Plasma Water Treatment of Emerging Contaminants: Assessing PFAS and 1,4-Dioxane in New Jersey

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Purafide

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Assessing PFAS and 1,4-Dioxane in New Jersey

For:
New Jersey Department of Environmental Protection
Division of Science and Research

By:
Purafide

March 3, 2025

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Re:

Project: 23-SR-19628 Plasma Water Treatment Pilot
Technical Services to the New Jersey Department of Environmental Protection Concerning Novel Treatment of Water Contaminants Using a Plasma-Based Technology

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Changelog:

v1.0	2024-04-29	Draft with initial results
v1.1	2024-11-13	Draft with higher sensitivity results
v2.0	2024-12-10	Draft with DSR comments and latest data
v2.1	2025-01-31	Draft with minor DSR edits (round 2)
v2.2	2025-02-18	Final after additional DSR edits (round 3), data tables, and abbreviations list

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  - Zahid Aziz
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  - Nick Procopio
  - Kathleen Rivera
  - Nadine Sheppard
  - Metthea Yepsen
- Sample Providers and Collectors

Thank you!

Abbreviations List

1,4-D	**1,4-d**ioxane
AIX	**A**n**i**on E**x**change
AOP	**A**dvanced **O**xidation **P**rocess
c_f	Final/Effluent Concentration (ppt)
c_i	Initial/Influent Concentration (ppt)
COD	**C**hemical **O**xygen **D**emand
ECO	**E**lectro**c**hemical **O**xidation
E_{EO}	**E**lectric **E**nergy Per **O**rder (kW h/m^3)
EPA	**E**nvironmental **P**rotection **A**gency
F	**F**low Rate (GPM)
GAC	**G**ranular **A**ctivated **C**arbon
GC-MS/MS	**G**as **C**hromatography/Tandem **M**ass **S**pectrometry
GPM	**G**allon(s) **P**er **M**inute (gal/min)
HALT	**H**ydrothermal **A**lkaline **T**reatment
HDPE	**H**igh-**D**ensity **P**oly**e**thylene
HFPO-DA	**H**exa**f**luoro**p**ropylene **O**xide **D**imer **A**cid
HI	**H**azard **I**ndex
IX	**I**on E**x**change
k_1	First-Order Reaction Rate (s^{-1})
LC-MS/MS	**L**iquid **C**hromatography/Tandem **M**ass **S**pectrometry
LGW	**L**eachate-Impacted **G**round**w**ater
LL	**L**andfill **L**eachate
MCL	**M**aximum **C**ontaminant **L**evel
MDL	**M**ethod **D**etection **L**imit
MS	**M**ass **S**pectrometer
ND	**N**on-**D**etect
NDMA	N-**N**itroso**d**i**m**ethyl**a**mine
NJDEP DSR	**N**ew **J**ersey **D**epartment of **E**nvironmental **P**rotection **D**ivision of **S**cience & **R**esearch
P	**P**ower (W)
PFAS	Per- and **P**oly**f**luoro**a**lkyl **S**ubstances
PFBS	**P**er**f**luoro**b**utane **S**ulfonate
PFHxA	**P**er**f**luoro**hex**anoic **A**cid
PFHxS	**P**er**f**luoro**hex**ane **S**ulfonate
PFNA	**P**er**f**luoro**non**anoic **A**cid

PFOA	**P**er**f**luoro**o**ctanoic **A**cid
PFOS	**P**er**f**luoro**o**ctane**s**ulfonic Acid
POE	**P**oint **o**f **E**ntry
POU	**P**oint **o**f **U**se
ppb	**p**art-**p**er-**b**illion (=µg/L)
ppm	**p**art-**p**er-**m**illion (=mg/L)
ppt	**p**art-**p**er-**t**rillion (=ng/L)
PWR	**P**lasma **W**ater **R**eactor
RO	**R**everse **O**smosis
RSD	**R**elative **S**tandard **D**eviation
RSE	**R**elative **S**tandard **E**rror
SCWO	**S**uper**c**ritical **W**ater **O**xidation
SPE	**S**olid-**P**hase **E**xtraction
t	**T**ime (min)
TOC	**T**otal **O**rganic **C**arbon
UV	**U**ltra**v**iolet [Light]
UVT	**UV T**ransmittance at 254 nm
WWE	**W**aste**w**ater **E**ffluent
WWI	**W**aste**w**ater **I**nfluent

Table of Contents

Summary

The New Jersey Department of Environmental Protection (NJDEP) wants to assess alternative technologies for the treatment of emerging contaminants. The primary contaminants of concern are state-regulated and include perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorononanoic acid (PFNA), and 1,4-dioxane (1,4-D). Purafide evaluated the initial concentrations and plasma-based destruction of these emerging contaminants in wastewater influent, wastewater effluent, leachate-impacted groundwater, and landfill leachate. Purafide performed time-resolved, bench-scale studies and varied the operating conditions to estimate the treatment efficacy and cost. Withstanding matrix effects, plasma demonstrated effective destruction of target contaminants, precursors, and transformation products. Purafide determined that the most efficient treatment occurred in landfill leachate and leachate-impacted groundwater samples. Future work could involve studying additional matrices and deploying pilots with NJDEP.

