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D3.4 – Assessing the treatment performance of PFAS degradation/immobilisation in the liquid and solid sediment fractions: a toxicity risk assessment

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Executive Summary

This report presents the outcomes of a comprehensive study on the removal of PFAS (Per- and Polyfluoroalkyl Substances) from contaminated sediments using thermal, chemical, mechanical, and immobilization techniques. The effectiveness of each method was evaluated through analytical chemistry, bioassays, and mechanical testing to assess environmental safety and the potential for material reuse.

Sediment washing using hydrogen peroxide (H_2O_2 , 2 mmol/g) combined with ultrasonic cavitation achieved the highest PFAS removal (72%) within 180 minutes, outperforming acid (23%) and alkaline (0%) treatments. The primary PFAS compounds detected in the washing solutions included 6:2 FTSA, 6:2 FTAB, and PFHxA. Ultrasonic cavitation was particularly effective when the initial PFAS concentrations were higher.

Pyrolysis effectively removed all detectable PFAS from both highly contaminated sediments (the Netherlands) and less contaminated sediments (Ancona) at temperatures ranging from 400°C to 800°C. No PFAS were detected in the treated solids, although a single detection of 6:2 FTS in the bio-oil occurred at 600°C for the Netherlands sediment. This thermal treatment demonstrated high efficiency, especially in reducing PFAS levels in solid matrices to below quantification limits.

Mechanical testing of the treated sediment mixtures (M1: 90% B + 10% A; M2: 80% B + 20% A, where B = granular mixture and A = sediments stabilized with lime) confirmed that they met the required strength standards for use in unbound foundation layers, embankments, and road sub-bases, supporting their reuse in civil engineering applications.

Leaching tests showed that PFAS release occurred only when acid or lime was introduced, not from the treated sediments themselves. PFAS contamination in leachates (e.g., 6:2 FTS and PFBS) was attributed to these additives rather than the sediment matrix. Stabilization with lime and cement successfully limited PFAS mobility under neutral and alkaline conditions.

Toxicity assessment using the PFAS CALUX bioassay indicated that H_2O_2 -treated sediments exhibited significantly reduced or undetectable PFAS-related toxicity for the less contaminated sediment (from Ancona). In contrast, the most contaminated sediments (from the Netherlands) retained moderate CALUX activity post-treatment due to their higher initial contamination levels. Leachates from ECOSEDRA-treated and immobilized sediments showed minimal bioactivity, with the lowest toxicity observed in acidic leachates.

In the DoA, the use of zero valent iron (ZVI) microparticles was initially planned for the reductive defluorination treatment of the sediment washing solution. However, a study conducted by Tur et al. (2025) [17] within the PROMISCES project demonstrated that nano-sized palladium-coated ZVI (nPd/ZVI) primarily removes PFAS—specifically PFOA and PFOS—through sorption, with minimal evidence of degradation. Based on these findings, the application of ZVI-based materials was deemed not suitable for achieving PFAS degradation in the sediment washing solution.

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List of abbreviations

4:2 FTSA : 4:2 Fluorotelomer Sulfonic Acid

6:2 FTAB : 6:2 Fluorotelomer sulfonamide betaine

6:2 FTS : *6:2-fluorotelomersulfonic acid*

6:2 FTSA : 6:2 Fluorotelomer Sulfonic Acid

8:2 FTSA : 8:2 Fluorotelomer Sulfonic Acid

ASTM : American Society for Testing and Materials

C6O4 : perfluoro([5-methoxy-1,3-dioxolan-4-yl]oxy) acetic acid (C₆HF₉O₆), commercially known as C6O4

DI Water : Deionised water

DMSO : Dimethyl Sulfoxide

DoA : Description of the Action

EPA : Environmental Protection Agency

EtFOSAA : N-ethyl perfluorooctane sulfonamido acetic acid

H₂O₂ : hydrogen peroxide

HFPO-DA (= GenX) : hexafluoropropylene oxide dimer acid

HNO₃ : Nitric acid

KOH : Potassium hydroxide

LC-MS/MS : Liquid Chromatography coupled to tandem Mass Spectrometry

LOQ : Limit of quantification

MeFOSAA : Methylperfluorooctane sulfonamidoacetic acid

meq/g : milliequivalent per gram

MRM : multiple reaction monitoring

NaDONA : Sodium dodecafluoro-3H-4,8-dioxanonanoate

NaOH : sodium hydroxide

nPd/ZVI : *nano-sized palladium-coated zero-valent iron microparticles*

PFAS : Per- and polyfluoroalkyl substances

PFBA : Perfluorobutanoic acid

PFBS : Perfluorobutane sulfonate

PFDA : Perfluorodecanoic acid

PFDoDA : Perfluorododecanoic acid

PFDoDS : Perfluorodecanesulfonic acid

PFDS : Perfluorodecanesulfonate

PFHpA : Perfluoroheptanoic acid

PFHpS : Perfluoroheptane sulfonic acid
PFHxA : Perfluorohexanoic Acid
PFHxS : perfluorohexane sulfonic acid
PFNA : Perfluorononanoic acid
PFNS : Perfluorononanesulfonic acid
PFOA : Perfluorooctanoic acid
PFOS : perfluorooctane sulfonate
PFOSA : *Perfluorooctanesulfonamide*
PFPeA : Perfluoropentanoic Acid
PFPeS : Perfluoropentane sulfonic acid
PFTeDA : Perfluorotetradecanoic acid
PFTrDA : Perfluorotridecanoic acid
PFTrDS : Perfluorotridecanesulfonic acid
PFUnDA : Per- fluoroundecanoic acid
PFUnDS : Perfluoroundecanesulfonic acid
RSD : Relative Standard Deviation
T4 : natural ligand thyroxine
THF MeOH : *Tetrahydrofuran (THF) and methanol (MeOH)*
TR β Calux : thyroid hormone receptor beta (TR β) Calux
TTR : transporter protein transthyretin
ZVI : Zero valent iron

1 Introduction

Dredged sediment comes from activities such as deepening waterways, harbour maintenance, or construction. When contaminated with PFAS, these sediments can act as reservoirs for persistent pollutants. Despite this, dredged sediments have the potential to support a circular economy by being repurposed in construction, land reclamation, or soil enhancement. However, the presence of pollutants like PFAS complicates their reuse due to environmental and health concerns. To align with circular economy principles, the PROMISCES project aims to develop a sediment treatment strategy based on sediment washing, which can help minimize PFAS impacts while enabling safe material recovery. As part of the national Italian project ECOSEDRA, a pilot-scale plant was developed to create and validate an innovative, eco-sustainable solution for the management of sediments from port dredging operations at a demonstrative scale (TRL > 7). Specifically, a prototype treatment facility processing 25–50 kg/h of dredged sediment from the Ancona Seaport was implemented to produce construction materials for reuse in road embankments. The ECOSEDRA process begins with mechanical separation of the sediments into coarse and fine fractions, followed by washing of the fine fractions using various cleaning solutions.

Deliverable D3.3, *“Overview of Transfer and Conversion of PFAS during Sediment Treatment/Valorisation,”* reports on the presence and behaviour of PFAS in dredged sediments collected from the Port of Ancona and a depot in the Netherlands, and examines their fate during the ECOSEDRA washing treatments. This current deliverable focuses on the treatment of the resulting washing solutions.

In the ECOSEDRA process, treated sediments are immobilized and solidified to produce concrete suitable for use in road embankments. This was achieved by adding lime to the sediments and mixing them with a granular aggregate and cement. In parallel, within the PROMISCES project, leaching tests were conducted to assess the risk of PFAS release from these recovered materials used in construction. While ECOSEDRA’s soil washing process reduced PFAS concentrations, complete removal was not achieved.

As an alternative to soil washing, pyrolysis (thermal degradation) was tested to treat dredged sediments. This deliverable includes:

- Treatment of sediment washing solutions via ultrasonic cavitation,
- A procedure for solidification/immobilization of treated sediments into concrete for road embankments,
- PFAS leaching test results for both treated sediments and solidified materials,
- PFAS removal performance through pyrolysis of low-contaminated sediments from Ancona and highly contaminated sediments from the Netherlands.

In the DoA, it was initially planned to apply the reductive defluorination treatment of sediment washing solution by using zero valent iron (ZVI) microparticles. In a study conducted by Tur et al. (2025) [17] within the PROMISCES project, an in-depth investigation was carried out on the interactions between nano-sized palladium-coated zerovalent iron microparticles (nPd/ZVI) and per- and polyfluoroalkyl substances (PFAS), specifically perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The results indicate that sorption is the predominant mechanism for PFAS abatement, with minimal degradation observed. Consequently, the application of ZVI-based materials for the treatment of the sediment washing solution was not considered to be of interest for the degradation of PFAS in the sediment washing solution.

2 Methodology

2.1 Sediments

The dredged sediments used for studying PFAS removal through thermal treatments, as well as PFAS leaching and immobilization, were sourced from two locations: the harbour of Ancona in Italy and a depot of fluvial sediments in the Netherlands. The Ancona sediments were collected from both a reclaimed sedimentation tank and the docks within the Harbor of Ancona (Figure 1).



Figure 1: Points of collection of the dredged sediments from Italy (Ancona)

The sediments from the Netherlands are of fluvial origin and were collected from a depot located on an artificial island within a lake. At the request of the sediment providers, the exact sampling location remains confidential. However, the area is known to be significantly impacted by PFAS contamination, as acknowledged in an official statement by the Dutch Ministry of Infrastructure and Water Management (RWS).

