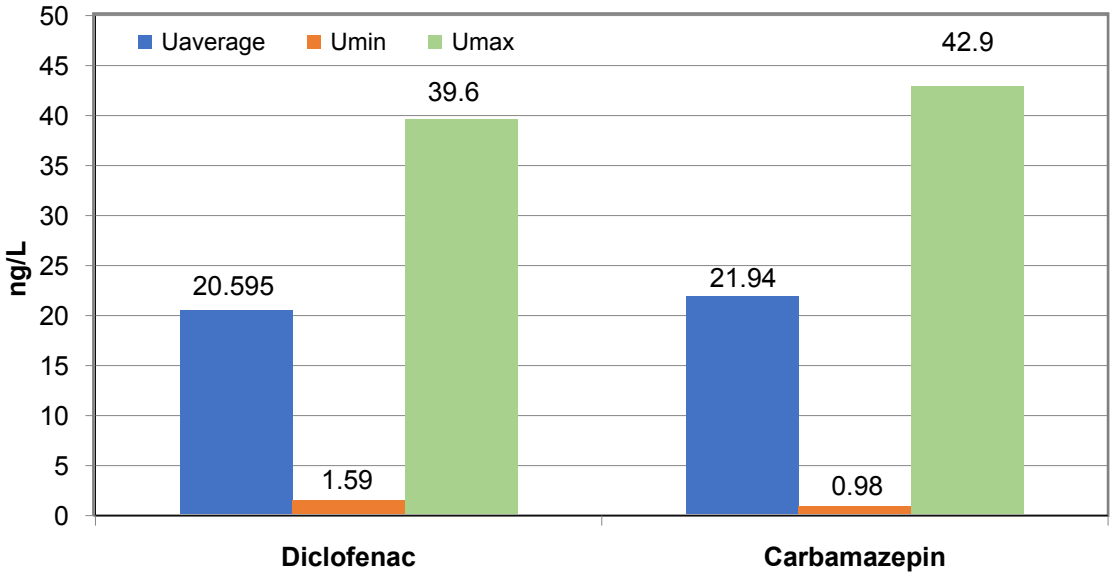
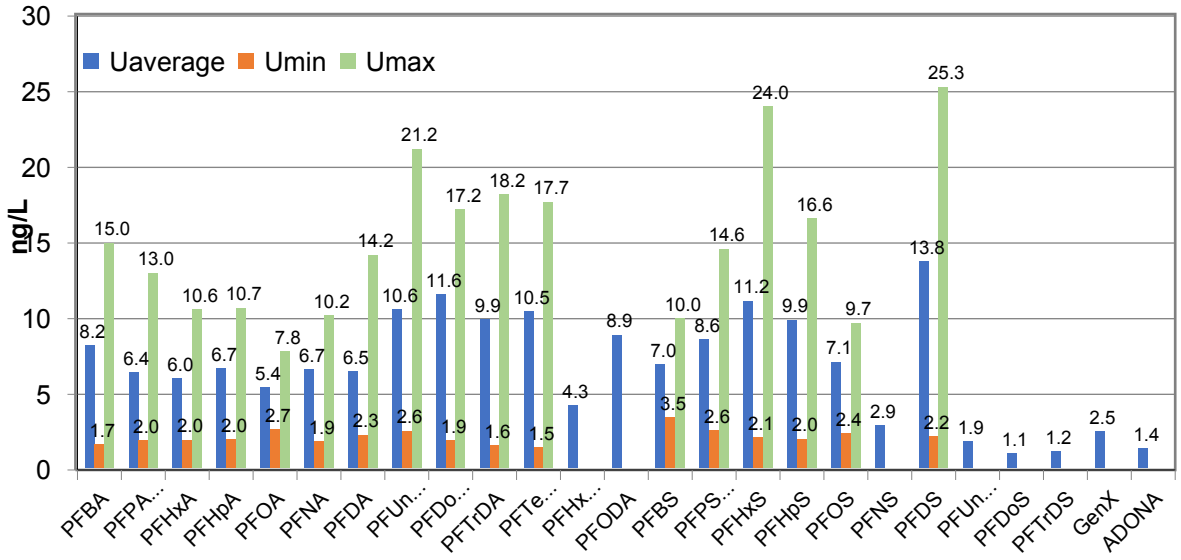


Fig. 7. Range of Extended Uncertainty (PFAS)



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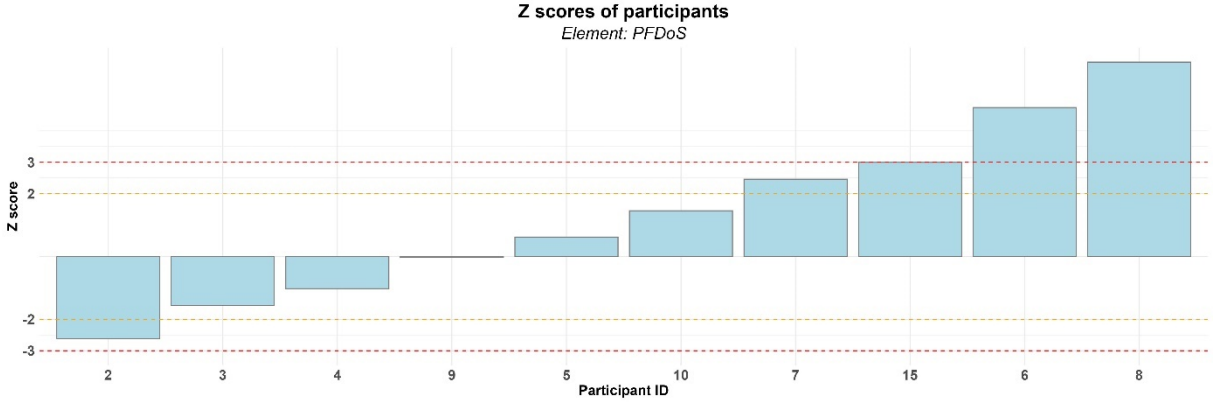