Introduction

The New Jersey Department of Environmental Protection (NJDEP) Division of Science and Research (DSR) collaborated with Purafide to conduct bench-scale investigations of a novel plasma-based water treatment technology. The highlighted contaminants of concern include 1,4-dioxane (1,4-D) and three per- and polyfluoroalkyl substances (PFAS): perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and perfluorononanoic acid (PFNA). Each of these compounds has a Maximum Contaminant Level (MCL), an enforceable limit, in New Jersey.[1]

Goal

Evaluate the concentrations and efficacy of plasma-based destruction of regulated PFAS and 1,4-dioxane in matrices relevant to water stakeholders in New Jersey.

Contaminants of Emerging Concern

Legacy and emerging contaminants threaten our natural resources and public health. Some of the most prevalent, persistent, and problematic pollutants include: 1,4-dioxane—a carcinogenic solvent known to be challenging for advanced treatment [1]; N-nitrosodimethylamine (NDMA)—a highly carcinogenic disinfection byproduct with many precursors in wastewater effluent [2]; and PFAS—a class of synthetic chemicals that are ubiquitous, refractory, and hazardous at very low concentrations [3]. While PFOA and PFOS are two well-studied long-chain global surfactants, short-chain PFAS, such as perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS), and hexafluoropropylene oxide dimer acid (HFPO-DA), are generally less understood, less toxic, but more refractory [4].

The scale of the PFAS problem is so severe that several states, including New Jersey, have taken proactive regulatory approaches. For instance, Maine became the first in the nation to ban PFAS-laden biosolids [5] and hesitancy for the land application of biosolids has caused a nationwide increase in residuals management costs, resulting in annual revenue losses of up to $1.9 million for utilities [6].

As listed in Table 2, NJ regulates three PFAS: PFOA (14 ppt),

Table 2: State MCLs for PFAS (Drinking Water) and 1,4-D (Groundwater) in units of part-per-trillion (ppt).

Contaminant	MCL
PFOA	14 ppt
PFOS	13 ppt
PFNA	13 ppt
1,4-D	400 ppt

Table 3: PFAS National Primary Drinking Water Regulations.

PFAS	MCL
PFOA	4 ppt
PFOS	4 ppt
PFNA	10 ppt
PFHxS	10 ppt
HFPO-DA	10 ppt

[1] Pursuant to the New Jersey Safe Drinking Water Act (N.J.A.C. 7:10), Ground Water Quality Standards (N.J.A.C. 7:9C), and Discharge of Petroleum and Other Hazardous Substances rules (N.J.A.C. 7:1E).

PFOS (13 ppt), and PFNA (13 ppt). 1,4-D currently has an MCL of 400 ppt in groundwater and a draft MCL of 0.33 ppb in drinking water [7]. Public health concerns over PFAS culminated to April 10, 2024 when the U.S. Environmental Protection Agency (EPA) finalized stringent standards under the Safe Drinking Water Act—the first time since the 1996 amendments [8]. In addition to the individual MCLs listed in Table 3, this regulation defines a Hazard Index (HI) for exposure to co-occurring select PFAS. The HI is the aggregate of several PFAS concentrations divided by their respective health-based values:

$$\mathrm{HI} = \frac{[\mathrm{PFNA}]}{10\,\mathrm{ppt}} + \frac{[\mathrm{PFHxS}]}{10\,\mathrm{ppt}} + \frac{[\mathrm{HFPO\text{-}DA}]}{10\,\mathrm{ppt}} + \frac{[\mathrm{PFBS}]}{2000\,\mathrm{ppt}} \leq 1 \qquad (1)$$

Existing Solutions & Their Limitations

Current state of practice for PFAS management is physical removal. Filtration technologies, including reverse osmosis (RO) and granular activated carbon (GAC), can remove PFAS and satisfy drinking water regulations [11]. RO can remove long- & short-chain PFAS, but it is very expensive & energy intensive and requires concentrate discharge. On the other hand, adsorption technologies have several advantages, primarily reduced costs and the elimination of reject water. GAC is a proven technology for long-chain PFAS. Ion exchange (IX) can remove short-chain PFAS and can be roughly half the cost of GAC, but IX does not perform well with water qualities containing high concentrations of dissolved solids and organics [12]. Alternatively, anion exchange (AIX) can also remove short- & long-chain PFAS and can be regenerable [13]. Overall, these technologies produce hazardous waste streams, such as concentrate and spent media, that must be properly disposed of, which is costly and introduces long-term liabilities. Hence, sustainable destruction is needed to break the contamination cycle.