2.2 Sediment washing procedure

The sediment washing procedure consisted of three main steps—acid washing, alkaline washing, and a final oxidative washing using demineralized water and hydrogen peroxide (H_2O_2)—along with preliminary pre-treatments. No replicated tests were performed.

Initially, the sediment samples underwent pre-treatment involving shredding and sieving (4 mm) to remove coarse materials. Following this, the acid washing step was performed by placing the sediment sample into a tank with water (mass-to-volume ratio: 1 kg sediment per 20 L water) and adding phosphoric acid (75%) at a concentration of 0.5 L per 1 m³ of water. The mixture was stirred for 30 minutes and then left to settle overnight. The resulting liquid was collected as the acid washing solution sample.

Next, the settled material was subjected to alkaline washing. The acid solution was removed and replaced with fresh water (1 kg/20 L) and sodium hydroxide (NaOH, 30%) at a dosage of 1 L per 1 m³ of water. As in the previous step, the mixture was stirred for 30 minutes and left to settle overnight. The supernatant from this step was collected as the alkaline washing solution sample.

In the final washing step, demineralized water (1 kg/20 L) containing 2 mmol H_2O_2 per gram of sediment was used. The sample was stirred for 30 minutes and allowed to settle overnight, generating the DI water + 2 mmol H_2O_2 washing solution sample.

An additional test was conducted using a higher concentration of H₂O₂ (8 mmol/g sediment) in demineralized water to enhance PFAS removal. This variant produced a fourth sample, the DI water + 8 mmol H₂O₂ washing solution.

In total, four distinct washing solutions were generated:

- Acid washing solution sample (Solution A)
- Alkaline washing solution sample (Solution B)
- DI water + 2 mmol H₂O₂ washing solution sample (Solution C)
- DI water + 8 mmol H₂O₂ washing solution sample (Solution D)

These solutions were subsequently analyzed for PFAS concentration and treated using ultrasonic cavitation.

2.3 Pyrolysis reactor and experimental conditions for sediments treatments

The thermochemical treatment reactor is a laboratory-scale fixed bed reactor with a screw conveyor, a controlled temperature, and a controlled sample resident time, in addition to the possibility of controlling nitrogen flux into the system to keep it under anaerobic conditions (Figure 2).

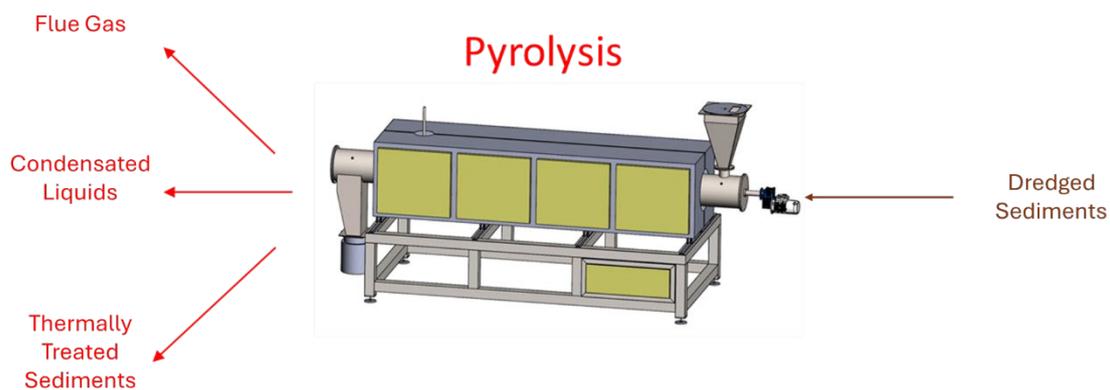


Figure 2: Schematic preview of Pyrolysis Reactor

Material feeding the reactor can be provided before running the reactor or even while it is running. The system generates two effluents: one for the solid phase product (Thermal treated sediments) and the other for the gas phase (Flue gas). To separate condensable liquids from flue gas in the stack emission stream, the gas effluent from the thermal reactor is sent to a condensation system (Figure 3).



Figure 3: Pyrolysis reactor in full setup – at a Laboratory of UNIVPM

2.4 Adopted procedure for sediments immobilization

The material coming from the ECOSEDRA plant was pre-treated before the process of immobilization/solidification utilized to produce concrete for road embankment. Particularly, sediments were crushed (Los Angeles “LA” equipment ASTM C131/C131M – 20) [1] and then passed to the ASTM No. 40 sieve (0.42 mm) (Figure 4).



Figure 4: ASTM C131 LA Abrasion Machine and product

The crushed sediments were stabilized with lime by adding 5% $\text{Ca}(\text{OH})_2$ as dry weight (Figure 5). The amount of lime to add was selected after evaluation of the plastic index according to the ISO/TS 17892-12:2004, which requires a plastic index higher than 10 (Atterberg Limits) [2] for the stabilized material. Nevertheless, the use of only stabilized sediments is not suitable for road embankment due to its limited particle distribution that required the addition of a granular mixture (Figure 6). Finally,

cement at different percentages of 2% and 4% was added to the final mixture of treated sediments with lime and granular mixture.

The final cement-stabilised mixture was therefore a granular mix made with dredged clay sediments treated by the ECOSEDRA plant and stabilised with lime.

Tests for the determination of indirect compressive/tensile strength (R_c , R_t) were accomplished using muds obtained using only granular mixture, and the granular mixture with addition of 10% and 20% of stabilized sediments in the mix. Cement at percentages of 2% and 4% was added to obtain the final testing samples (Table 1).

Table 1: Mixtures Testing Programme for the determination of R_c , R_t (indirect compressive/tensile strength)

Sample	2% Cement	4% Cement
M0 = 100% B	R_c , R_t	R_c , R_t
M1 = 90% B + 10% A	R_c , R_t	R_c , R_t
M2 = 80% B + 20% A	R_c , R_t	R_c , R_t

B = granular mixture; A = sediments stabilized with lime

Samples were poured into cylinder specimens and left to solidify before starting the experiments, as visible in Figure 7.



Figure 5: Lime Stabilization



Figure 6: Granular Mix B



Figure 7: Indirect compressive and tensile strength samples

2.5 Leaching test from stabilized sediments

Leaching test was done on 3 matrices produced by the different stages of the sediments' stabilisation process:

- ECOSEDRA treated sediments as it is
- ECOSEDRA stabilised sediments with lime
- ECOSEDRA stabilised sediments with lime, granular mixture and cement

The goal of the leaching test was to check for the possibility of PFAS leaching from the treated sediments in different scenarios as it will be reused for road embankment.

After doing a comparison between different leaching methods and checking what is mentioned in literature [3–5]. It was decided to go with EPA 1313 LEAF [6], which is appropriate for assessing the leaching of organic compounds.

Testing started following the steps as mentioned in the EPA method (Figure 8) by selecting the matrix and making sure it is of a suitable size as mentioned in the method, then checking for moisture content inside each sample. After this, a titration curve was established for the prepared samples (Pre-Test in Figure 8), and an extraction procedure was planned for different pH conditions. Particularly, it was verified that each sample reached the same pH as indicated in the titration curve proving a stable testing environment. The final extracted samples were sent to ACEA infrastructure for PFAS analysis.

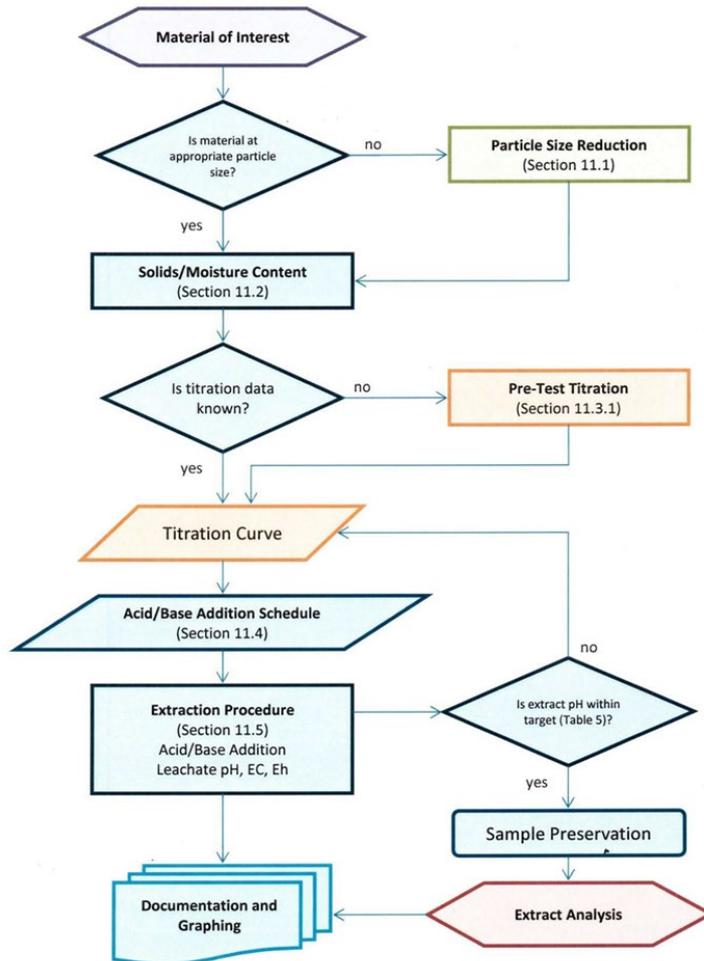


Figure 8: EPA METHOD 1313 Flowchart

Following the EPA 1313 method, a particle size of 0.3 mm was selected due to the fact that the treated sediments were characterized by a particle size around and lower than 0.3 mm; this choice complies with the method's requirement for particles to be smaller than 9.5 mm. Samples containing the granular mixture, lime, and cement were crushed to the same size for consistency, considering the worst-case scenario, since smaller particles have a higher surface area in contact with the leaching liquid.