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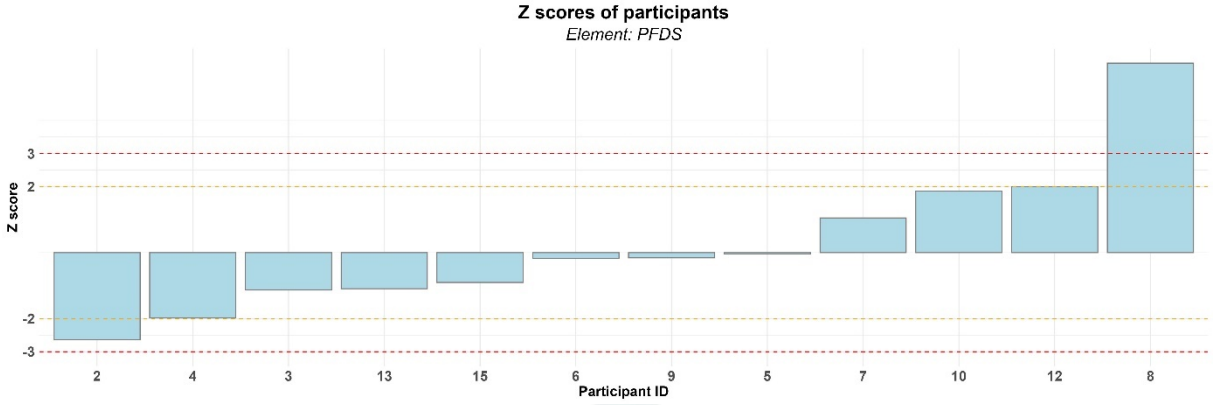

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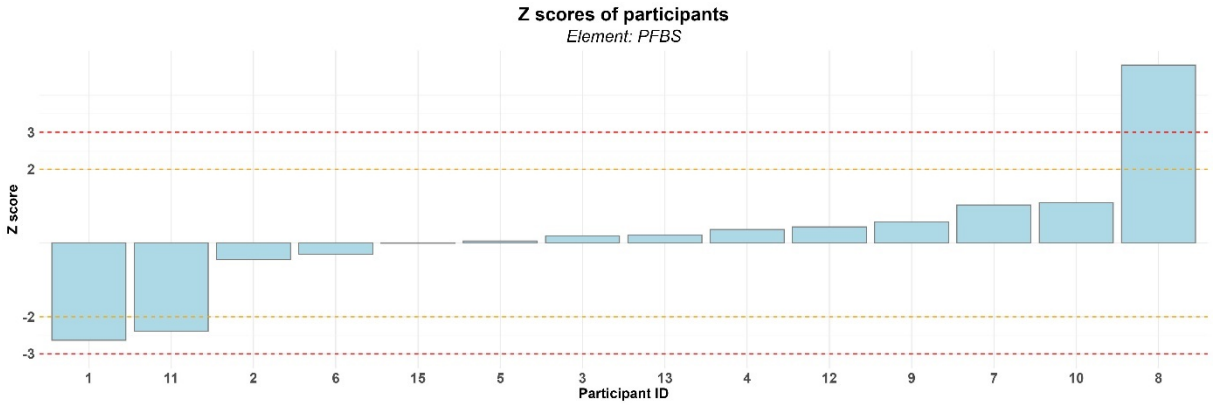

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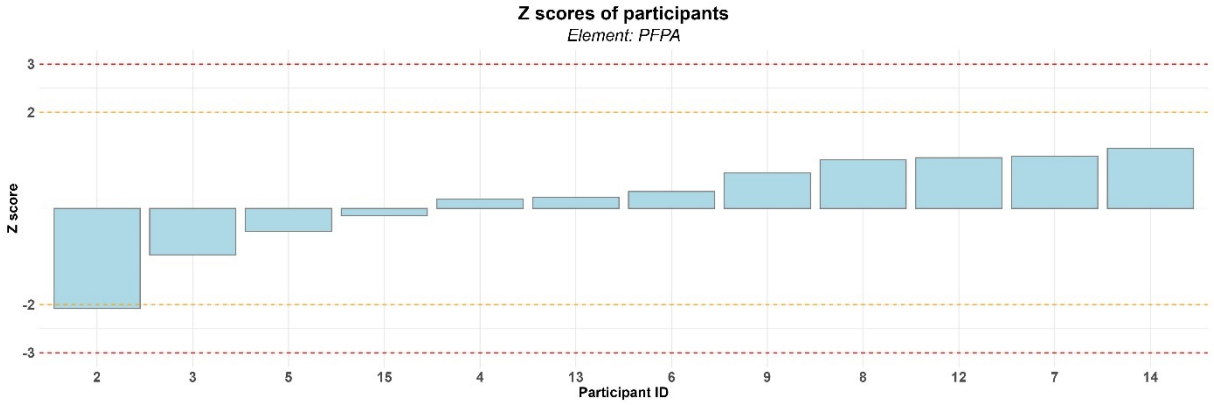

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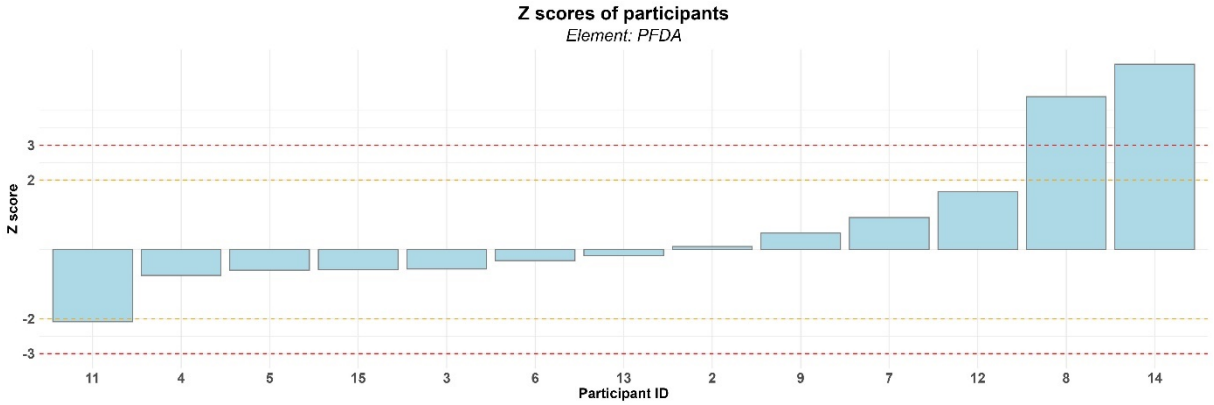