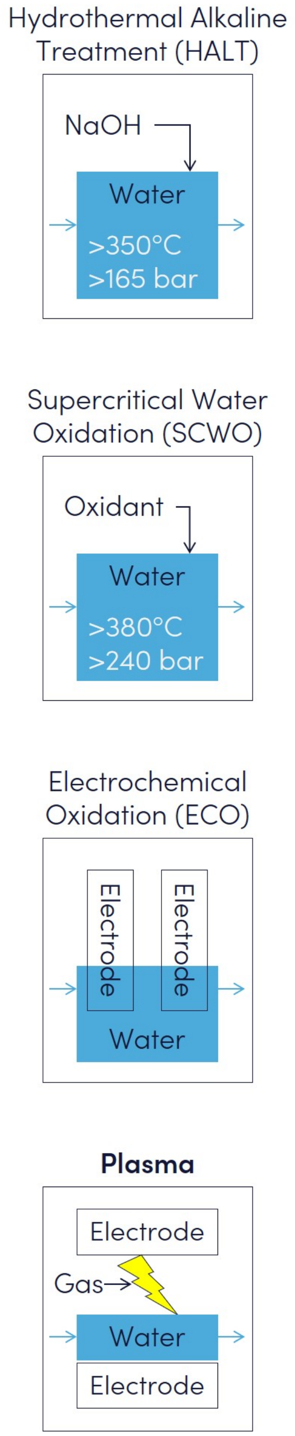

Figure 1: Illustrations of novel destruction technologies. [9, 10]

Destruction

Advanced oxidation processes (AOPs) are established destruction technologies that can disinfect and destroy a wide range of legacy and emerging contaminants, such as 1,4-dioxane and NDMA, that serve as health- and performance-based indicator compounds [14]. However, AOPs are inadequate for several contaminants of concern, particularly PFAS; PFHxS and PFBS, for instance, did not exhibit any degradation with a ultraviolet light (UV)/hydrogen peroxide AOP in groundwater [15]. On the other hand, incineration is the only approved destruction method for PFAS, but it is associated with hazards and high average costs of approximately $4.50/gal [16]. Therefore, while some technologies prove effective, none are truly sustainable and versatile enough to handle PFAS across various water qualities.

Emerging destruction technologies include thermal and non-thermal approaches, as illustrated in Figure 1. Hydrothermal alkaline treatment (HALT) and supercritical water oxidation (SCWO) require high temperatures and pressures in the presence of an oxidant whereas electrochemical oxidation (ECO) and plasma use high voltage to produce reactive species. Each approach has benefits and limitations, such as cost, scale, and resource recovery, but universally, the scavenging capacity of the background matrix hinders efficacy.

Plasma's Place in the Water World

UV and ozone, AOP technologies that use plasma indirectly, do not take advantage of strong yet short-lived species. The plasma-water interface efficiently creates energetic electrons that induce reduction and oxidation, which produce additional radicals and enable a multitude of destructive pathways. As a result, plasma-based systems can be more energy efficient[2] than AOPs, as demonstrated with various trace organics of concern [18]. Unlike separation-based technologies, plasmas can effectively inactivate pathogens and break down the most recalcitrant contaminants, including PFAS [19, 20]. Preliminary studies suggest that plasma can be an effective and energy efficient destruction alternative, as shown in Table 4 for PFOA [10, 21]. Plasma-based water treatment is fairly resilient over ranges of water quality parameters and scavenger loads. Consequently, plasma could be applied to many water qualities since it can function despite interferences. This is especially valuable in matrices where other destruction technologies are severely limited. For example, the presence of leachate co-contaminants does not hinder plasma treatment of long-chain PFAS [22]. Thus, plasma can support sustainable, simultaneous, and synergistic treatment of emerging contaminants.

Plasmas have been studied in a limited capacity on relevant water matrices at bench- & pilot-scale and should be vetted across matrices and advanced treatment trains [18, 23, 24]. However, previous plasma-based water purifiers, such

[2] The electric energy per order (E_{EO}) is defined as the amount of energy needed for 90% (one-log) reduction of a specific compound in a given volume [17]. A function of power (P), flow rate (F), and influent (c_i) and effluent (c_f) concentrations, E_{EO} is a useful metric for technology comparisons of a given matrix.

$$E_{EO} = \frac{P}{F \log_{10} \frac{c_i}{c_f}} \tag{2}$$

Table 4: Example E_{EO} for PFOA [10, 21]

Technology	PFOA E_{EO} (kW h/m^3)
Incineration	440
HALT	130
ECO	15
Plasma	4.0

as the point-source plasma jet [25], do not easily scale. At atmospheric pressure, plasmas are filamentary and cannot treat large volumes of water due to the very small discharge contact area. Thus, the diffusion of radicals into water is a transport-limited challenge. Simple designs that maximize plasma-water surface area, such as bubbles [24] or packed bed dielectric barrier discharges [26], could improve contaminant destruction in the bulk fluid.

Purafide's Plasma Water Reactor

Figure 2: PWR active region.

Purafide's Plasma Water Reactor (PWR), as pictured in Figure 2, enhances plasma ignition and propagation while minimizing energy consumption. Without consumables, this platform product couples innovative power systems and geometric configurations to address site-specific water qualities. The PWR has been parametrically assessed on various water matrices from across the U.S., ranging from drinking water to RO concentrate of landfill leachate. For instance, ECO and the PWR were compared in bench-scale studies of a challenging groundwater at an industrial remediation site in New Jersey. ECO was ineffective due to high iron, organics, and total suspended solids whereas the PWR achieved customer-defined E_{EO}s for particular PFAS. Similarly for groundwater at an industrial remediation site in Michigan, spent media management was environmentally and economically infeasible due to high background concentrations whereas the PWR destroyed PFAS and other emerging contaminants [27]. Thus, the PWR can ensure resilience against current, emerging, and future contaminants while offering savings, convenience, and regulatory compliance for water treatment managers.