According to the method suggestions available in Table 2, 20 g of the sample was used with contact time of 24 hours to perform the leaching test. The liquid-to-solid ratio (L/S) of 10 mL extractant/g dry sample (g-dry) was used in agreement with the method.

Table 2: Extraction Parameters as function of Maximum Particle Size as indicated by EPA 1313 method

Particle Size (85 wt% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Suggested Vessel Size (mL)
0.3	50	20 ± 0.02	24 ± 2	250
2.0	10	40 ± 0.02	48 ± 2	500
5.0	4	80 ± 0.02	72 ± 2	1000

As mentioned above, preliminary tests were also carried out to pre-determine the neutralization capacity of the sediments. **PRE-TEST:**

Taking the selected L/S ratio (10 mL solvent / 1 g dry sample), ten samples were made for each pre-test. Following the preliminary test, the Moderate Alkalinity test type was selected as indicated in Table 3. The test therefore began with an acid addition of -2 meq/g dry and ended at +10 meq/g dry. The negative symbol indicates an addition of Alkaline solution while the positive indicates the addition of Acid solution.

Table 3: Pre-Test Titration: Acid Equivalent Schedule by EPA 1313 method

Neutralization Classification	Bottle 1 - Equivalents of Acid (meq/g-dry)	Bottle 2 - Equivalents of Acid (meq/g-dry)	Bottle 3 - Equivalents of Acid (meq/g-dry)	Bottle 4 - Equivalents of Acid (meq/g-dry)	Bottle 5 - Equivalents of Acid (meq/g-dry)
Low Alkalinity	-2.0	-1.0	0	1.0	2.0
Moderate Alkalinity	-2.0	0	2.0	5.0	10.0
High Alkalinity	0	5.0	10.0	15.0	25.0

NOTE: 1) Base additions shown as opposite sign of acid equivalents.
2) Additional pre-test point(s) interpolating or extrapolating from the pre-test schedule may be necessary to provide adequate resolution in the titration curve.

Titration curves were built to serve as a base for the selection of the amount of Acid/Base that should be added to samples to reach the requested pH at the end of each test.

Actual Test:

For the actual test, only three samples were selected covering three ranges of values. The pH value has been selected for each test based on the indications provided in Table 4 and according to the obtained titration curve.

Table 4: Final Extracts pH Targets according to EPA 1313 method

pH Target	Rationale
?	Natural pH at L/S 10 mL/g-dry (no acid/base addition)
2.0 ± 0.5	Provides estimates of total or available COPC content
4.0 ± 0.5	Lower pH limit of typical management scenario
5.5 ± 0.5	Typical lower range of industrial waste landfills
7.0 ± 0.5	Neutral pH region; high release of oxyanions
8.0 ± 0.5	Endpoint pH of carbonated alkaline materials
9.0 ± 0.5	Minimum of LSP curve for many cationic and amphoteric COPCs
12.0 ± 0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
13.0 ± 0.5	Upper bound (field conditions) for amphoteric COPCs
10.5 ± 0.5	Substitution if natural pH falls within range of a mandatory target

To control and check for contaminations during execution of tests, three blanks of reagent were added to the series of samples with the same additions of Acid/Base that was used for the samples but with no solid. HNO₃ was used as the Acid solution with a normality of 2 meq/mL, and KOH was used as the Alkaline solution with a normality of 1 meq/mL.

The selected samples and blanks for leaching tests with the added Acid/Base solutions are described in Table 5 and Table 6, where **R** = Raw Treated Sediments, **L** = Raw Treated Sediments after mixing with Lime, **C** = Raw Treated Sediments after mixing with lime, granular mixture and Cement, **B** = Blanks of reagent. In Table 5 and Table 6, samples were indicated by letter (L, R, C, B) and numbers, where **1** = the addition of **Base** with a dose of **1 meq/g-dry** of sample, **2** = No addition of Acidic or Basic solution, **3** = the addition of **Acid** with a dose of **7 meq/g-dry** of sample.

Table 5: Selected Samples for Leaching Test

Raw Sediment	R1	R2	R3
Raw + Lime	L1	L2	L3
Raw + Lime + Cement	C1	C2	C3
Selected Samples	1	2	3
Acid Addition [meq/g-dry]	-1 (base)	0	7 (acid)
“As Tested” Solid [g] (±0.05g)	20	20	20
Reagent Water [mL] (±5%)	180	200	130
Acid Volume [mL] (±1%)	-	-	70
Base Volume [mL] (±1%)	20	-	-
Acid Normality [meq/mL] HNO ₃	-	-	2
Base Normality [meq/mL] KOH	1	-	-

Table 6: Selected Blanks for Contamination check without solids

Blanks	B1	B2	B3
3 Blanks with No Solids	1	2	3
Acid Addition [meq/g-dry]	-1	0	7
“As Tested” Solid [g] (± 0.05 g)	0	0	0
Reagent Water [mL] ($\pm 5\%$)	180	200	130
Acid Volume [mL] ($\pm 1\%$)	-	-	70
Base Volume [mL] ($\pm 1\%$)	20	-	-
Acid Normality [meq/mL] HNO_3	-	-	2
Base Normality [meq/mL] KOH	1	-	-

2.6 Sonochemical treatment of sediment washing solutions

Experiments on sediment washing solutions using ultrasonic cavitation equipment supplied by SinapTec were conducted in a bath-type reactor (500 mL capacity) with 300 mL reaction volumes, operated at a frequency of 500 kHz. Sonochemical treatments were applied for 180 minutes across all sample types, with aliquots collected at regular intervals for UPLC-MS/MS analysis. The reaction temperature was maintained at 25°C using a chiller connected to a recirculating water bath, and the ultrasonic power density was set at 333 W/L. All experiments were performed under ambient air conditions and repeated in triplicate to ensure reproducibility. After treatment, all samples underwent identical mass spectrometry analysis to quantify PFAS removal percentages over time.

2.7 Analytical methods

2.7.1 Target PFAS analysis in sediments and washing waters

Target PFAS in sediments and washing water were analysed following the method described in WP1 (reported in D1.1), which developed a cost-effective testing method for PFAS analysis in complex matrices. The test method was designed to be easily replicable and transferable to any testing laboratory operating in support of industrial operators. The developed procedure and the obtained performance ensure robustness, reliability, and fast turnaround time, with low material costs, high throughput (more than 20 samples per day) and meet the needs for continuous PFAS control and monitoring in complex matrices. Particularly, the repeatability of the obtained analytical results was verified on N.10 aliquots of 1 g each taken from actual sediment sample. Standard deviation of replicates (RSD) was <20% for the identified PFAS.

Samples are prepared using an appropriate sample preparation method (e.g., solvent dilution or extraction) to determinate n. 30 analytes of the perfluoroalkyl family of substances from environmental matrices of interest, liquid or solid. The laboratory set the LOQ values starting from lowest point on the calibration curve:

- 0.050 $\mu\text{g}/\text{kg}$ on the sediment matrix.
- 0.015 $\mu\text{g}/\text{L}$ on the washing water, deemed free of concentrated interfering substances.

Table 7: Analysed target PFAS and LOQ

30 target PFAS	PFDA, PFHpA, PFHxS, PFNA, PFOA, PFOS, PFDoDA, PFDoDS, PFDS, PFHpS, PFHxA, PFPeA, PFTrDA, PFTeDA, PFUnDA, PFBA, PFBS, 4:2 FTSA, 6:2 FTSA, 8:2 FTSA, NADONA, EtFOSAA, PFOSA, MeFOSAA, PFNS, PFPeS, PFTrDS, PFUnDS, HFPO-DA (= GenX), C6O4
LOQ wastewater liquid	15 ng/L
LOQ solids	50 ng/kg

Before analytical measurements, sediments were dried at 40°C to remove humidity. Then, it was decided to apply a solid-liquid extraction procedure to extract PFAS from the solid matrix (sediments), using 10 mL of Methanol and sonicating at room temperature for 30 minutes, then the samples are centrifuged to separate suspended solids from the liquid phase. After that the extraction solvent is ready for instrumental analysis. The extract from sediment is concentrated at 1 mL by using a gentle stream of nitrogen gas. Two Extracted Internal Standard (EIS) are also added to monitor the analytical process.

Permeate and washing waters are directly prepared in the glass sampling container and then transferred into a vial, ready to be analysed, in order not to lose PFAS adhered to the container wall.

All sample concentrations are determined by isotope dilution, according to the project-specific requirements, using isotopically labelled compounds added to the samples before injection. All the solutions prepared during the analysis must necessarily contain at least 30% methanol to keep under control the filming process on the walls of the containers. Analysis is conducted by LC-MS/MS in the multiple reaction monitoring (MRM) and negative ionization mode.

The target compounds are qualitatively identified in samples by comparing retention times (RTs) to RTs of isotopically labelled surrogates in the same samples or to RTs of target analytes in standards, as applicable, and by comparing product ion ratios to those in standards development. Qualitatively identified target compounds are then quantified based on their primary product ion responses utilizing NIS.

Possible interferents can be caused by the matrix, solvents, reagents, analytical standards, and glassware contamination. Method Blanks (MB) and Reagent Blanks (RB) are prepared and analyzed with all samples and are used to demonstrate that laboratory supplies, preparation, and analysis steps do not introduce interferences or PFAS artifacts at levels that would prevent the proper identification and integration of target analytes or bias quantitation, especially near the Limit of Quantitation (LOQ) or any project-specific concentration levels of interest. Careful selection of reagents and consumables is necessary because even low levels of PFAS contamination may alter the precision and bias of the method; background introduced by these materials (and variability thereof) is cumulative.