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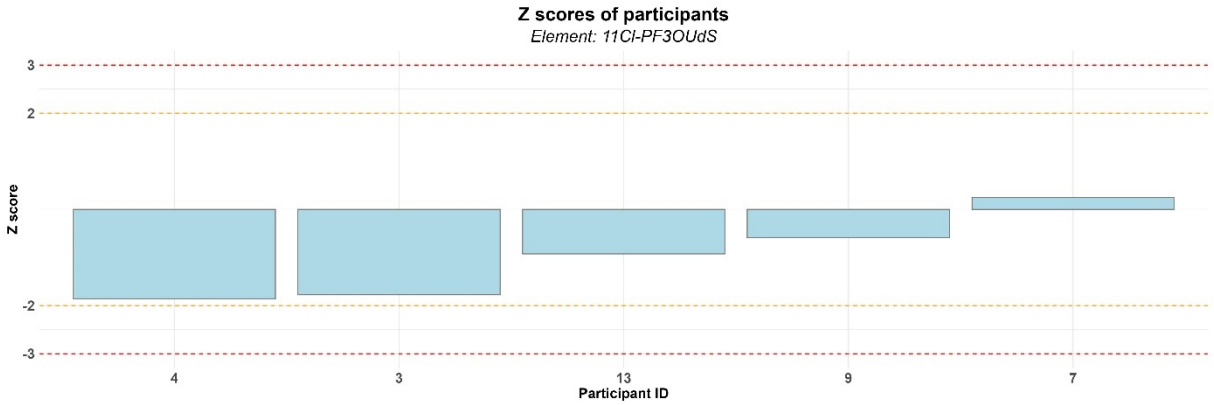

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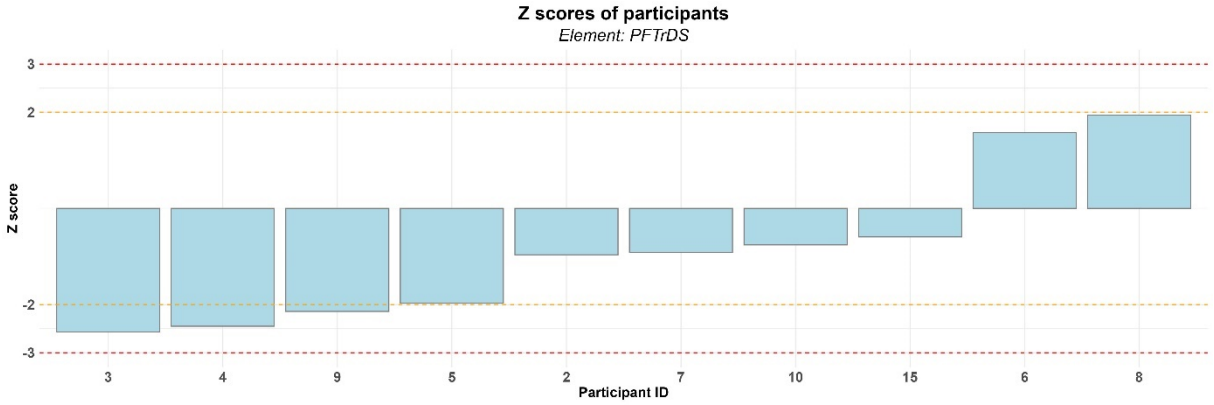

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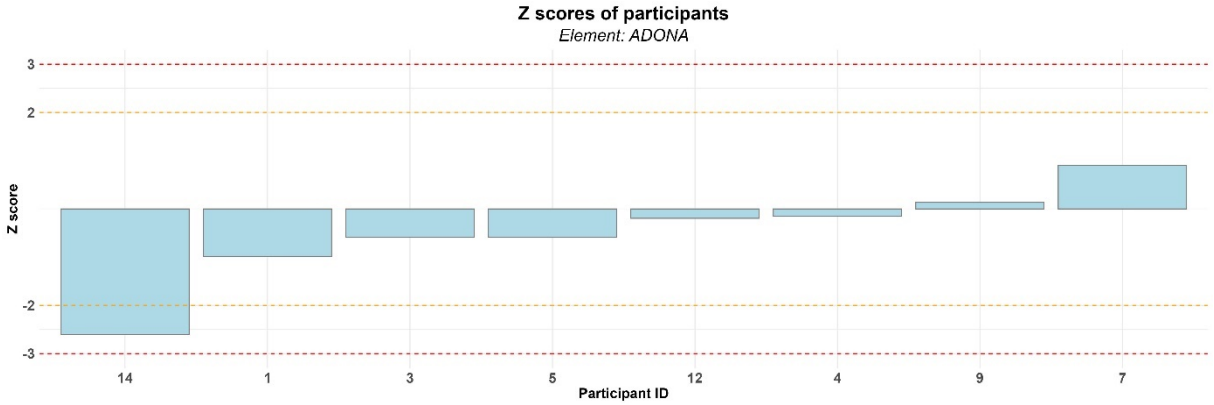