This novel platform product should enable scale to industrial flow rates, but applications must be validated and prioritized prior to field deployment. NJDEP DSR partnered with Purafide to conduct bench-scale investigations of the PWR.

Experimental Design

Illustrated in Figure 3, the bench-scale PWR system was parametrically assessed to optimize kinetics and to demonstrate the tradeoff between effectiveness and energy efficiency. Purafide varied the geometry, flow, and power to select the operating conditions based on how the PWR interacted with various matrices. The system operated in batch mode, send-

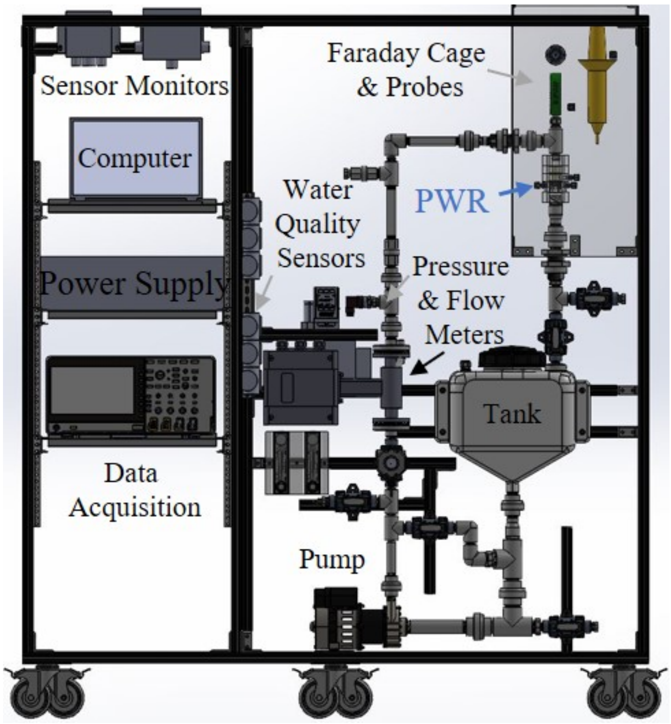

Figure 3: Bench-scale PWR system (5' x 5' x 2').

ing the bulk of the recirculated water through the PWR and a fraction of water through the water quality sensors. The online sensors monitored pH, oxidation-reduction potential, conductivity, dissolved oxygen, ozone, hydrogen peroxide, turbidity, and UV transmittance at 254 nm (UVT). Along with contaminant concentrations, these surrogate parameters provided insight into basic water chemistry, scavenger capacity, matrix interference, membrane integrity, and advanced oxidation metrics. Power characteristics were also real-time measured with high voltage and current probes.

Matrices & Methods

The technical objective was to achieve state MCLs (Table 2) for emerging contaminants in an effective and sustainable manner. NJDEP DSR focused on matrices[3] that may be impacted by PFAS and 1,4-D. A landfill, a remediation site, and a wastewater treatment plant volunteered to share samples with NJDEP DSR and Purafide staff under the condition of anonymity. Field samples were collected in high-density polyethylene (HDPE) containers without preservatives and stored at 4 °C upon arrival at Purafide's lab.

Compared to other PFAS methods, EPA Method 1633 can re-

[3] **Matrices of Interest:**

- Wastewater Influent (WWI)
- Wastewater Effluent (WWE)
- Leachate-Impacted Groundwater (LGW)
- Landfill Leachate (LL)

liably measure the most analytes (40) at trace concentrations in matrices beyond drinking water (aqueous, biosolids, soil, tissue). EPA Method 1633 calls for solid-phase extraction (SPE) followed by liquid chromatography/tandem mass spectrometry (LC-MS/MS). For 1,4-D, EPA Method 8270E is performed using headspace solid-phase microextraction followed by gas chromatography/tandem mass spectrometry (GC-MS/MS). The corresponding Method Detection Limit (MDL) for each analyte is listed in Table 5. Note that 1633 MDLs are defined for non-leachate aqueous samples, which undergo SPE and nitrogen blowdown (250 mL → 2.5 mL), and should be roughly five times higher for leachate samples, which just undergo SPE (100 mL → 5 mL).

Table 5: MDLs for in-house EPA Method 1633 (PFAS) and EPA Method 8270E (1,4-D).

Analyte	MDL (ppt)
1,4-D	160
PFOA	0.23
PFOS	2.9
PFNA	0.28
PFBA	0.49
PFPeA	0.41
PFHxA	1.2
PFHpA	0.20
PFDA	0.38
PFUnA	0.39
PFDoA	0.40
PFTrDA	0.44
PFTeDA	0.76
PFBS	0.47
PFPeS	0.58
PFHxS	1.6
PFHpS	0.21
PFNS	0.52
PFDS	1.1
PFDoS	0.70
4:2FTS	1.1
6:2 FTS	0.93
8:2FTS	0.98
PFOSA	0.35
NMeFOSA	0.55
NEtFOSA	0.56
NMeFOSAA	0.53
NEtFOSAA	1.1
NMeFOSE	3.4
NEtFOSE	3.2
HFPO-DA	0.88
ADONA	0.91
PFMBA	0.31
PFMPA	0.36
NFDHA	0.54
9Cl-PF3ONS	1.8
11Cl-PF3OUdS	2.3
PFEESA	2.4
3:3FTCA	0.30
5:3FTCA	4.5
7:3FTCA	7.5