Sediment washing solutions were analyzed at BRGM according to the following protocol. The samples were then analyzed via LC-MS/MS to determine the PFAS contents via the following protocol. The sample is mixed with methanol to obtain a methanol content of 50%. The sample with methanol is diluted with water/methanol 50/50 (v/v) so that the PFAS levels in the samples are within the calibration range (5 to 5000 ng/L). A volume of 0.44 mL from the previous preparation is transferred to a polypropylene vial with a cap, then spiked with 10 µL of 5% acetic acid and 50 µL of the internal standard solution (2 µg/L in methanol). This process yields a surrogate concentration of

200 ng/L and 0.5% acetic acid in the diluted solution. Samples underwent analysis using LC-MS/MS. To prevent cross-contamination, methanolic blanks are injected between high-concentration samples, and water are analyzed to ensure the absence of contamination.

PFAS analyses utilized a Waters TQXS system in conjunction with a Waters UHPLC system, featuring an Acuity BEH C18 Column (100 × 2.1 mm, 1.7 μm, Waters) maintained at 35 °C, along with a delay column (Atlantis Premier BEH C18 AX 50mm x 2.1mm, 5 μm, Waters) to prevent PFAS contamination from the chromatographic system. The injection volume was 10 μL, and the mobile phase consisted of a mixture of 2 mM Ammonium Acetate in H₂O (A) and 2 mM Ammonium Acetate in ME OH (B) at a flow rate of 0.3 mL/min. The gradient expressed as changes in solvent A was as follows: 0-1 min, 95% to 75% A; 1.0-23 min, 75% to 0% A; 23.0-27.0 min, 0% A; 27.0-27.1 min, 0% to 95% A and 27.1-30.0, 95% A.

The TQXS mass spectrometer was utilized for MS analysis, functioning in negative and positive Electrospray Ionization (ESI) mode. The source conditions were established as follows: desolvation temperature of 500 °C, desolvation gas flow at 1100 L/hr, cone gas flow at 150 L/hr, and capillary voltage set to -1000 V (ESI⁻) and 1000 V (ESI⁺). The chromatograms underwent processing using Target Lynx software. PFAS quantification utilized 10-point calibration curves ranging from 10 to 5000 ng/L, achieving R² values greater than 0.99 for all compounds. Labeled internal standards were used to provide an adequate correction compensating for matrix effects.

2.7.2 Toxicity test PFAS CALUX performed on water and sediment samples

Toxicity testing of PFAS using the effect- and non-animal based PFAS CALUX bioassay was performed. Mechanism-based bioassays provide insight in the modes of action of toxicants. They can be used as alternative methods to detect the presence of chemicals and their transformation products and to assess the hazard posed by chemicals and chemical mixtures (see also at CWA 18201, 2025). For the detection of PFAS, the PFAS CALUX bioassay was developed.

The PFAS CALUX bioassay is based on competition between PFAS and the thyroid hormone T4 for binding sites on transthyretin (TTR) transport proteins in combination with the TRβ CALUX bioassay as a functional readout (Collet et al. 2020; Behnisch et al. 2021; De Scheper et al. 2023; CWA 18201, 2025). In the TTR-binding assay, binding competition between a fixed concentration of T4 and dilution series of test item or sample extracts (e.g., PFOA or extracts water samples) is studied. Increasing concentrations of test item capable of competing with T4 for TTR-binding sites, will result in a decreased amount of TTR-bound T4. Following separation of TTR-bound and unbound compounds (T4 and test items) on a Biogel column, the amount of TTR-bound T4 is determined using the TRβ CALUX bioassay (Figure 9). Disruption of T4-TTR binding is benchmarked against the reference compound perfluorooctanoic acid (PFOA).

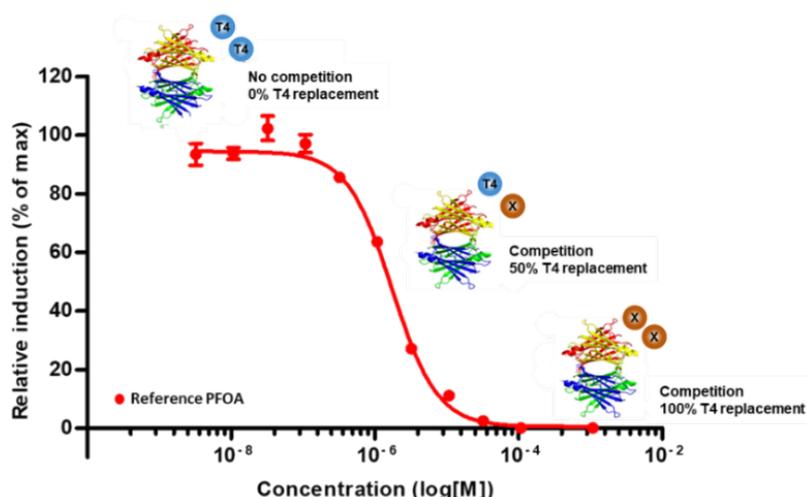


Figure 9: Dose-response curve of TTR-bound thyroid hormone T4. TTR-T4 complex is collected following BioGel column separation and exposed to TR β CALUX cells. T4 bound to TTR is detected by the TR β cells and results in a TR β CALUX response. In case increasing concentrations of a competitor are present in the TTR/T4 incubation mixture (e.g., PFAS), T4 is gradually replaced from TTR-binding sites. As a result, less TTR-bound T4 is present in the final BioGel column eluate, and a lower TR β CALUX bioassay response is observed.

The TR β CALUX bioassays comprise human bone cell lines (U2-OS) incorporating the firefly luciferase gene coupled to “thyroid responsive elements” as a reporter gene for the presence of compounds activating these responsive elements (Collet et al. 2020; CWA 18201, 2025). Cells that are exposed to compounds of interest not only express proteins that are under normal circumstances associated with responsive elements but also luciferase. By addition of the appropriate substrate for luciferase, light is emitted (Figure 10). The amount of light produced is proportional to the amount of ligand-specific receptor binding, which is benchmarked against the relevant reference compound L-thyroxine (T4).

Processing of water and sediment samples

For PFAS analysis in water samples, 0.5-1 liter of water was extracted by means of solid-phase extraction on a weak-anion-exchange cartridge (WAX-SPE). After conditioning the WAX-SPE cartridge with subsequently MeOH:0.1% NH₄OH, MeOH and ultrapure water, the samples were loaded on the columns and washed with NH₄Ac (pH 4) and THF:MeOH (75:25) (v/v). Finally, PFAS were eluted with MeOH:0.1% NH₄OH and collected in tubes containing ENVI-Carb. Following vortexing (10 sec.), the eluates were centrifuged (10 minutes at 1800 g), and collected supernatants were evaporated under a gentle flow of N₂. The final extracts were reconstituted in DMSO (generally 30 μ L), and serial dilutions in DMSO were prepared with log increments of 0.5 (1, 3, 10, 30, and 100-times dilutions).

Either sediment samples or sediment sample extracts in solvent (methanol) were received for analysis. In the case of sediment samples, they were dried by means of freeze-drying. Next, approximately 5 grams of dried sample was extracted by means of shake extraction after the addition of 2 mL of 200 mM NaOH and 20 mL MeOH. Samples were shaken thoroughly for 30 minutes. Following centrifugation (10 min; 1800 g), the supernatant was collected. This extraction was repeated with 10 mL MeOH and 200 μ L 2 M HCl was added to the final collected extracts. The combined extracts were evaporated to approximately 0.5 mL using a gentle stream of nitrogen gas N₂ (45 $^{\circ}$ C) and reconstituted in 100 mL ELGA (super-demi) water. The reconstituted samples were

centrifuged (10 min; 1800 g) and filtered through a glass-fiber filter to remove particles. The pH of the samples was adjusted to 4 with acetic acid. Next, the samples further processed by loading them on conditioned WAX-SPE columns as described above. After eluting the PFAS from the WAX-SPE, they eluates were evaporated under a gently stream of nitrogen gas N₂ (45 °C) and reconstituted in DMSO (generally 30 µL) after which serial dilution in DMSO were prepared with log increments of 0.5 (1, 3, 10, 30 and 100-times dilutions).

TTR-binding assay

Serial sample dilutions were incubated in Tris-buffer (pH 8.0) overnight at 4°C in the presence of TTR (0.058 µM) and a fixed concentration of T₄ (0.052 µM) (3.2% sample dilution in incubation mixture). After incubation, TTR-bound and free T₄ were separated on a Bio-Gel P-6DG column. The eluate was added to assay medium after which TR_β CALUX cells were exposed for 24 hours.