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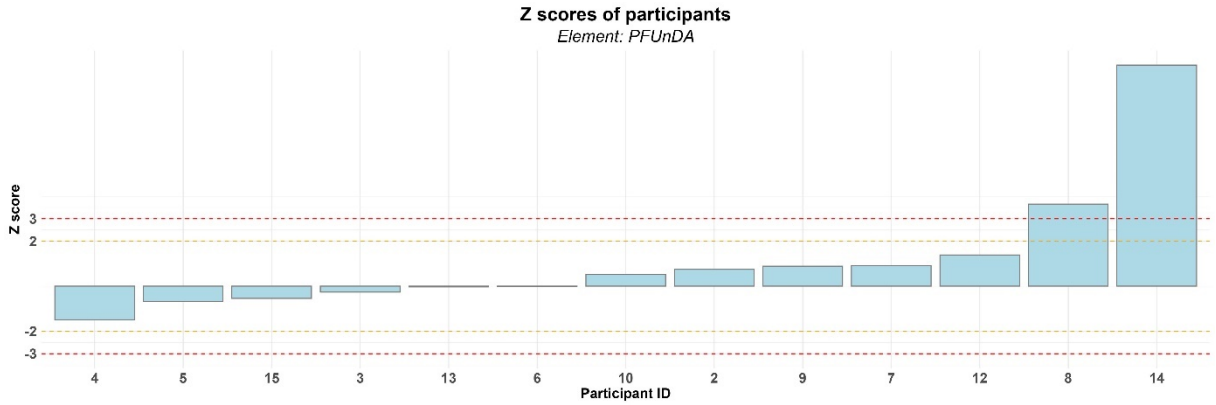

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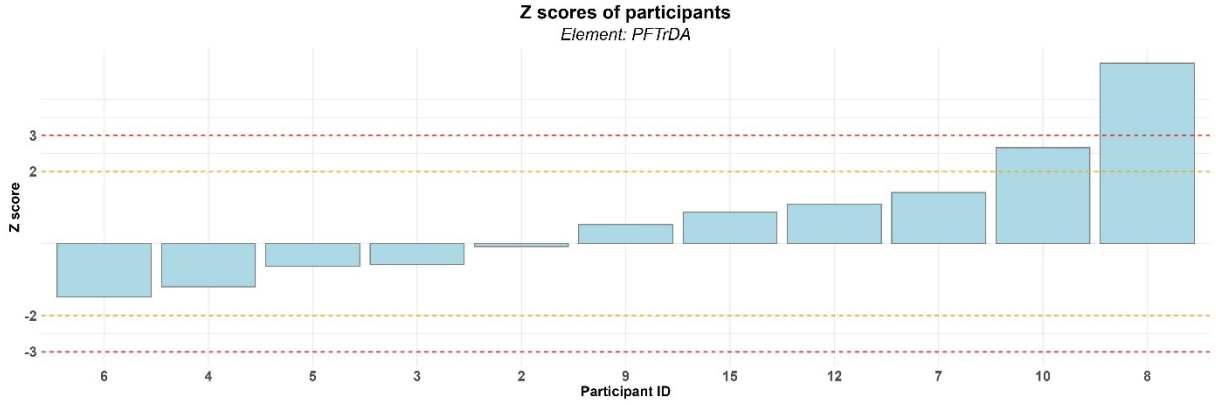

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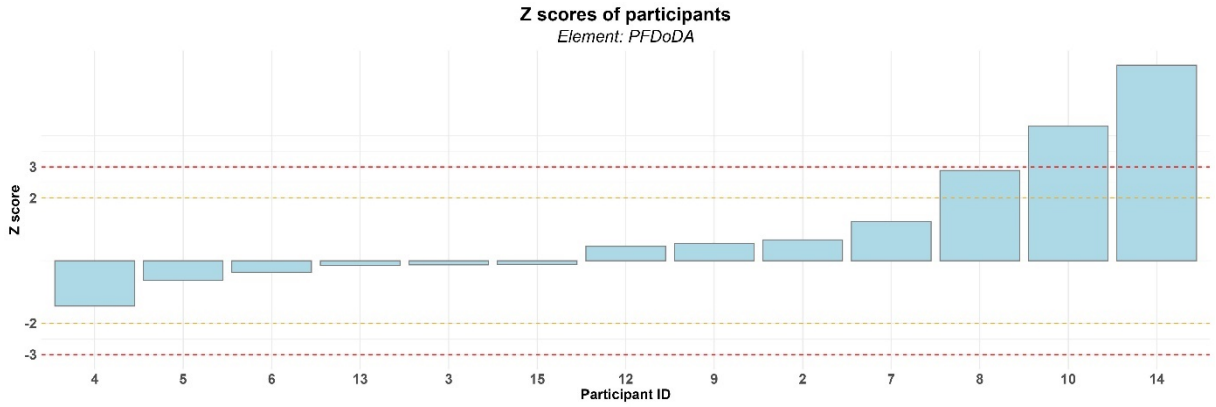

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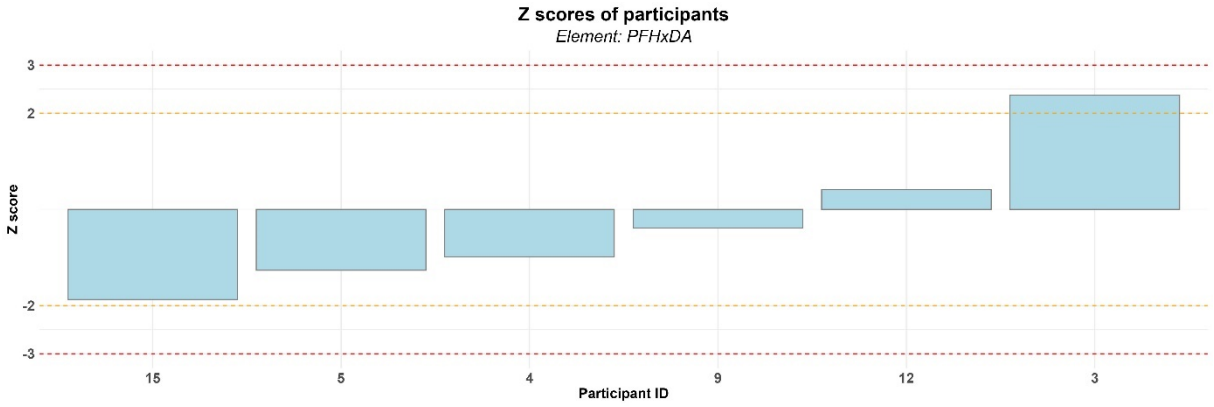