Quality Criteria

The data collected during this project will **not** be used for regulatory/compliance purposes. The data can be used to characterize emerging contaminants in relevant water matrices and evaluate the efficacy of plasma-based destruction. Criteria for quality assurance and control have been developed in accordance with modifications to EPA Method 1633 and EPA Method 8270E. When appropriate, both methods involve instrument, sample, and method blanks, internal standards, 7+ calibration standards, and check standards for instrument sensitivity and calibration verification. For 1633, given the difficulty of PFAS analysis, additional check samples include low- and medium-level ongoing precision & recovery; also, compounds exhibiting polynomial behavior would use relative standard error (RSE) instead of relative standard deviation (RSD). To improve analysis, 1633 used automated SPE and 8270E was modified to include selected reaction monitoring.

Data sets were considered acceptable when blanks were non-detect, internal standards were within recovery ranges (extracted) and deviations $\leq$ 20% (non-extracted), calibration curve RSD/RSE $\leq$ 20%, and check standards deviated $\leq$ 30% for PFAS and $\leq$ 20% for 1,4-D. Data quality occasionally failed for some PFAS due to recoveries falling outside of the acceptable ranges and these results were indicated as estimates accordingly. After extensive troubleshooting, recovery failures were determined to be unavoidable due to matrix interferences. PFAS troubleshooting took so long that extracted samples were analyzed outside of the method-defined holding time, but the detector counts appear to negligibly vary in and outside the holding time. Also, counts did not substantially deviate between duplicate extractions of untreated samples; these duplicates were treated like check standards and the highlighted PFAS varied $\lesssim$ 10%. Hence, the analytical results were deemed accurate and reported based on the average of triplicate analysis from a given eluent.

Parametric Bench Studies

The system operated at an approximate flow rate of 4 gal/min (GPM) with a working volume of 3 L, except for LL (2.5 L) due to excessive foaming; this corresponded to cycle times between 10 s and 30 s. The sampling volume was 250 mL (100 mL for leachate) in HDPE or polypropylene for 1633 and 10 mL in borosilicate glass for 8270E. Untreated samples were collected from (1) the sample container directly and (2) the system sample valve with the recirculation pump on and the plasma off. Treated samples were collected via the sample valve at several time steps ($0 < t < 99$ min) during each closed-loop parametric experiment.

At least three treatment studies were performed in each matrix. For two experiments, the power supply settings were selected such that the same power was applied ($\approx$ 220 W) while using different operating conditions. This involved varying user-controlled variables, namely voltage and frequency, until similar applied powers were achieved. The third experiment fixed one variable while increasing another parameter, applying greater power ($\approx$ 280 W). These settings were investigated to demonstrate the wide range in kinetics and the need to optimize operating conditions for maximum destruction. LGW and LL were further evaluated in a fourth experiment that used a more efficient power supply at maximum settings ($\leq$ 200 W).

Results

These experiments were performed in two batches: (1) the initial three configurations analyzed with a lower resolution mass spectrometer (MS) and (2) the fourth, and presumably best, operating condition analyzed with a higher resolution MS. The latter studies are predominantly discussed herein.

Table 6: PFAS and 1,4-D initial concentrations in matrices of interest (prior to treatment) with MCLs, if applicable. ND denotes non-detect and * indicates an estimate due to recovery failure.

Analyte	WWE	LGW	LL	MCL
1,4-D	1.5 ppb	2.8 ppm	89 ppb	400 ppt
PFOA	57.6 ppt	10.6 ppb	2.07 ppb	14 ppt
PFOS	18.0 ppt	89.9 ppb	444 ppt	13 ppt
PFNA	4.92 ppt	9.87 ppt	137 ppt	13 ppt
PFBA	62.1 ppt	13.3 ppb	1.84 ppb	
PFPeA	69.6 ppt	15.5 ppb	5.27 ppb	
PFHxA	110 ppt	62.6 ppb	4.18 ppb	
PFHpA	17.9 ppt	9.96 ppb	914 ppt	
PFDA	9.42 ppt	2.27 ppt	140 ppt	
PFUnA	ND	ND*	8.03 ppt	
PFDoA	ND	ND*	10.4 ppt	
PFTrDA	ND	ND	3.38 ppt	
PFTeDA	ND	ND	5.46 ppt	
PFBS	84.5 ppt	16.4 ppb*	4.77 ppb	
PFPeS	1.22 ppt	29.1 ppb	44.7 ppt	
PFHxS	14.8 ppt	157 ppb	702 ppt	
PFHpS	0.50 ppt	1.33 ppb*	5.59 ppt	
PFNS	ND	1.84 ppt*	ND	
PFDS	ND	ND	1.91 ppt	
PFDoS	ND	ND	ND	
4:2FTS	ND*	3.84 ppt*	8.38 ppt	
6:2 FTS	1.43 ppt	32.5 ppt*	341 ppt*	
8:2FTS	ND	ND*	36.3 ppt	
PFOSA	0.56 ppt	2.65 ppt	15.3 ppt	
NMeFOSA	ND	ND*	2.95 ppt	
NEtFOSA	ND	122 ppt	143 ppt	
NMeFOSAA	2.25 ppt	92.2 ppt	255 ppt	
NEtFOSAA	1.43 ppt	ND*	3.30 ppt	
NMeFOSE	ND	ND	188 ppt	
NEtFOSE	ND	ND	143 ppt	
HFPO-DA	ND	3.35 ppt	1.63 ppt	
ADONA	ND	ND*	ND*	
PFMBA	ND	56.5 ppt	1.30 ppt	
PFMPA	ND	34.8 ppt	1.33 ppt	
NFDHA	ND	ND	0.72 ppt	
9Cl-PF3ONS	ND	ND*	ND	
11Cl-PF3OUdS	ND	ND*	ND	
PFEESA	ND	5.31 ppt	ND	
3:3FTCA	0.53 ppt	33.7 ppt	40.4 ppt	
5:3FTCA	ND	51.6 ppt	4.16 ppb	
7:3FTCA	ND	ND	173 ppt	