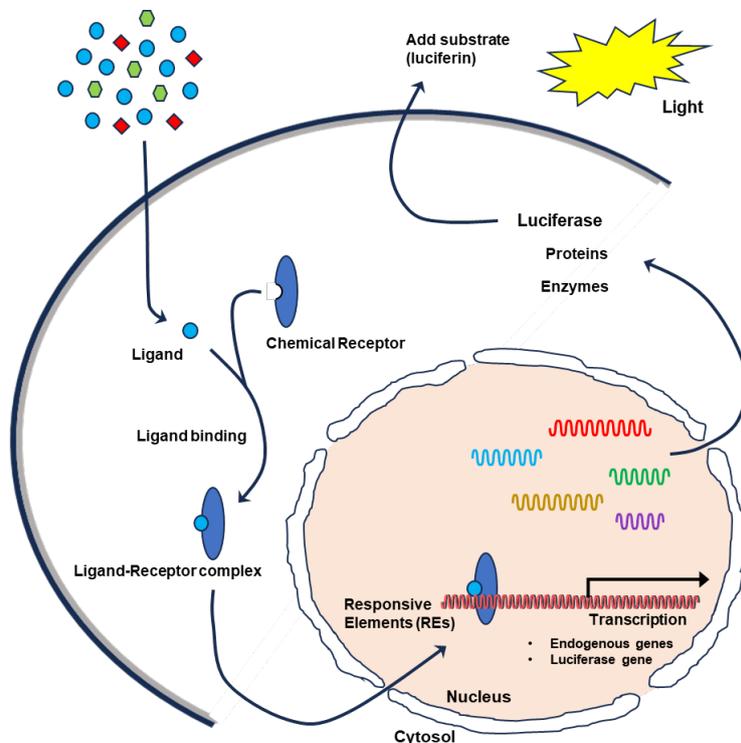


Figure 10: Principle of a CALUX assay. Exposure of cells to chemicals leads to a change in gene expression.

This response is mediated through the binding of transcription factors to promoter elements such as receptor binding elements that drive expression of endogenous genes. In a CALUX reporter gene assay, this response is modulated. Activation of a signalling pathway is linked to transcription of a stably introduced luciferase gene. Upon addition of a substrate, a light signal is generated that is proportional to the amount of biological chemical in a sample (adapted from Van der Burg et al., 2013).

CALUX bioassays

For determination of TR_β CALUX activity, TR_β CALUX cells were seeded in 96 wells plates in assay medium. Following exposure of the CALUX cells to serial dilutions of eluate after TTR-binding assay, the induction of luciferase production is quantified by measuring luminescence (Berthold luminometer) following addition of the substrate luciferin. In a series of four 96-well microtiter plates, one complete PFOA calibration curve was analysed. In Table 8 the exposure conditions for TR_β CALUX are given.

Table 8: CALUX cell culture and exposure information

Assay	TTR-TRb
Cell type	U2OS
Species	Human
%DMSO	3%
Fold dilution	31.25
%CO ₂	5%
Exposure time	24 hrs
Confluence	10000 cells per well
Medium used	DMEM/F12
Additions to medium	- Non essential amino acids

Note: TR_β CALUX incubations do not contain (stripped) serum

Data analysis

Analysis results of sample extracts, expressed as induction relative to the standard PFOA reference compound, are interpolated in the calibration curves of TR_β CALUX bioassay for quantitative determination of disruptive potential using the statistical software package GraphPad Prism V5.03. Only dilutions that do not show any signs of cytotoxicity are used for the final evaluation of analysis results. All analysis results are expressed as the amount of PFOA equivalents per liter of processed water or PFOA equivalents per gram of processed sediment.

3 Results

3.1 PFAS removal by non-oxidative thermal treatments (Pyrolysis)

The operation of the Pyrolysis reactor was similar to a thermal treatment in the absence of oxygen. Several experiments were done using different temperatures with the same residence time. In Table 9, it is reported a characterization of treated samples, the indication of the operational conditions of the thermal test, and characterization of obtained products.

Table 9: Pyrolysis products with different matrices and temperatures

Sediment Source	Sediment (g)	Organic Content (g)	Temperature (°C)	Retention time (min)	Treated sediments (g)	Bio-Oil (g)
The Netherlands	378	51	600	20	327	11
The Netherlands	630	86	800	20	531	5
Ancona	433	19	400	20	410	13
Ancona	448	20	600	20	399	16
Ancona	458	20	800	20	386	23

The two types of sediments (i.e., Ancona and the Netherlands) were different in their PFAS contamination level, as The Netherlands sediments were much more contaminated in PFAS compared to the sediments of Ancona (Table 10).

Table 10: PFAS concentrations in the sediments with their limits of quantification (LOQ)

LOQ µg/kg	0.05	0.05	0.05	0.05
Samples	N-EtFOSAA	N-MeFOSAA	PFOA	PFOS
Ancona sediments	<	<	<	0.08
The Netherlands sediments	0.4	0.08	0.06	1.12

After the treatment with the pyrolysis reactor, no PFAS were detected in treated sediments in all experiments with a difference in LOQ between Ancona and The Netherlands sediments due to a difference in sample pollution levels, as presented in Table 10.

Table 11: PFAS concentrations and LOQ in treated sediments

Sediment Source	Temperature	LOQ $\mu\text{g}/\text{kg}$	0.05	0.05	0.05	0.05
-	($^{\circ}\text{C}$)	Samples	N-EtFOSAA	N-MeFOSAA	PFOA	PFOS
Ancona	400	Treated sediments	<	<	<	<
Ancona	600	Treated sediments	<	<	<	<
Ancona	800	Treated sediments	<	<	<	<
-	-	LOQ $\mu\text{g}/\text{kg}$	1	1	1	1
-	-	Samples	N-EtFOSAA	N-MeFOSAA	PFOA	PFOS
The Netherlands	600	Treated sediments	<	<	<	<
The Netherlands	800	Treated sediments	<	<	<	<

In Bio-oil samples, PFAS concentrations were only detected in one sample as 6:2 FTS resulting from the treatment of The Netherlands sediments at 600 $^{\circ}\text{C}$ (Table 12).

Table 12: PFAS concentrations and LOQ in Bio-oil

Sediment Source	Temperature	LOQ $\mu\text{g}/\text{L}$	1
-	($^{\circ}\text{C}$)	Samples	6:2 FTS
The Netherlands	600	Bio-oil	1.4
The Netherlands	800	Bio-oil	<
Ancona	400	Bio-oil	<
Ancona	600	Bio-oil	<
Ancona	800	Bio-oil	<

3.2 Sediment washing solution PFAS content and ultrasonic cavitation treatment

Based on the analytical outcome, 6:2 FTSA and 6:2 FTAB, were found to be present in the four solutions studied. Whereas, 6:2 FTSaAM was found in solution A, solution C, and solution D (Table 13).

Table 13: Detected PFAS compounds in the Netherlands sediment washing solutions (n=1)

Compounds	PFAS concentration (ng/L)				LOQ (ng/L)
	Solution A	Solution B	Solution C	Solution D	
6:2 FTSA	107	40	520	113	20
6:2 FTAB	132	30	1012	270	20
6:2 FTSaAM	82	-	495	116	20
PFHxA	-	-	48	-	20
PFHpA	-	-	20	-	20
8:2 FTSA	-	-	20	-	20
10:2 FTSA	-	-	22	-	20

After performing identical UPLC-MS/MS analysis on the treated solutions, the following conclusions can be drawn. Considering individual solutions, solution C witnessed a 72% cumulative PFAS removal within 180 min of treatment time. At the same time, solution A and solution D have shown 23% and 51% removal. However, solution B did not witness any removal over the treatment time. Figure 11 presents the progress in PFAS removal over the treatment duration, as analyzed via mass spectrometry. When targeted PFAS analysis (here displayed as negative percentage of the sum of PFAS removal in Figure 11) shows an increase in total PFAS over treatment time, it strongly indicates the presence of PFAS precursors in the studied samples, which are transforming into measurable PFAS compounds during the treatment.

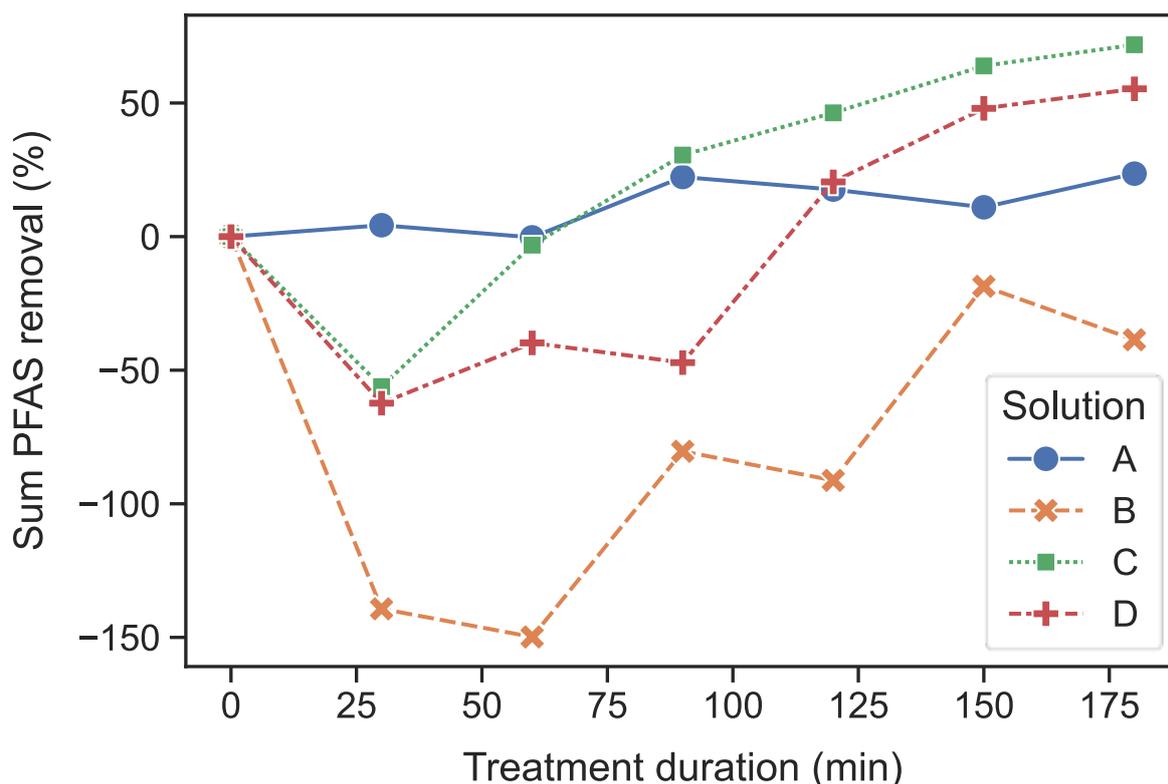


Figure 11: PFAS removal over 180 min treatment time

Solution C, which demonstrated the highest number of PFAS compounds and their elevated concentrations compared to the other washing methods, suggests that the addition of H₂O₂ enhanced PFAS extraction from the solid matrix. In contrast, the alkaline washing (Solution C) resulted in a minimal removal of PFAS, both in terms of the number of compounds and their concentrations, compared to the other treatments. Additionally, the sonochemical treatment showed increased removal efficiency with higher initial PFAS concentrations, a trend that aligns with our previously published findings on PFOS (Panda et al., 2025) [16]. The concentrations analyzed by mass spectrometry for all PFAS and each time are given in Table 14.