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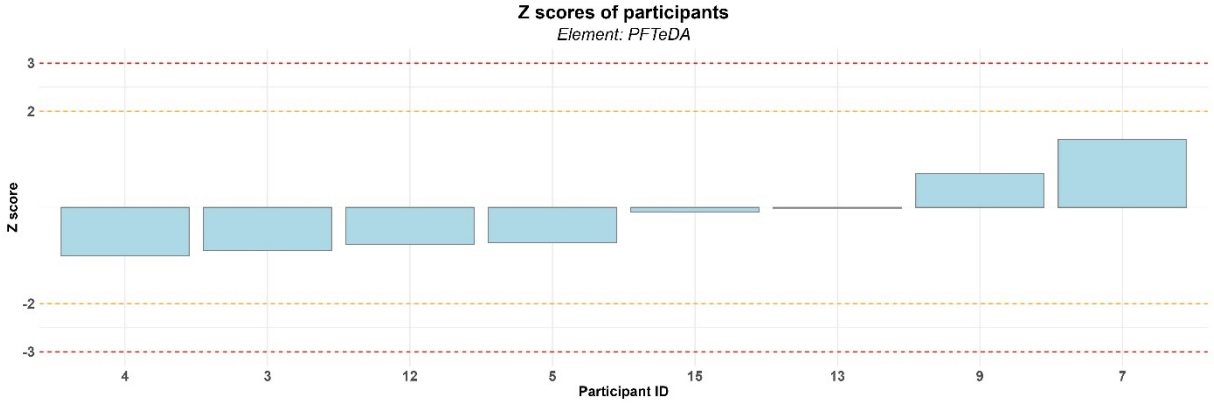

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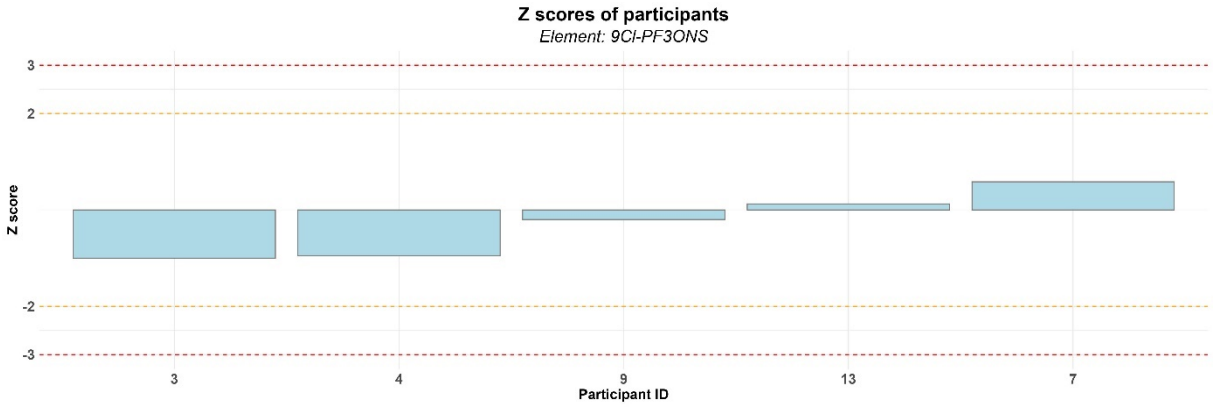

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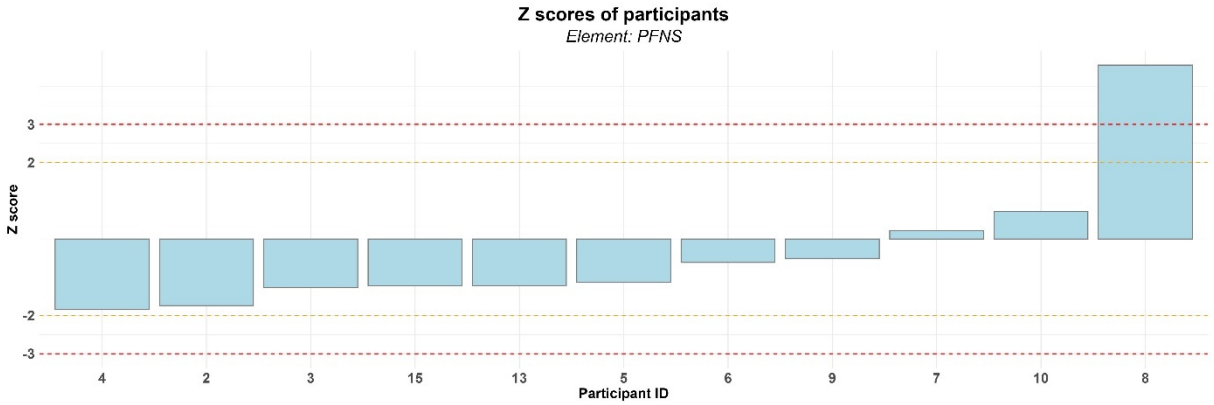

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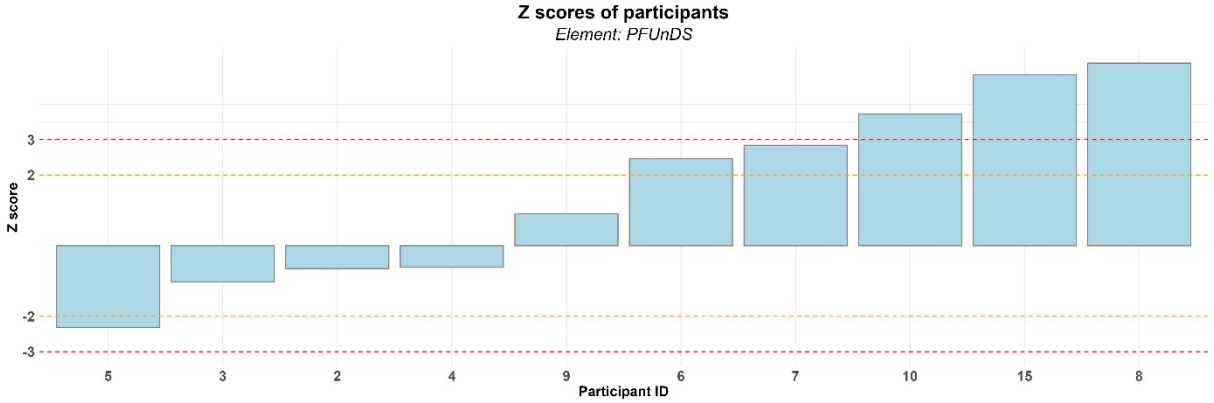