Initial Concentrations of Emerging Contaminants

Particulates in WWI clogged the sample lines, resulting in incomplete 1633 extractions for untreated samples directly from the sample container. Instead, untreated WWI was sampled from the bench-system after running through a 70 µm polyethylene strainer: PFOA (3ppt), PFOS (17ppt), and PFNA (5ppt) were near or below the federal & state drinking water MCLs. On the other hand, the headspace analysis in 8270E enabled analysis of untreated sample directly from the sample container, resulting in non-detect (ND) for 1,4-D.

The other matrices (WWE, LGW, and LL) were successfully extracted via 1633. As evident in Table 6, each matrix exceeded the state MCL for the contaminants of concern, except for PFNA in WWE and LGW. Each of these matrices also exceeded the federal health-based valve for PFHxS, signaling that the matrix is hazardous (HI $>$ 1) by drinking water standards. LGW and LL also exceeded the federal health-based valve for PFBS. Overall, matrix interferences caused failed recoveries for certain contaminants and plasma treatment generally improved the passing rate of recoveries.

Destruction Efficacy

In this particular investigation, the PWR was most cost-effective in LL, but this does not imply that this will always be the case. For example, prior work revealed that matrices on opposite ends of the pollution spectrum, specifically drinking water and RO concentrate of LL, exhibited similar E_{EO} though they had initial concentrations orders of magnitude apart. Assuming first-order reaction rates, treatment of matrices with higher concentrations are expected to be more energy efficient, yet this was not the case in this study where LGW had initial concentrations orders of magnitude greater than LL. Operating conditions, background constituents, and initial concentrations play critical roles as evident during plasma treatment in WWI, where unexpected kinetics occurred for PFOS—one configuration yielded steady decay while the other two settings resulted in first production then decay. This suggests that unidentified precursors are responsible for the changes in concentrations as they increase the complexity of these practical matrices. Therefore, given the unique nature of each matrix, it is difficult to confidently claim which matrix the plasma will perform best in and bench-scale studies are required. Regardless of the matrix, the PWR demonstrated destruction of each of the highlighted pollutants and the capability to achieve non-detect.

For 1,4-D, LGW and LL surprisingly achieved similar log reductions (≈0.14, or 27% removal) for the same treatment time; on the contrary, WWE achieved non-detect in all three experimental configurations while some timesteps revealed detectable 1,4-D concentrations, suggesting unknown transformations. This further indicates the need for future work to involve developing a technoeconomic model that incorporates the added benefit of synergistic destruction.

Plasma-based destruction of the highlighted contaminants was demonstrated in each matrix even though competing kinetics interfered with contaminant destruction. For instance, the highlighted PFAS displayed overall decomposition in LGW (Fig. 4, Table 9) and LL (Fig. 5, Table 10). For the same operating condition, PFOS had the best and worst effective reaction rate in LGW and LL, respectively, which is attributed to the different orders of magnitudes between contaminant & scavenger concentrations. The background constituents affected both the PFAS destruction rates and sample extraction success rates.

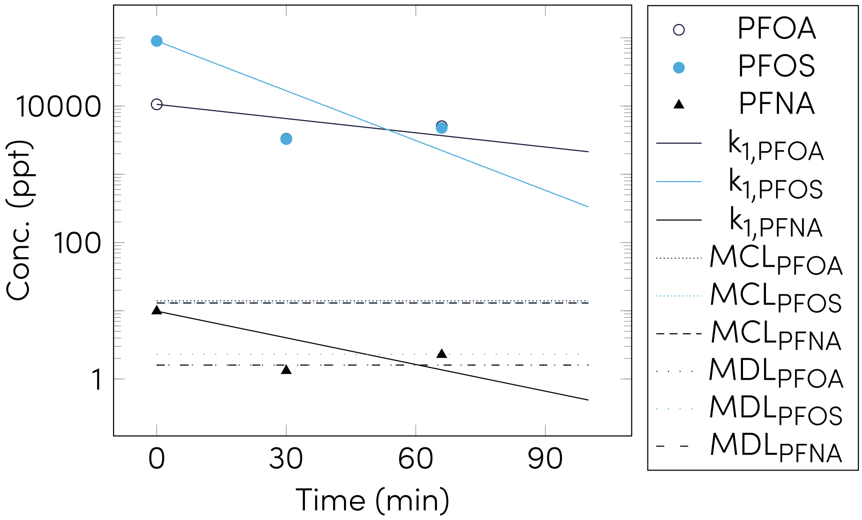

Figure 4: Plasma-based destruction of regulated PFAS in LGW.