Table 14: Evolution of PFAS concentration during Ultrasonic cavitation treatment for samples A, B, C and D

Solution A (ng L⁻¹)							
Time	6:2 FTAB	6:2 FTSA	8:2 FTSA	10:2 FTSA	6:2 FTSaAM	PFHxA	PFHpA
0	132	39	<	<	82	<	<
30	92	107	<	<	44	<	<
60	71	147	<	<	36	<	<
90	35	128	<	<	34	<	<
120	50	130	<	<	29	<	<
150	55	137	<	<	34	<	<
180	33	138	<	<	23	<	<
Solution B (ng L⁻¹)							
Time	6:2 FTAB	6:2 FTSA	8:2 FTSA	10:2 FTSA	6:2 FTSaAM	PFHxA	PFHpA
0	29	<	<	<	<	<	<
30	34	35	<	<	<	<	<
60	25	46	<	<	<	<	<
90	17	35	<	<	<	<	<
120	21	34	<	<	<	<	<
150	<	34	<	<	<	<	<
180	<	40	<	<	<	<	<
Solution C (ng L⁻¹)							
Time	6:2 FTAB	6:2 FTSA	8:2 FTSA	10:2 FTSA	6:2 FTSaAM	PFHxA	PFHpA
0	1012	520	19	<	495	<	<
30	1162	1153	61	22	748	48	<
60	539	1091	48	22	339	54	20
90	224	894	29	32	160	56	27
120	231	653	25	23	106	38	23
150	99	488	29	30	62	32	<
180	123	361	<	22	43	27	<
Solution D (ng L⁻¹)							
Time	6:2 FTAB	6:2 FTSA	8:2 FTSA	10:2 FTSA	6:2 FTSaAM	PFHxA	PFHpA
0	180	41	<	<	65	<	<
30	277	113	<	<	116	<	<
60	167	173	<	<	96	<	<
90	178	214	<	<	67	<	<
120	65	163	<	<	20	<	<
150	47	116	<	<	<	<	<
180	33	107	<	<	<	<	<

3.3 Results of mechanical tests for the use of recovered material in road embankments

A full technical characterization about the suitability of produced concrete with dredged sediments for road embankments was accomplished during the national ECOSEDRA project. In this document, results from tests for the determination of indirect compressive/tensile strength (R_c , R_t) are reported in Table 15.

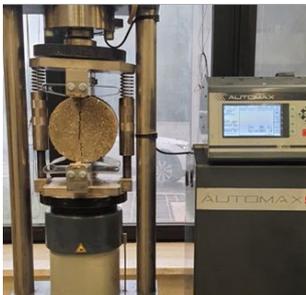
According to the obtained results and technical requirements for road constructions [7]:

- The M1 mixture (90% B + 10% A) is suitable¹ for use in unbound foundation layers
- The M2 mixture (80% B + 20% A) is suitable² for use in unbound foundation layers and sub-bases
- Both M1 and M2 mixtures are suitable for embankments and road sub-bases constructions.

Table 15: Indirect compressive and tensile strength results



R_c [MPa]	Cement 2%	Cement 4%
M0	2.82	2.58
M1	2.25	3.54
M2	1.29	2.46



R_t [MPa]	Cement 2%	Cement 4%
M0	0.134	0.121
M1	0.188	0.292
M2	0.136	0.221

More details and results of technical tests to evaluate the suitability of the obtained mixture for road constructions are reported in the final report of project ECOSEDRA [8].

¹ According to the CNR catalogue and the most recent specifications

² According to the CNR catalogue

3.4 Leaching of PFAS from treated and stabilized sediments

Figures 12, 13 and 14 show the pH calibration curves obtained during preliminary tests, where the resulting pH is plotted against the specific amount of Acid/Base solution added. Figures 15, 16 and 17 present the titration curves obtained for ii) ECOSEDRA treated sediments, ii) sediments stabilized with lime, and iii) sediments immobilized with lime, granular mixture and cement, respectively.

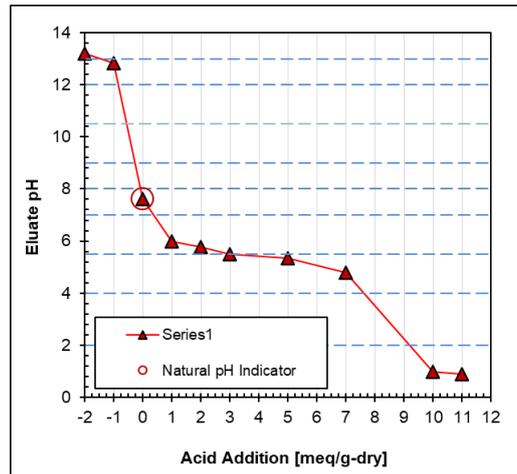


Figure 12: Titration Curve for ECOSEDRA Treated sediments

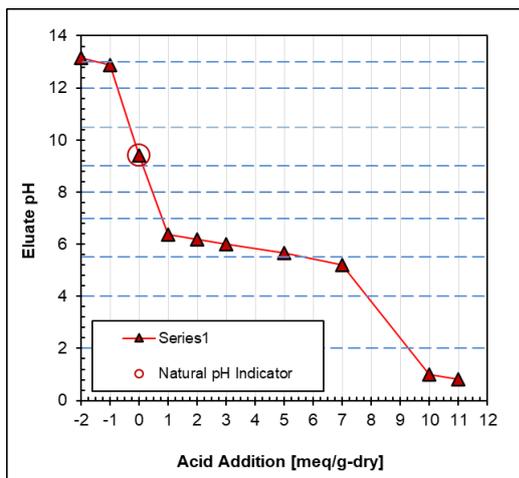


Figure 13: Titration Curve for ECOSEDRA stabilised sediments with lime

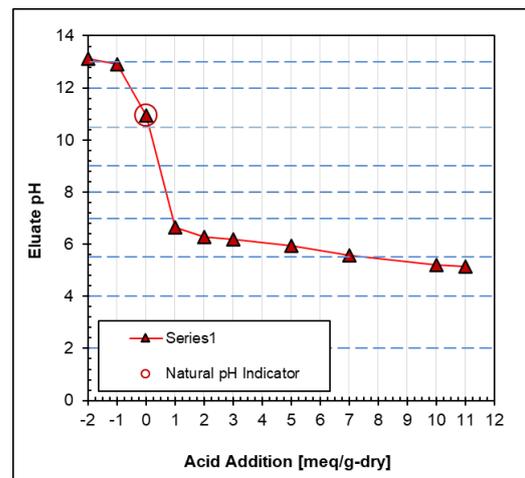


Figure 14: Titration Curve for ECOSEDRA stabilised sediments with lime, granular mixture & Cement

Using the results of the titration curve, the amount of acid/base to be added to the sample was determined in order to achieve the different pH values selected for the PFAS leaching assessment.

Following the parameters described in Tables 5 and 6 and using a contact time of 24 hours, the tests yielded the pH values shown in Table 16.

Table 16: pH of Leaching liquids after testing

Sample	R1	R2	R3	L1	L2	L3	C1	C2	C3	B1	B2	B3
pH	12.76	7.61	5.33	12.9	8.52	5.63	12.89	10.91	6.23	12.97	8.83	0.67

The leaching liquids from all samples and blanks collected after 24 hours were sent to ACEA Infrastructure for PFAS analysis. Results are presented in Table 17.

Table 17: PFAS in Leaching liquids after the tests

Washing water													
LOQ (ng/L)	type	R1	R2	R3	L1	L2	L3	C1	C2	C3	B1	B2	B3
20	6:2 FTS	<	<	90	<	<	80	<	<	80	<	<	80
20	PFBS	<	<	<	<	80	<	<	20	<	<	<	<

PFAS are almost never found in leachates. When present, contamination of the acid solution and lime used in the tests is suspected. Indeed, the presence of 6:2 FTS in samples number **3** (R3, L3, C3) is systematic, including in blank B3. Furthermore, concentrations of PFBS were detected in samples **L2** and **C2**, indicating contamination due to the addition of lime. PFBS was not detected in leachates obtained from sediments alone.

3.5 PFAS CALUX toxicity tests on treated sediments

PFAS CALUX bioassays were used to determine toxicity related to the presence of PFAS analytes in sediments and fractions obtained from treated sediments. Particularly, tests were conducted on different samples:

- Untreated sediments and sediments treated by ECOSEDRA lab processes.
- Leachate samples obtained from leaching experiments of treated sediments before and after stabilisation and solidification at different pH levels.