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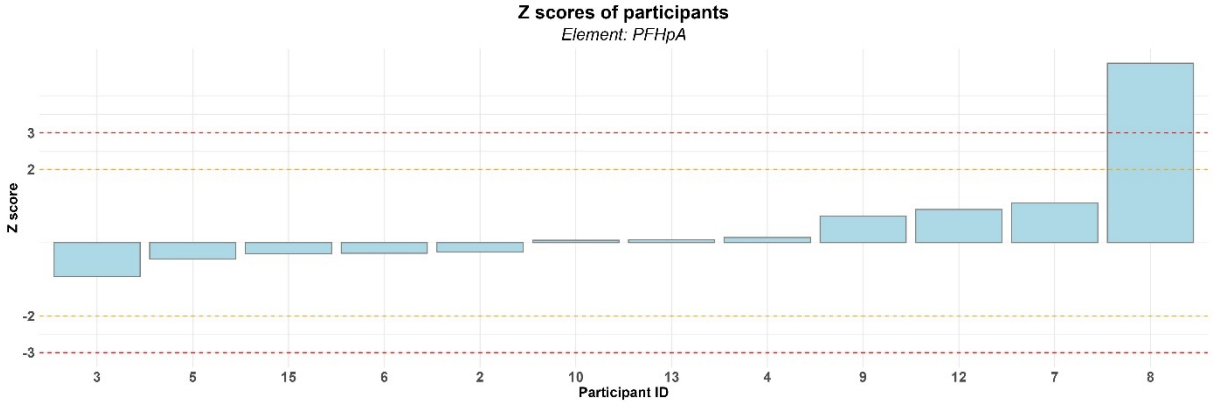

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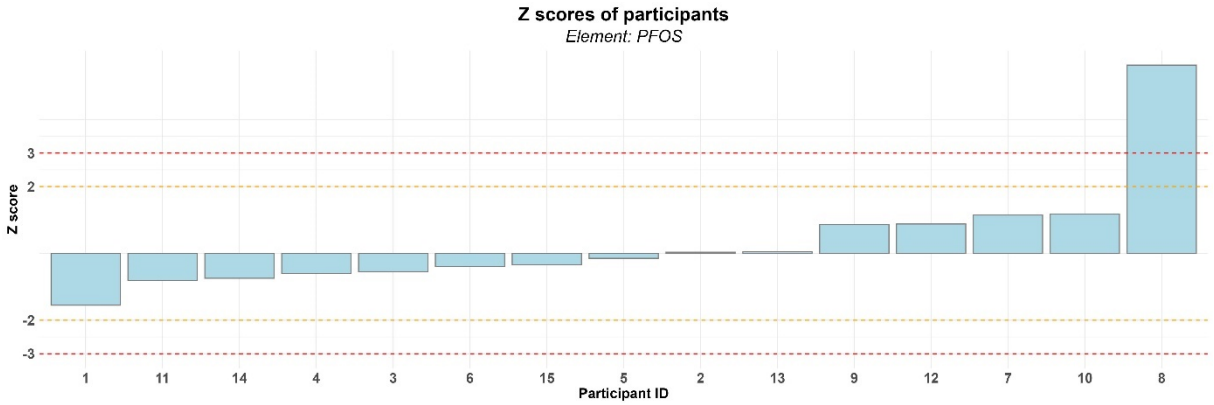

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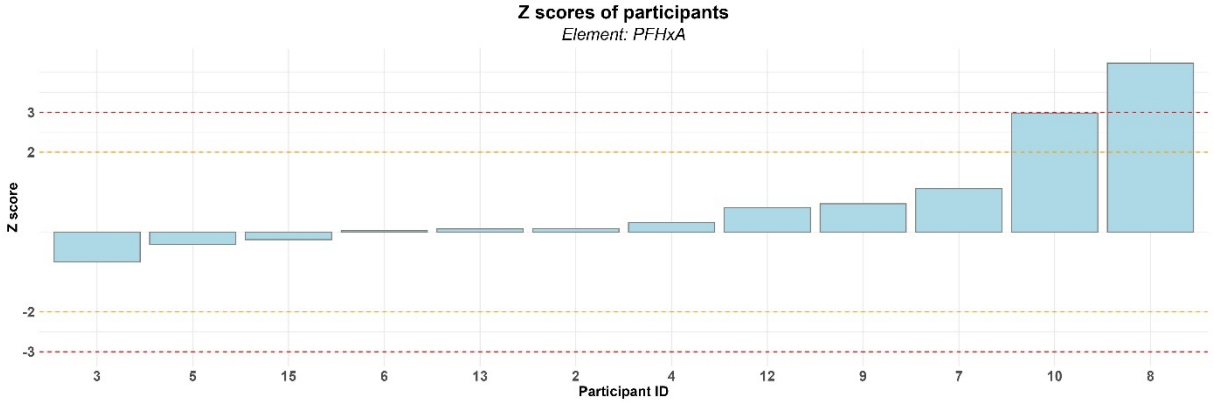

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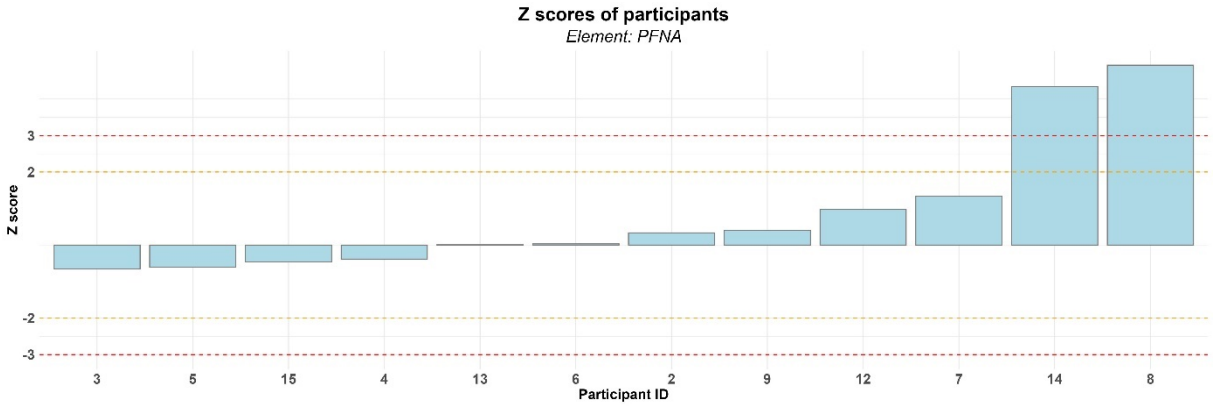