Table 7: Energy & electric cost [28] ranges for regulated PFAS in LGW.

E_{EO}	Cost
17–170 $\mathrm{kW\,h/m^3}$	\$32–240 /kgal

LL exhibited first-order (k_1) reaction rates for all the selected PFAS ($R^2 > 0.94$) whereas the high initial concentration and transformation products of PFOA in LGW significantly competed with decomposition, resulting in non-first-order behavior ($R^2 > 0.62$). In both cases, the effects caused by the background matrix and transformation products are clear in the data's deviation from the fitted curves. First-order kinetics assume scavenger concentrations are much greater than contaminant concentrations and enough treatment time will eventually result in the desired effluent concentration. The effective reaction rate should still be pseudo-first-order for long-chain PFAS and can be used to determine the minimum contact time necessary for a given log reduction or effluent concentration. As for short-chain PFAS, their reaction rates should be predominately a function of their concentrations and the reaction rates of long-chain PFAS precursors. When comparing matrices, the change in the effective reaction rate of a given PFAS can be accredited to the matrices' respective scavenging capacities, which can be seen in the deviations from first-order and vastly different reaction rates. This proves difficult especially for intermediate-sized PFAS, such as PFHxA and PFBS, that oscillate in concentration as complex matrix effects take hold.

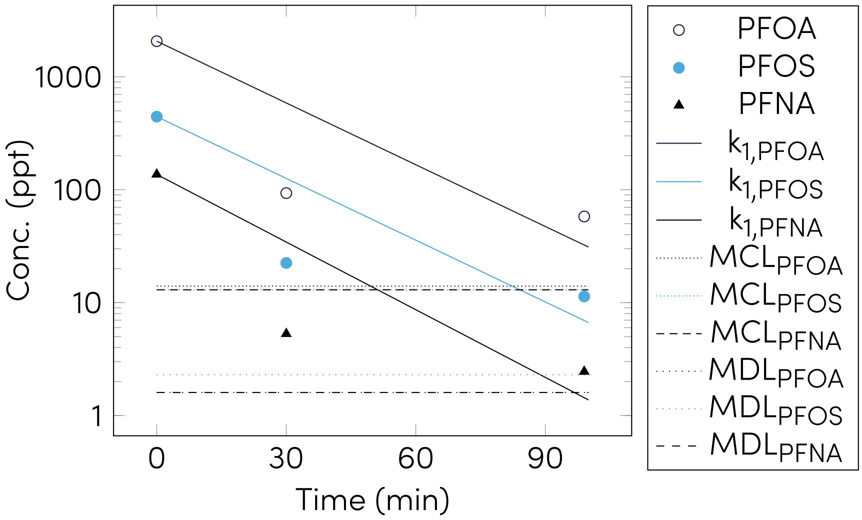

Figure 5: Plasma-based destruction of regulated PFAS in LL.

Table 8: Energy & electric cost [28] ranges for regulated PFAS in LL.

E_{EO}	Cost
27-64 kW h/m^3	\$14-69 /kgal

For each pollutant, the E_{EO} can be evaluated and the lowest E_{EO} will correspond to the most energy efficient configuration for the PWR. The variations in oxidants and PFAS E_{EO} provide insight into how water quality impacts plasma performance and demonstrate that PFAS concentrations can be tailored using different geometric, power, and flow configurations. Since PFAS analysis is costly, surrogate parameters may be used to imply adequate PFAS destruction, similar to how standard AOPs use oxidant dose and UVT to indirectly indicate sufficient treatment of 1,4-dioxane. Though the reaction rates and initial concentrations were substantially different in LGW and LL, they yielded a similar order of magnitude for E_{EO} and electric cost for each PFAS, as listed in Tables 7 and 8. In both matrices, generally, the E_{EO} will creep up as more power is drawn and parasitic reactions proliferate. If the desired E_{EO} cannot be attained or PFAS destruction transitions away from first-order decay, power parameters can be real-time varied to tailor kinetics, hence energy efficiency. Thanks to cost savings from in-house analysis, if unexpected reaction rates occur, samples at intermittent time intervals will be taken to better fit the kinetic curves and reveal the dominant contribution to the reaction rate.

The short-chain PFAS and other recalcitrant contaminants expectedly exhibited lower effective reaction rates than long-chain PFAS and compounds susceptible to oxidation. PFOA unexpectedly first decreased then increased in concentration, implying that precursors are present. As for general water quality, there was a minimal impact on pH and ammonia remained below the federal MCL. Furthermore, organic matter measurements, such as chemical oxygen demand (COD) and total organic carbon (TOC), are believed to falsely increase due to excess aqueous hydrogen peroxide, suggesting the need for quenching prior to analysis. Nonetheless, the complexity of the chemistry is evident as higher contaminant concentrations and lower background concentrations do not necessarily indicate better effective reaction rates. The non-ordinary kinetics and nearly order of magnitude range in the E_{EO} between experiments reinforce the need for more optimization studies.