3.5.1 PFAS CALUX tests for sediment treated by ECOSEDRA process

PFAS CALUX tests were performed in raw sediments and sediments treated by ECOSEDRA process to evaluate the effectiveness of the treatment on reducing toxicity levels in sediments. Sediments used for the experiments were sampled at Ancona port and in the Netherlands.

PFAS CALUX test was performed in sediment extracts in methanol (Table 18), which were produced to perform PFAS analytical determination as described by Zietzschmann et al. (2024) at ACEA laboratories and shipped to BDS to accomplish toxicity tests. Particularly, the methanol extracts were further processed by extraction of PFAS using a WAX-SPE column. Final extracts were dissolved in 30 µL of DMSO. Following preparation of serial dilution series of the final sample extracts, the bioactivity in PFAS CALUX bioassays was determined.

Table 18: Sample coding and sample processing volumes

Sample name	Sample extract processed	Description
(-)	(mL)	
ECOSSEDRA Treated Sediments (N) E2	9	Sediments from the Netherlands treated by ECOSSEDRA lab process (second experiment)
Untreated Sediments (A)	9.3	Untreated sediments from Ancona
ECOSSEDRA Treated Sediments (N) E1	9.2	Sediments from the Netherlands treated by ECOSSEDRA lab process (first experiment)
Untreated Sediments (A)	9.1	Untreated sediments from Ancona
Untreated Sediments (N)	7.6	Untreated sediments from the Netherlands
Modified ECOSSEDRA with H ₂ O ₂ (A) R2	8.9	Ancona sediment treated by ECOSSEDRA lab process with addition of H ₂ O ₂ in the final step (replicate 2)
Modified ECOSSEDRA with H ₂ O ₂ (A) R1	9.3	Ancona sediment treated by ECOSSEDRA lab process with addition of H ₂ O ₂ in the final step (replicate 1)

Note: (A) = Ancona, (N)= The Netherlands, R1 = Replicate 1, R2= Replicate 2, E1= First Experiment, E2= Second Experiment

The sample dose-response curves of the PFAS CALUX bioanalysis results of the sediment extracts are presented in Figure 15.

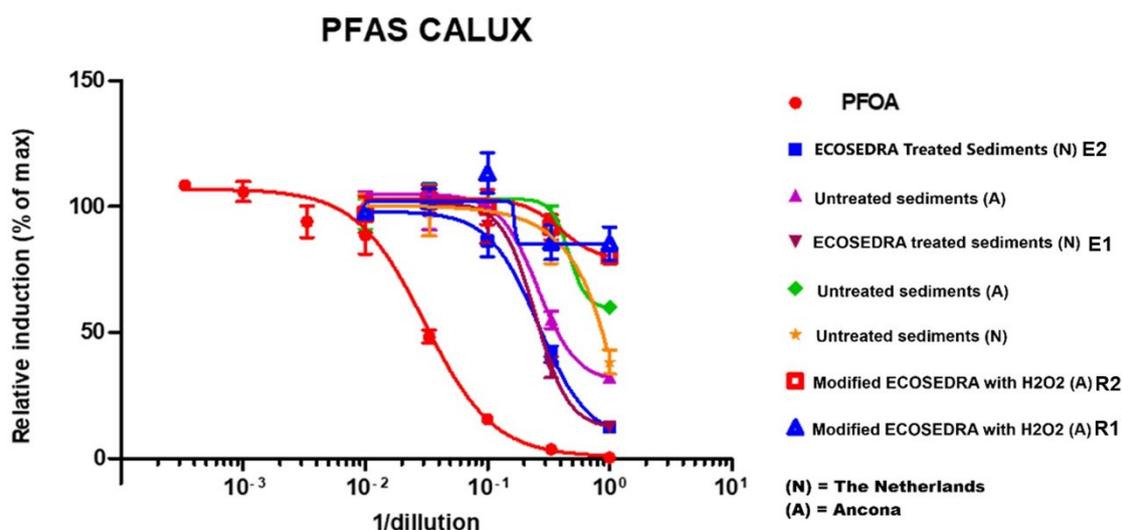


Figure 15: Graphical representation of PFAS CALUX analysis results of samples

The quantified PFOA equivalent content of total sum PFAS in the PFAS CALUX in the analysed samples are summarised in Table 19.

Table 19: Total sum PFAS in PFOA-BEQ by PFAS CALUX bioanalysis results of samples extracts received from ECOSEDRA

Sample name	PFAS CALUX activity	LOQ	Description
(-)	($\mu\text{g PFOA-BEQ/g sample}$)		
ECOSSEDRA Treated Sediments (N) E2	4.6	0.64	Sediments from the Netherlands treated by ECOSEDRA lab process (second experiment)
Untreated Sediments (A)	3.2	0.64	Untreated sediments from Ancona
ECOSSEDRA Treated Sediments (N) E1	3.7	0.64	Sediments from the Netherlands treated by ECOSEDRA lab process (first experiment)
Untreated Sediments (A)	1.3	0.64	Untreated sediments from Ancona
Untreated Sediments (N)	1.3	0.64	Untreated sediments from the Netherlands
Modified ECOSEDRA with H ₂ O ₂ (A) R2	<LOQ	0.64	Ancona sediment treated by ECOSEDRA lab process with addition of H ₂ O ₂ in the final step (replicate 2)
Modified ECOSEDRA with H ₂ O ₂ (A) R1	<LOQ	0.64	Ancona sediment treated by ECOSEDRA lab process with addition of H ₂ O ₂ in the final step (replicate 1)

Considering samples collected in Ancona, PFAS CALUX activity was reduced to <LOQ as observable in Table 19 and Figure 15. Two different samples of untreated sediments were assessed by PFAS CALUX test for Ancona port. The toxicity levels determined correspond to the variability of PFAS concentrations detected in this solid matrix (Table 20).

Table 20: PFAS concentration in raw and treated sediments for 30 PFAS

	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
	6332 LOQ=50 ng/kg The Netherlands	6336 LOQ=50 ng/kg The Netherlands	7243 LOQ=50 ng/kg The Netherlands	16664 LOQ=50 ng/kg Ancona	16665 LOQ=50 ng/kg Ancona	16667 LOQ=50 ng/kg Ancona	16668 LOQ=50 ng/kg Ancona
	Sediment non-treated	Sediment treated by ECOSEDRA	sediment treated by ECOSEDRA	Sediment non- treated	Sediment treated by ECOSEDRA + H ₂ O ₂ (4 mmol)	Sediment non- treated	Sediment treated by ECOSEDRA + H ₂ O ₂ (4 mmol)
BDS code	46244	46242	46240	46243	46245	46241	46246
PFBA	125	100	<	90	<	90	<
PFBS	55	<	<	<	<	<	<
PFOA	110	55	50	<	<	<	<
N-MeFOSAA	110	65	165	<	<	<	<
PFOS	1205	400	780	220	<	350	<
N-EtFOSAA	720	500	1260	<	<	<	<
PFUdA	50	<	<	<	<	<	<
PFDS	<	<	75	<	<	<	<
ΣPFAS	2375	1120	2330	310	0	440	0

On the other side, PFAS CALUX activity in sediments from the Netherlands was not reduced. It may be related to the high load of PFAS compounds in this matrix, which was still high after treatment (see Table 14 in Deliverable D3.3 by Lancioni et al. (2024)).

3.5.2 PFAS CALUX test for sediments leaching test samples

PFAS present in ECOSEDRA treated sediments and sediments stabilized by different reactants (lime, cement) were subject to leaching experiments at different pH-levels (alkaline, neutral and acidic pH). Subsequently, the leachates were tested for total PFAS content using the PFAS CALUX bioassay.

Following extraction of PFAS from produced samples, serial dilutions of the final extracts in DMSO were prepared and analysed on the human cell-based PFAS CALUX bioassay for total PFAS content. Table 21 lists the names and descriptions of the leachate samples received.

Table 21: Sample coding of leachate samples and sample volumes processed.

Leaching Code	Sample Type	Leaching Condition	Volume processed (L)
B-1	Blank	Alkaline	0.03553
B-2		Neutral	0.03986
B-3		Acidic	0.03997
R-1	Sediment	Alkaline	0.03306
R-2		Neutral	0.03357
R-3		Acidic	0.03713
L-1	Sediment + Lime	Alkaline	0.0345
L-2		Neutral	0.03611
L-3		Acidic	0.03724
C-1	Sediment + Cement + lime	Alkaline	0.04571
C-2		Neutral	0.04091
C-3		Acidic	0.04595

In Table 21, letters were used to indicate different samples: **R** = Raw Treated Sediments, **L** = Raw Treated Sediments after mixing with Lime, **C** = Raw Treated Sediments after mixing with lime, granular mixture and Cement, **B** = Blanks of reagent water and no solids. In addition, different numbers were used to indicate **1** = the addition of **Base** with a dose of **1 meq/g-dry** of sample; **2** = No addition of Acid or Basic solution; **3** = the addition of **Acid** with a dose of **7 meq/g-dry** of sample.

The final PFAS CALUX results for the leachate samples are presented in Table 22. For all samples, the PFAS CALUX results are expressed as the concentration of PFOA equivalents per liter of processed leachate. Graphical representations of all PFAS CALUX bioanalysis results are presented in Figure 16. Comparison between the different stabilizing treatments of sediment and different leaching conditions (alkaline, neutral, acidic) is visualized in Figure 17.

Table 22: PFAS CALUX bioanalysis results of leachate samples. Analysis results are expressed as PFOA equivalent concentration per volume of leachate ($\mu\text{g PFOA-BEQ/L sample}$).

Leaching Code	Sample Type	Leaching Condition	PFAS CALUX activity	LOQ	Unit
B-1	Blank	Alkaline	<LOQ	8.7	$\mu\text{g PFOA-BEQ/L sample}$
B-2		Neutral	<LOQ	7.7	$\mu\text{g PFOA-BEQ/L sample}$
B-3		Acidic	<LOQ	7.7	$\mu\text{g PFOA-BEQ/L sample}$
R-1	Sediment	Alkaline	210	9.3	$\mu\text{g PFOA-BEQ/L sample}$
R-2		Neutral	68	9.2	$\mu\text{g PFOA-BEQ/L sample}$
R-3		Acidic	<LOQ	8.3	$\mu\text{g PFOA-BEQ/L sample}$
L-1	Sediment + Lime	Alkaline	200	8.9	$\mu\text{g PFOA-BEQ/L sample}$
L-2		Neutral	100	8.5	$\mu\text{g PFOA-BEQ/L sample}$
L-3		Acidic	20	8.3	$\mu\text{g PFOA-BEQ/L sample}$
C-1	Sediment + Cement + lime	Alkaline	83	6.7	$\mu\text{g PFOA-BEQ/L sample}$
C-2		Neutral	42	7.5	$\mu\text{g PFOA-BEQ/L sample}$
C-3		Acidic	93	6.7	$\mu\text{g PFOA-BEQ/L sample}$

The obtained results show a high level of PFAS content in alkaline leachate samples whereas neutral leachate samples contained moderate PFAS concentrations. The acid-treated leachate samples had the lowest PFAS content. In addition, the PFAS content in the sediments treated with cement/lime was significantly lower than in raw sediments and the sediments treated with lime alone.

These results are not easy to interpret and may be affected by the reagents/materials used for sediment stabilization and leaching tests. In addition, analytical measurements of 30 target PFAS in leachate samples did not show PFAS leaching from the treated sediments, but only contamination issues related to the materials and reagents used during the experiments.

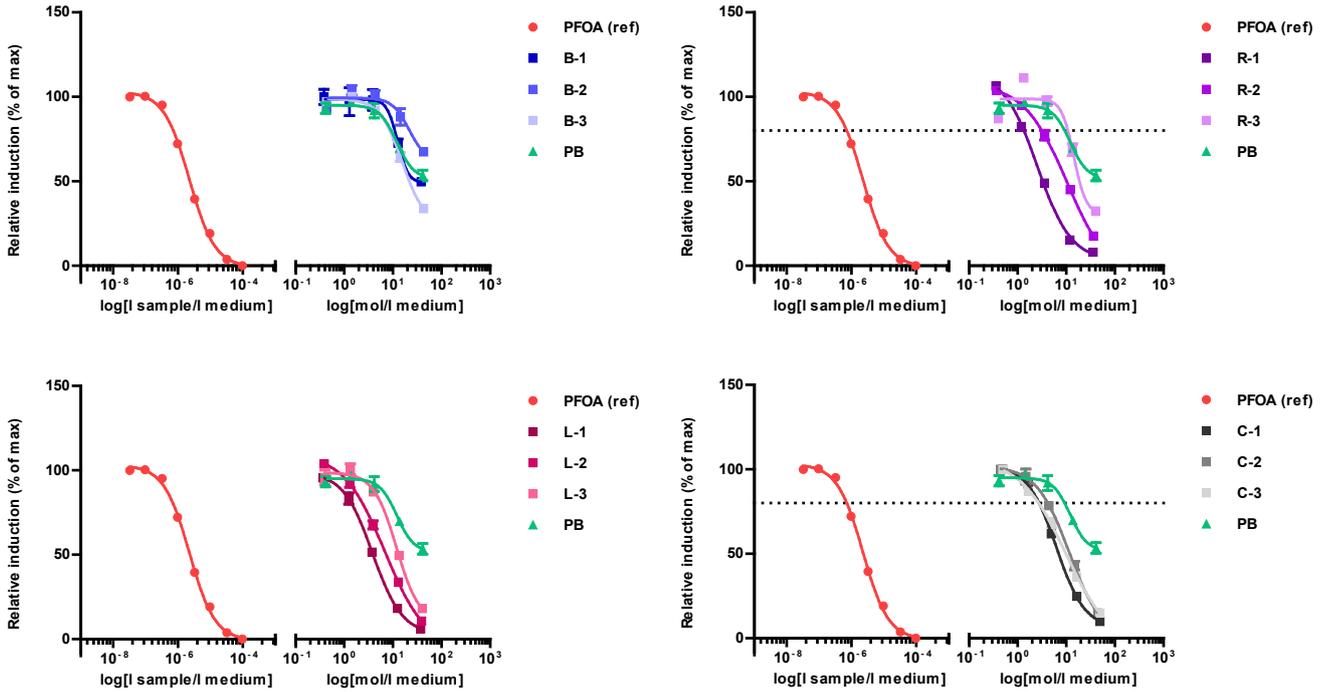


Figure 16: Graphical representation of PFAS CALUX bioanalysis results of leachate samples

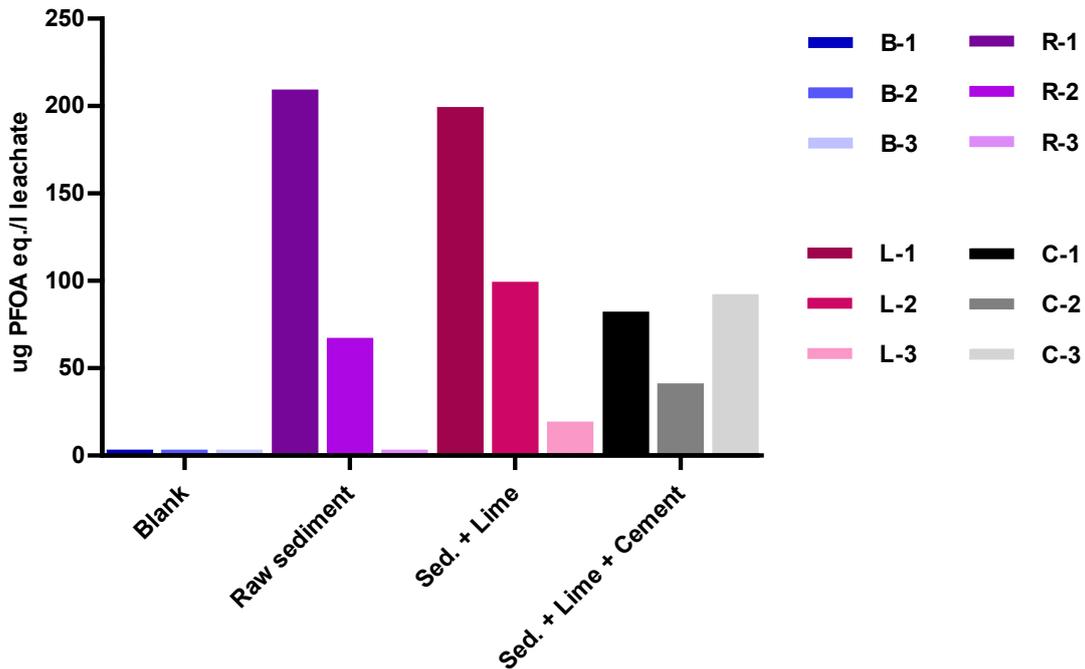


Figure 17: Concentration of PFOA bio-equivalents measured by PFAS CALUX in leachates subject to different leaching conditions (alkaline, neutral, acidic) and following PFOA immobilisation on sediment and additional stabilisation with lime or lime + cement.

4 Conclusions

This work demonstrates the effectiveness of various treatment processes for the removal and immobilization of PFAS from contaminated sediments, with a particular focus on pyrolysis, ultrasonic cavitation, and solidification techniques, alongside a thorough assessment of residual toxicity using PFAS CALUX bioassays.

Pyrolysis proved to be highly effective in removing detectable PFAS from sediments originating from the Netherlands and Ancona. Regardless of initial contamination levels or pyrolysis temperature, no PFAS were detected in the treated solids. A minor presence of PFAS was observed only in the bio-oil fraction from one condition (@600 °C for the Netherlands sample), confirming the effectiveness of PFAS destruction during thermal treatment under anoxic conditions. Sonochemical treatment of washing solutions showed variable results in terms of PFAS removal. The highest efficiency (72%) was achieved for sample C, which had the highest initial PFAS concentration and was subjected to alkaline washing combined with H₂O₂. These results highlight the role of oxidizing species and initial PFAS loading in improving treatment results, consistent with previously published data. Sediment-derived mixtures tested for road embankment applications demonstrated adequate mechanical properties. Both formulations M1 and M2 met the requirements for use in unbound foundation layers and sub-bases, indicating a viable pathway for the reuse of sediment after treatment. Leaching tests did not reveal any release of PFAS from sediments treated solely with the ECOSEDRA process. The PFAS detected in leachates from samples treated with acid or lime were linked to contaminants introduced by the reagents rather than release from the sediments. This finding highlights the importance of reagent purity and demonstrates the high immobilization of PFAS post-treatment. PFAS toxicity was significantly reduced in Ancona sediments after treatment, particularly when H₂O₂ was added, with CALUX activity falling below the limit of quantification. In contrast, sediments from the Netherlands still showed detectable toxicity, likely due to higher residual levels of PFAS, reinforcing the need for treatment strategies tailored to the contamination load. Overall, the integrated approach combining pyrolysis, washing, cavitation, and solidification effectively reduced PFAS concentrations and associated toxic effects in sediments. Moreover, the potential for safe reuse of treated sediments in construction aligns with circular economy principles and environmental remediation goals.

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