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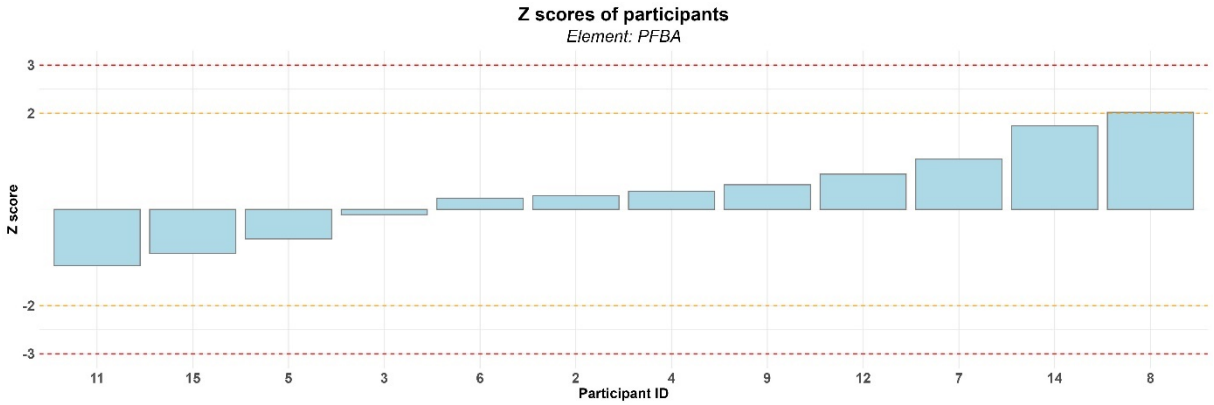

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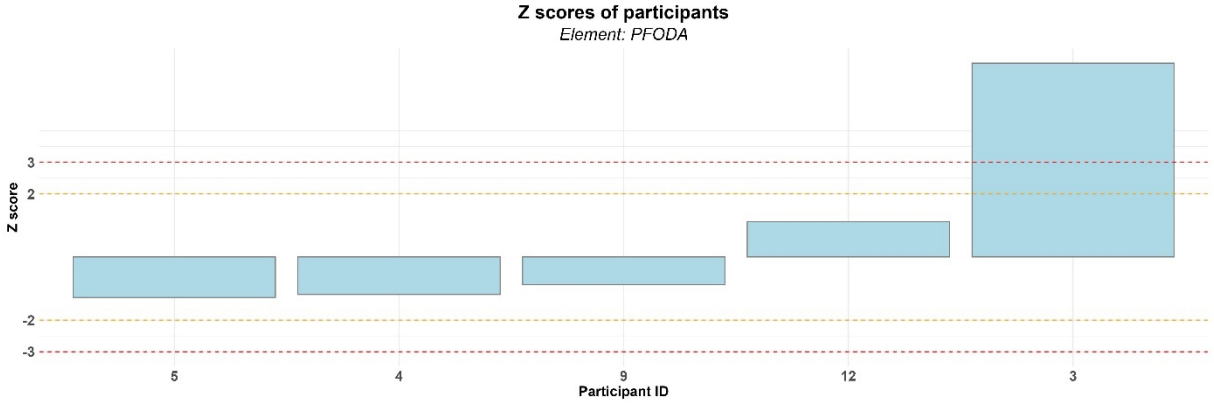

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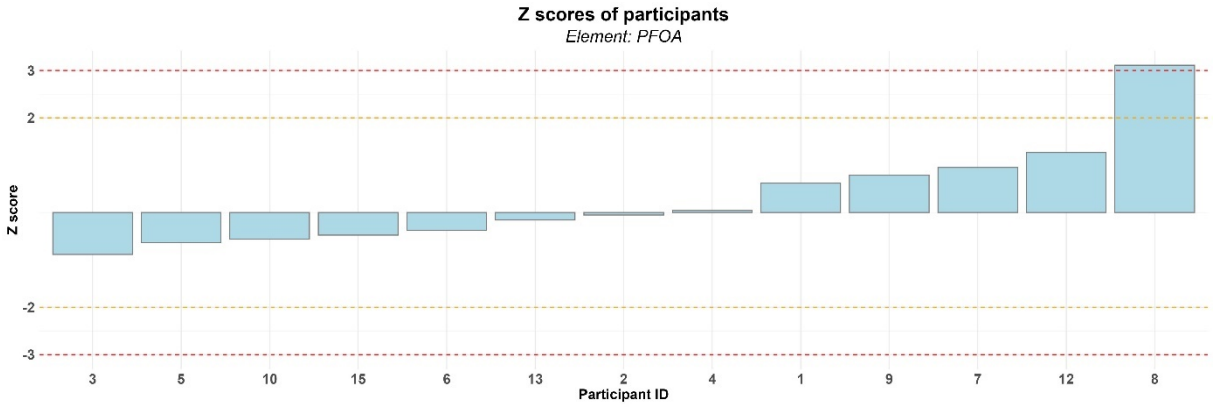