Conclusions

Purafide is an environmental startup that destroys and analyzes emerging contaminants. Purafide uses plasma to mineralize pollutants and develop the latest analytical methods to confirm their destruction. Purafide performs lab studies, deploys onsite pilots, then helps organizations manage their water quality via commercial installations. Our commitment to environmental justice is only further demonstrated by the work of our Water Equity Fund, which provides pro bono analysis and treatment system installations for marginalized communities.

These preliminary investigations reaffirmed that plasma can be a viable destruction alternative. The PWR efficiently destroyed concerning contaminants and reliably operated regardless of matrix interferences. Plasma was effective in the tested matrices, ranging from wastewater effluent to landfill leachate, most of which had hazardous concentrations of PFAS and 1,4-D. More importantly, plasma can replace unsustainable practices, such as leachate solidification and deep well injection that can cost roughly \$200/kgal. These initial plasma bench-scale studies achieved the target destruction cost of < \$100/kgal.

Applications

Plasmas can eliminate emerging contaminants in effluent and reject streams. They can enhance contaminant destruction, pathogen inactivation, electrocoagulation, and biodegradation, which is why their synergy with other technologies should be explored in advanced treatment trains. Plasmas could complement existing systems in remediation, source control, and decentralized treatment, such as point of entry (POE) and point of use (POU). Due to the high initial cost barrier for citizens, planned pilots include (1) remediation sites, particularly those employing pump-and-treat, and (2) water utilities, namely those with industrial pretreatment programs. As the technology scales, cost is projected to drop enough to the point that the average citizen can afford decentralized plasma-based treatment. Using online sensors, the ultimate goal would be to real-time monitor and dynamically treat water.

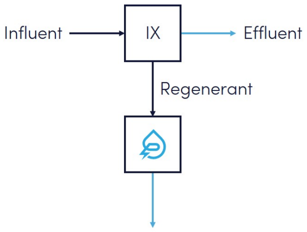

Figure 6: IX-based treatment train.

For near-term applications, plasmas are better suited for 1,4-D and long-chain PFAS since their reaction rates are higher than those of short-chain PFAS.

Point of Entry Treatment Systems

POE or POU treatment systems typically involve separation. The simplest small-scale technologies for separation are sorption-based, such as IX and GAC, though RO has gained traction. If destruction is also included, the established technology is AOP, usually UV. Plasma can be applied to reject streams, like regenerant or concentrate, or replace destruction approaches. For example, as illustrated in Figures 6 and 7, the sorbent can be periodically regenerated and that liquid waste stream can be treated by the plasma.

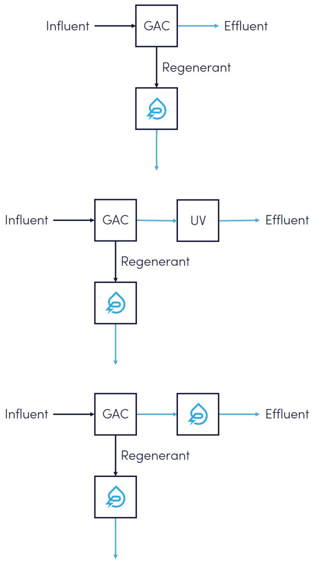

Figure 7: GAC-based treatment trains.

Also, plasmas can replace UV in GAC-based treatment trains (Fig. 7) for added benefits including enhanced pathogen inactivation and destruction of emerging contaminants, such as short-chain PFAS, 1,4-D, and other trace organics.

Since RO removes long- and short-chain PFAS, plasma can be incorporated into concentrate management (Fig. 8) and help reduce PFAS entering water resource recovery facilities. Furthermore, plasmas could replace the AOP for improved 1,4-D destruction and pathogen inactivation.

The next step involves prioritizing matrices and treatment trains to pursue in the field.

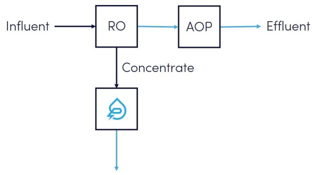

Figure 8: RO-based treatment train.

Next Steps

Purafide is eager to continue to collaborate with NJDEP DSR to deploy plasma pilots at a landfill and a remediation site, such as the leachate-impacted groundwater. On another note, the biggest challenge during this project was sample analysis due to matrix-induced complications and the latest method improvements should be used to reassess the investigated matrices.

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Appendices

Data Tables

Figure 4 plots the data listed in Table 9.

Table 9: Regulated PFAS concentrations in LGW.

Analyte	**Time** (min)	**Concentration** (ppt)
PFOA	0	10600
	30	3310
	66	5060
PFOS	0	89900
	30	3280
	66	4780
PFNA	0	9.87
	30	1.32
	66	2.27

Figure 5 plots the data listed in Table 10.

Table 10: Regulated PFAS concentrations in LL.

Analyte	**Time** (min)	**Concentration** (ppt)
PFOA	0	2070
	30	93.4
	99	58.0
PFOS	0	444
	30	22.5
	99	11.4
PFNA	0	137
	30	5.30
	99	2.45