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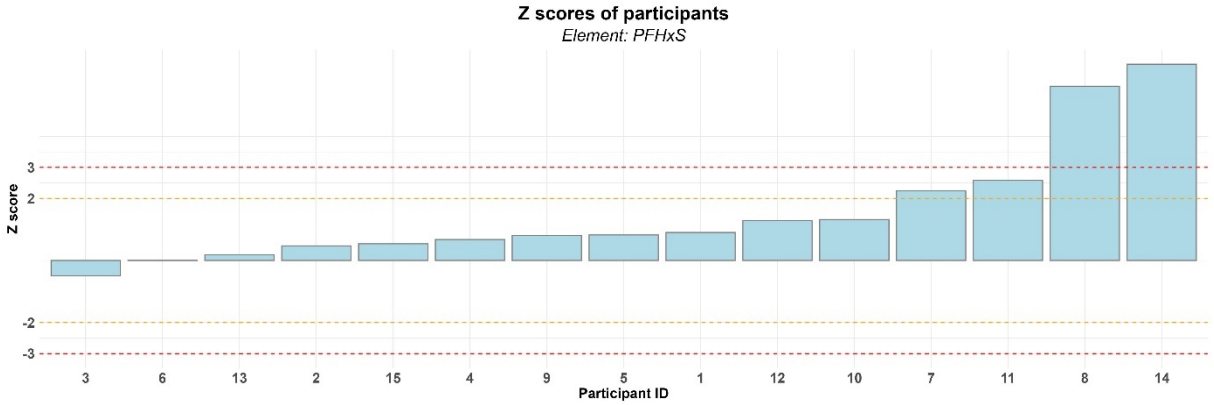

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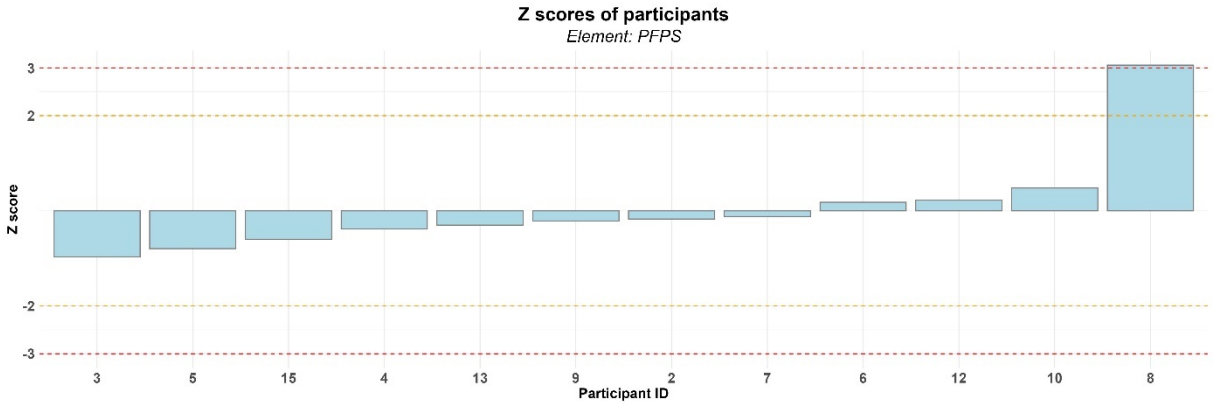

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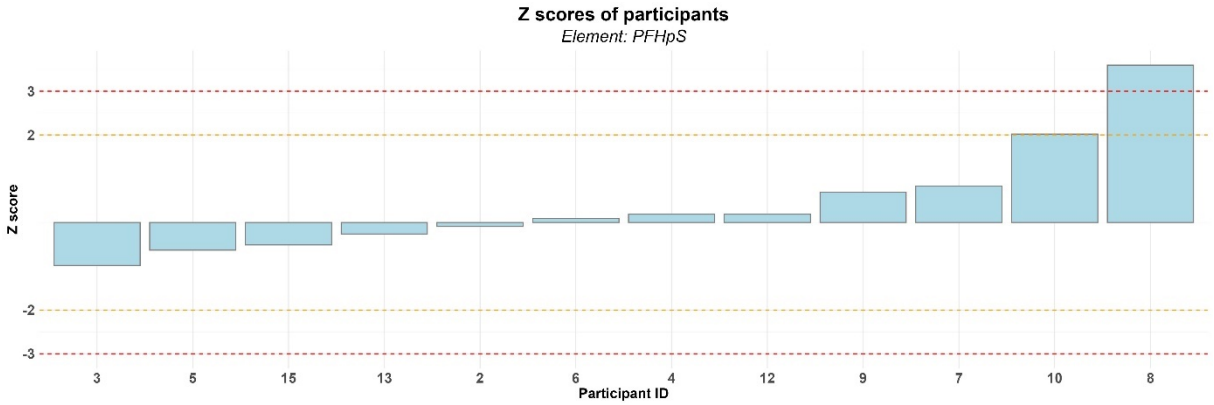

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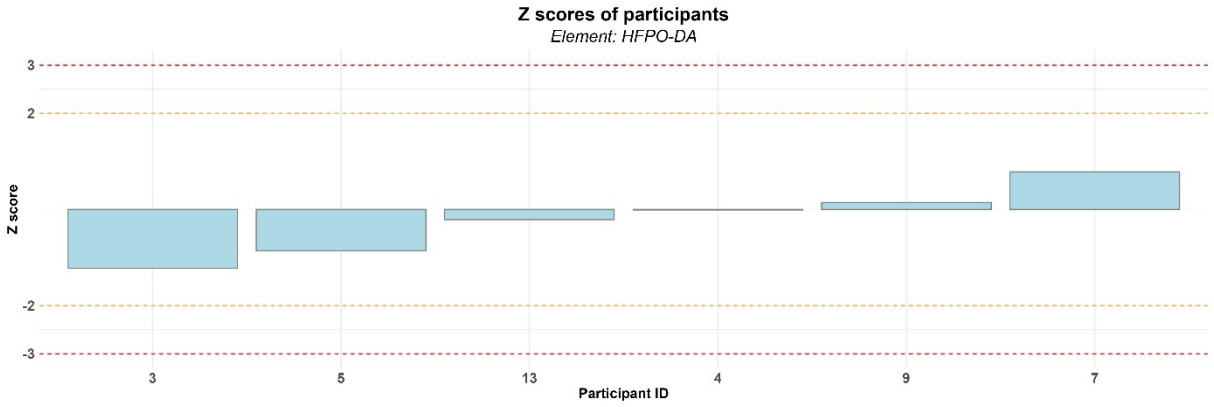

Figure 35: