



The State of New Hampshire
Department of Environmental Services

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Robert R. Scott, Commissioner

September 9, 2020

His Excellency, Governor Christopher T. Sununu
and the Honorable Council
State House
Concord, NH 03301

REQUESTED ACTION

Authorize Department of Environmental Services (DES) to enter into a **Sole Source** agreement with the U.S. Geological Survey (USGS), Pembroke, NH (VC# 175772), in the amount of \$420,000 to study the occurrence and behavior of per- and poly-fluoroalkyl substances (PFAS) in soils and biosolids in New Hampshire, effective upon Governor and Council approval through January 31, 2022. Funding is 100% Drinking Water/Groundwater Funds.

Funding is available in the following account.

	<u>FY 2021</u>
03-44-44-444001-8873-102-500731	\$420,000
Dept. Environmental Services, Emerging Contaminants, Contracts for Program Services	

EXPLANATION

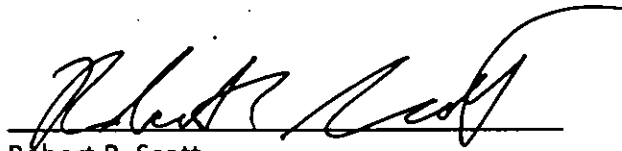
The purpose of this agreement is to fund a study to assess the occurrence of PFAS in shallow soils and biosolids in New Hampshire, and evaluate the risk to groundwater that may be caused by leaching of these contaminants from both soil and biosolids. The work will involve an extensive sampling and analysis effort of soils statewide and selected biosolids, and additional laboratory and field studies to characterize leaching behavior. DES would like to enter into a **Sole Source** agreement with USGS for this study because of their unique capabilities and previous extensive experience conducting statewide studies of the occurrence of emerging contaminants. Previous work conducted by USGS in New Hampshire includes statewide studies of methyl tertiary-butyl ether (MtBE), which were key to understanding the scope of that contamination problem. USGS's extensive knowledge of New Hampshire soils, geology, and aquifers, along with their high quality assurance standards, make them uniquely qualified to conduct this study. In addition to these advantages, \$180,000 in project matching funds will be provided by USGS. Laboratory analytical costs associated with this study will be paid separately and directly by DES to the contract labs under previously approved contracts.

The study is necessary to support DES's efforts to develop protective standards governing soil cleanup and land application of biosolids. Ultimately, such standards are vitally important to

protecting groundwater and drinking water quality in New Hampshire. The study will result in an improved understanding of the occurrence and behavior of PFAS in New Hampshire soils and biosolids, and help to position DES to develop appropriate protective standards, thus advancing DES's mission to protect human health and the environment.

This agreement has been approved by the Department of Justice as to form, content, and execution. In the event that other funds are no longer available, General Funds will not be requested to support this contract.

We respectfully request your approval.



Robert R. Scott
Commissioner

U.S. Department of the Interior
U.S. Geological Survey
Joint Funding Agreement
FOR
Water Resource Investigations

Customer #: 600000093
Agreement #: 20LGJFANH000015
Project #:
TIN #: 02-6000618

Fixed Cost Agreement YES[X] NO[]

THIS AGREEMENT is entered into as of the September 22, 2020, by the U.S. GEOLOGICAL SURVEY, New England Water Science Center, UNITED STATES DEPARTMENT OF THE INTERIOR, party of the first part, and the New Hampshire Department of Environmental Services party of the second part.

1. The parties hereto agree that subject to the availability of appropriations and in accordance with their respective authorities there shall be maintained in cooperation a study called New Hampshire PFAS concentrations in soils and some biosolids in the State of New Hampshire, herein called the program. The USGS legal authority is 43 USC 36C; 43 USC 50, and 43 USC 50b.

2. The following amounts shall be contributed to cover all of the cost of the necessary field and analytical work directly related to this program. 2(b) include In-Kind-Services in the amount of \$0.00

- (a) \$180,000 by the party of the first part during the period September 22, 2020 to January 31, 2022
- (b) \$420,000 by the party of the second part during the period September 22, 2020 to January 31, 2022
- (c) Contributions are provided by the party of the first part through other USGS regional or national programs, in the amount of: \$0

Description of the USGS regional/national program:

- (d) Additional or reduced amounts by each party during the above period or succeeding periods as may be determined by mutual agreement and set forth in an exchange of letters between the parties.
- (e) The performance period may be changed by mutual agreement and set forth in an exchange of letters between the parties.

3. The costs of this program may be paid by either party in conformity with the laws and regulations respectively governing each party.

4. The field and analytical work pertaining to this program shall be under the direction of or subject to periodic review by an authorized representative of the party of the first part.

5. The areas to be included in the program shall be determined by mutual agreement between the parties hereto or their authorized representatives. The methods employed in the field and office shall be those adopted by the party of the first part to insure the required standards of accuracy subject to modification by mutual agreement.

6. During the course of this program, all field and analytical work of either party pertaining to this program shall be open to the inspection of the other party, and if the work is not being carried on in a mutually satisfactory manner, either party may terminate this agreement upon 60 days written notice to the other party.

7. The original records resulting from this program will be deposited in the office of origin of those records. Upon request, copies of the original records will be provided to the office of the other party.

8. The maps, records or reports resulting from this program shall be made available to the public as promptly as possible. The maps, records or reports normally will be published by the party of the first part. However, the party of the second part reserves the right to publish the results of this program, and if already published by the party of the first part shall, upon request, be furnished by the party of the first part, at cost, impressions suitable for purposes of reproduction similar to that for which the original copy was prepared. The maps, records or reports published by either party shall contain a statement of the cooperative relations between the parties. The Parties acknowledge that scientific information and data developed as a result of the Scope of Work (SOW) are subject to applicable USGS review, approval, and release requirements, which are available on the USGS Fundamental Science Practices website (<https://www.usgs.gov/about/organization/science-support/science-quality-and-integrity/fundamental-science-practices>).

U.S. Department of the Interior
U.S. Geological Survey
Joint Funding Agreement
FOR
Water Resource Investigations

Customer #: 6000000093
Agreement #: 20LGJFANH000015
Project #:
TIN #: 02-6000618

9. Billing for this agreement will be rendered quarterly. Invoices not paid within 60 days from the billing date will bear Interest, Penalties, and Administrative cost at the annual rate pursuant the Debt Collection Act of 1982, (codified at 31 U.S.C. § 3717) established by the U.S. Treasury.

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U.S. Geological Survey
United States
Department of Interior

New Hampshire Department of Environmental
Services

Signature

By  Date: 09/08/2020
Name: Matt Ely acting for Johnathan Bumgamer
Title: Director

Signatures

By  Date: 9/9/20

Name:
Title:

By  Date: 9/9/2020

Name:
Title: Attorney General (Form, Substance, & Execution) (if applicable)

By _____ Date: _____

Name:
Title:



Per- and Polyfluoroalkyl Substances (PFAS) Partitioning to Soils and Biosolids in New Hampshire

U.S. Geological Survey, New England Water Science Center
September 2020

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a diverse class of thousands of compounds that have been produced since the 1940s and are frequently found in the environment. Exposure to some PFAS has been associated with adverse human health outcomes. Many PFAS are hydrophobic surfactants that are chemically, thermally, and biologically stable at ambient conditions, which allows for a range of surfactant and non-stick applications. As in many areas, PFAS have been released to the environment in New Hampshire through several pathways including industrial releases, commercial uses, waste management applications (wastewater effluent, biosolids application, landfill leachate), and from the use of Class B firefighting foams, including aqueous film-forming foams (AFFF). There is a high level of public concern over PFAS in New Hampshire following discoveries of drinking water contamination at the former Pease Air Force Base in 2014 and in several southern New Hampshire towns in 2016, which prompted statewide investigations of PFAS impacts to drinking water quality and the environment. Throughout this text, PFAS refers to the targeted compounds measured by a New Hampshire Department of Environmental Services (NHDES) contract laboratory.

Problem Statement

As adverse human health effects have been associated with exposure, New Hampshire has promulgated groundwater and drinking water quality standards for some PFAS. Additionally, several states in New England have set standards and/or guidance values for some PFAS in drinking water. New Hampshire has established guidance values for direct contact with soil impacted by select PFAS. There is currently (2020) a need to set maximum allowable soil and biosolid PFAS concentration(s) that are protective of human health due to the potential for leaching of some PFAS to groundwater that is used as a drinking water source. Biosolids are a known source of some PFAS to the environment, and soils can contain some

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PFAS from atmospheric input or due to discharges from local PFAS sources. Therefore, precipitation over areas with contaminated biosolids or soils can result in contaminated surface water runoff and infiltration of contaminated water to underlying aquifers. A 2018 soil sampling effort in Vermont found select PFAS concentrations ranged from 540 nanograms per kilogram (ng/kg, equivalent to parts per trillion) to 35,000 ng/kg.¹ Given the large range in PFAS concentrations observed in the Vermont study, as well as the range observed at site-specific PFAS investigation areas in New Hampshire, it will be useful for New Hampshire to have an overview of PFAS concentrations across the state. Therefore, the first objective of this proposal is for the U. S. Geological Survey (USGS) to conduct a state-wide survey to evaluate the range of PFAS concentrations that occur in shallow soils and selected biosolids.

In addition to soil and biosolid PFAS occurrence concentrations in New Hampshire, underlying partitioning data is needed to understand potential concentrations in water in contact with soils or biosolids. Sediment/water distribution coefficient (K_d) values are available in the literature for certain PFAS compounds, but are not specific to soils and biosolids in New Hampshire. If the fraction of organic carbon (f_{oc}) is known, organic carbon normalized sediment/water partition coefficient (K_{oc}) values could be used to estimate K_d values in New Hampshire through the following equation:

$$K_{oc} = \frac{K_d}{f_{oc}}$$

However, it has been shown that PFAS sorption is not necessarily dependent on organic carbon, and can also be significantly influenced by other factors, including, but not limited to protein, anion exchange capacity, oxide content of the solids, etc.² Therefore, K_d values specific to major types of New Hampshire soils and biosolids need to be investigated in both laboratory and field settings.

Objectives and Scope

The primary objectives of this project are as follows:

- 1. Characterize shallow soil PFAS concentrations in New Hampshire, and quantify PFAS concentrations in selected biosolids samples.**
- 2. Investigate PFAS sediment/water partitioning for selected soils and biosolids.**
- 3. Conduct a field-scale investigation of PFAS transport to compare to the laboratory observed values.**

Approach

The proposed work will involve a combination of field sampling, laboratory experiments, and a field-scale investigation. Note that the technical details of the following tasks are subject to revision as the project develops as the project team reviews and incorporates the data generated by this study. Major changes will be discussed with NHDES before implementation. Changes to the technical details of the work scope will not result to an increase in the project budget.

Objective 1. Characterize soil PFAS concentrations in New Hampshire, and quantify PFAS concentrations in selected biosolids samples.

Rationale for Objective 1: Knowledge of the PFAS concentrations in soils and biosolids in New Hampshire is necessary to understand the extent and scale of PFAS contamination.

Furthermore, knowledge of the range of PFAS concentrations will allow evaluation of whether nonlinear sorption regimes need to be considered. Nonlinearity in sorption isotherms can arise from heterogeneity of adsorption sites or from interactions between PFAS molecules at high concentrations (for example, electrostatic repulsion). Typically, nonlinearity arises at high concentrations of PFAS, and can result in higher-than-expected water concentrations if the expected concentrations were calculated based under the assumption of linearity. An example of such a non-linear sorption isotherm is shown in Figure 1.²

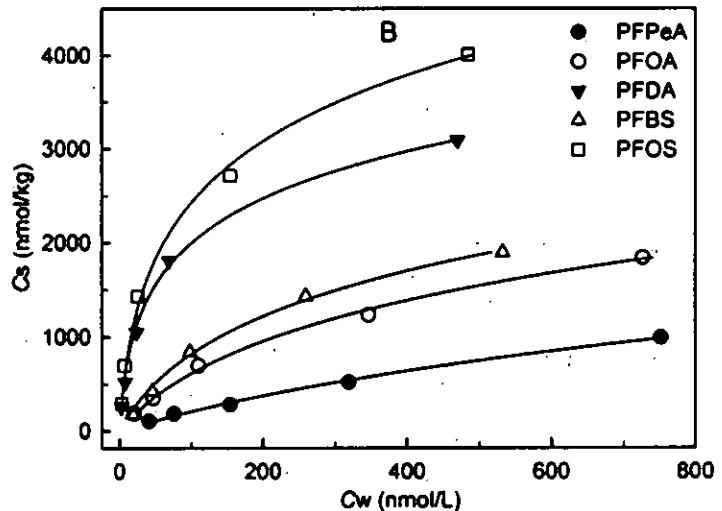


Figure 1. Example of a non-linear sorption isotherm in soil. C_s is the concentration in the soil and C_w is the concentration in the water. Figure from Li et al., 2019².

Tasks for Objective 1: The goal of this objective is to provide information on

shallow soil and selected biosolid PFAS concentrations in New Hampshire. Site locations for soil sampling will be determined following an equal area grid approach³ to allow quantification of the proportion of soil greater than laboratory reporting limits. Soils sampling protocols will be established and documented in consultation with NHDES prior to sampling. All soils will be sampled in the 0–6 inch depth interval. 50% of the samples will additionally be sampled in the 6 – 12 inch interval to investigate whether PFAS have migrated from the top surface soil. Deeper

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soil profiles will be collected at six locations in 6 inch intervals, down to the water table or a maximum depth of 3 feet to investigate vertical migration of PFAS. Selected representative biosolids also will be analyzed. USGS will provide PFAS-free water as needed for blanks and equipment decontamination. The following soil characterization and analyses will be completed for all soil and biosolids samples (see also Non-PFAS Analyses section of proposal):

In the field or laboratory by USGS:

- Soil sampling
- Visual classification of soils using the modified Burmister Soil Classification System
- Soil pH

By NHDES or in a contract laboratory to NHDES:

- Biosolids sampling
- Percent solids (soil moisture content)
- PFAS analysis, including PFHxS, PFOA, PFOS, and PFNA (See PFAS Analysis section)
- Concentrations of select perfluoroalkyl carboxylic acid (PFCA) and perfluoroalkyl sulfonic acid (PFSA) precursors via total oxidizable precursor assay (TOPA) will be analyzed for the 0-6 inch interval at the locations selected for additional subsurface sampling.
- Sediment organic carbon content (total organic carbon using the Lloyd Kahn method)

Table 1. Sample Numbers for Objective 1

	Depth Interval (in)	Number of Samples	Soil pH	% Solids	PFAS Analysis	TOPA	Sediment Organic Carbon	Protein Content
Top soil samples	0-6	100	100	100	100	50	100	100
Field duplicate/triplicates for top soil samples	0-6	10	10	10	10	5	10	10
Shallow subsurface soil samples	6-12	50	50	50	50	0	50	50
Field duplicate/triplicate for shallow subsurface soil samples	6-12	5	5	5	5	0	5	5
Soil profile (max 3 ft) samples	0-36	36	36	36	36	0	36	36
Field duplicate/triplicate for soil profile (max 3 ft) samples	0-36	4	4	4	4	0	4	4
Soil quality control (equipment blanks, field blanks, etc.)*	N/A	20	N/A	N/A	20	5	20	20
Biosolids	N/A	5	5	5	5	5	5	5
Field duplicate biosolids	N/A	5	5	5	5	5	5	5
Biosolid quality control (equipment blanks, field blanks)*	N/A	5	N/A	N/A	5	5	5	5
Total Sample Numbers		240	245	245	240	75	240	240

*Field blanks are assumed to be in the same matrix as the primary samples, whereas equipment blanks and other QA/QC samples are in the aqueous phase.

Objective 2. Investigate PFAS sediment/water partitioning for selected soils and biosolids

Rationale for Objective 2: K_d values are critical sorption parameters required for assessment of aqueous mobility of contaminants and are inputs for a variety of methods to determine allowable soil concentrations. K_d values are also critical parameters for SESOIL—a SEasonal SOIL one-dimensional vertical transport (and fate) model for unsaturated zone flow, used by NHDES to evaluate potential for soil contaminant leaching for certain contaminants. Because K_d values are soil-specific, the objective of this task is to identify values for soils and biosolids that may be representative of New Hampshire conditions.

Tasks for Objective 2: As Objective 2 will start soon after Objective 1, prior information on PFAS concentrations and soil types from NHDES will be used to select 5 soils for partitioning experiments that have a range of characteristics. Soils will be chosen in consultation with NHDES. Additionally, 5 biosolids will be chosen based on input from NHDES. Soil selection will be chosen with the aid of resources like the Natural Resources Conservation Service soil types and will concentrate on samples that fall into the major soil type categories in New Hampshire, including stratified drift-derived soil and glacial till-derived soil. The soils derived from stratified drift would ideally consist of one fine-grained (glacial lake deposit parent material) and one coarse-grained (outwash or deltaic parent material) site. The glacial till-derived soils would ideally be chosen based on those that are typical for agriculture in the state. For each of the 5 types of soils chosen, a location without PFAS contamination (or with low concentration of PFAS) (e.g., PFAS concentrations are less than 1 ppb or below the laboratory reporting limit for measured PFAS and TOPA analysis) and with known PFAS (e.g., at least 3 analytes detected at concentrations at least one to two orders of magnitude greater than the uncontaminated soil for measured PFAS pre-TOPA analysis) will be selected. From here on, references to “uncontaminated soil” refer to soil with low concentrations of PFAS as described above. Effort will be made to ensure the soil characteristics are similar between sites with and without PFAS contamination to facilitate comparison.

Uncontaminated soil will be used for control experiments. Further, uncontaminated soils will be artificially spiked with a range of PFAS at a range of concentrations and the K_d values compared to soils already containing PFAS. See PFAS Analysis section for list of PFAS compounds in the spike solution. Although there will inevitably be differences in PFAS concentrations/composition, this will allow for comparison in sorption between soils containing an in situ PFAS population, and soils artificially spiked with PFAS (i.e. adsorption vs. desorption experiments). There is

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evidence in the literature indicating that soils containing PFAS (desorption experiment) leach much more slowly than predicted from adsorption experiments.⁴ Therefore, we will test both artificially spiked uncontaminated and contaminated soils to provide a range of K_d values. The following steps outline the tasks for this objective.

Subtask 2.1: Prepare laboratory experiments, including characterization of soil and biosolids

1. Select 5 soil types and 5 biosolids. Obtain a contaminated soil sample and an uncontaminated soil sample from each of the 5 chosen soil types. A total of 15 solid samples will be obtained: 5 uncontaminated soils, 5 contaminated soils, and 5 biosolids. Samples will be collected using the same procedures as in Objective 1, dried, and sieved with a 2 mm sieve to remove large materials. Samples will be stored at 4 °C or frozen when not in use.
2. As outlined in Objective 1, the selected 15 samples will be characterized for soil pH, sediment organic carbon, percent solids, individual PFAS, and TOPA. Other desired analyses include cation and anion exchange capacity, protein content, iron content, aluminum content, and grain size (%sand, %silt, and %clay).
3. Batch reactors will be set up in triplicate in polypropylene or HDPE containers and will contain a 1:10 soil:water ratio, likely using 4 g soil and 40 mL artificial water. The reactors must have room for head space to prevent oxygen from being consumed too quickly, but also need to contain enough liquid and sediment to maintain low PFAS reporting limits (see PFAS Analyses section) during laboratory analysis. The 1:10 soil:water ratio is one of the recommended ratios outlined by the U.S. Environmental Protection Agency document on "Batch-Type Procedures for Estimating Soil Adsorption of Chemicals",⁵ and will allow for K_d evaluation of most compounds. Artificial water will likely be constructed to be similar to the inorganic composition of soil water/stream water in Hubbard Brook, New Hampshire to replicate environmental conditions.⁶⁻⁸ The artificial water will contain more dissolved ions than precipitation. This is because the batch reactors contain more water per gram of soil than occurs naturally, and therefore low ionic strength water would cause the soils to leach ions excessively. All reactors will be put on a shaker table at room temperature after all components are added.

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Subtask 2.2: Kinetics Experiment

- First, a kinetics experiment will be undertaken to determine the time needed to reach steady state in the system. The following experimental design will be undertaken (Table 2). 1 uncontaminated soil, 1 contaminated soil, and 1 biosolid will be chosen. Dissolved oxygen (DO), cations, anions, and pH will be monitored in separate control reactors (one for each of the 3 solid samples) throughout the experiment. The sterile and non-sterile reactors will be used to monitor the impact that live microbes have on partitioning. Further, sterile controls are needed to monitor precursor degradation and precursor contribution to the perfluoroalkyl acid concentrations in the reactors.

Table 2. Kinetics experimental design.

Sample Time (days)	2 Blank Reactors, No PFAS, No Solids	1 Blank reactor, Spiked (Aqueous Phase Starts at 1000 ng/L), not solids	Uncontaminated Soil, no additional PFAS spike	Uncontaminated Soil, Spiked (Aqueous Phase Starts at 1000 ng/L)	Contaminated Soil, no additional PFAS spike	Biosolids, Spiked (Aqueous Phase Starts at 1000 ng/L)	Sum at each time point
0 (Initial aqueous phase)	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	0	0	0	0	12 Aq.
2		3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	30 Aq. / 24 Solid
4		3 sterile/ 3 non-sterile	0	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	24 Aq.
6	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	0	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	30 Aq. / 24 Solid
10		3 sterile/ 3 non-sterile	0	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	24 Aq.
16	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	3 sterile/ 3 non-sterile	36 Aq. / 24 Solid
Total	18 Aq.	36 Aq. / 18 Solid (container walls)	12 Aq.	30 Aq. / 18 Solid	30 Aq. / 18 Solid (PFAS) 30 Aq. / 18 Solid (TOPA)	30 Aq. / 18 Solid (PFAS) 30 Aq. / 18 Solid (TOPA)	156 Aq. / 72 Solid 30 Aq. / 36 Solid (TOPA)

*All above aqueous samples will be measured for targeted PFAS. TOPA will be conducted for the contaminated soil and biosolids samples (spiked and not spiked) that are expected to contain PFAA precursor concentrations. The PFAS spike of 1000 ng L⁻¹ will be from a perfluoroalkyl acid standard mix from Wellington Laboratories and will contain no precursor compounds (see PFAS Analyses section). The spike concentration (1000 ng L⁻¹) is the concentration of each compound before anion concentration correction. All sample cells highlighted in light blue will be measured for aqueous and solid phase.

- At each sampling time point, samples will be removed from the shaker table and centrifuged before transferring the aqueous phase to a new container. Samples will be weighed throughout the process to record soil/biosolid and water weights to enable correction for water concentrations. The separated aqueous and solid phases will be

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sent for PFAS analysis. PFAS loss to the side walls will be monitored through the spiked control reactors that contains no solids.

- The above kinetics experiment will allow for evaluation of the effectiveness of the experimental setup. Further, the impact of sterilization and the contribution of PFAA precursors will be evaluated to decide on whether the following set of batch experiments need to be sterilized. If necessary, parameters will be adjusted after evaluation of the results. The results will also determine the time needed to reach steady state.

Subtask 2.3: Batch Experiments

- Following the kinetics experiment, the batch sorption experiments outlined in Table 3 will be undertaken. All reactors will be measured after the number of days required to reach steady state, as determined from the kinetics experiment.

Table 3. Batch sorption experiments.

Initial Aqueous Spike Concentration (ng/L)*	3 Control Reactors, No Sediment	Uncontaminated Soil, Spiked	Contaminated Soil, no additional PFAS spike	Biosolids, Spiked	Sum at Each Concentration
0	9 (blanks)	3*5 soils	3*5 soils	3*5 biosolids	54 Aq. / 54 Solid
300	3	3*5 soils	0	3*5 biosolids	33 Aq. / 33 Solid
500	3	3*5 soils	0	3*5 biosolids	33 Aq. / 33 Solid
750	3	3*5 soils	0	3*5 biosolids	33 Aq. / 33 Solid
1000	3	3*5 soils	0	3*5 biosolids	33 Aq. / 33 Solid
2000	9	3*5 soils	0	3*5 biosolids	39 Aq. / 39 Solid
Total	30 Aq. / 30 Solid	90 Aq. / 90 Solid	15 Aq. / 15 Solid (PFAS) 15 Aq. / 15 Solid (TOPA)	90 Aq. / 90 Solid (PFAS) 90 Aq. / 90 Solid (TOPA)	225 Aq. / 225 Solid (PFAS) 105 Aq. / 105 Solid (TOPA)

*Methanol content of each reactor will be ≤0.1%. All above samples will be measured for PFAS. TOPA will be conducted for all contaminated and biosolids samples. Both aqueous and solid phases will be measured for all samples. The PFAS spike of 1000 ng L⁻¹ will be from a perfluoroalkyl acid standard mix from Wellington Laboratories and will contain no precursor compounds (see PFAS Analyses section). The spike concentration (300 – 2000 ng L⁻¹) is the concentration of each compound before anion concentration correction.

- Dissolved oxygen (DO) will be monitored in separate control reactors (one for each of the 15 soil and biosolid samples) throughout the experiment. Selected cations, selected anions, pH and DOC will be measured in the artificial water (before being distributed to

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different reactors) and in the aqueous phase of the reactors at the end of the batch experiment. One reactor will be set up for each of the 15 solids tested to allow for measurement of selected cations, selected anions, pH and DOC.

Subtask 2.4: Ion concentrations

- Partitioning can be impacted by ion concentrations. Therefore, a range of ion concentrations relevant to NH precipitation and groundwater will be evaluated (Table 4) using the same batch experiment setup as described above.

Table 4.

Two different background ion concentrations					
Initial Aqueous Spike Concentration (ng/L)*	Control Reactors, No Solids	Uncontaminated Soil, Spiked	Contaminated Soil, no additional PFAS spike	Biosolids, Spiked	Sum at Each Concentration
0	3	3*1 soil	3*1 soil	3*1 soil	12 Aq. / 12 Solid
1000	3	3*1 soil	0	3*1 soil	9 Aq. / 9 Solid
2000	3	3*1 soil	0	3*1 soil	9 Aq. / 9 Solid
Total	9	9	3	9	30 Aq. / 30 Solid
Total for 2 Background Ion Concentrations	18 Aq. / 18 Solid	18 Aq. / 18 Solid	6 Aq. / 6 Solid (TOPA) 6 Aq. / 6 Solid (TOPA)	18 Aq. / 18 Solid (TOPA) 18 Aq. / 18 Solid (TOPA)	60 Aq. / 60 Solid 24 Aq. / 24 Solid

*Methanol content of each reactor will be $\leq 0.1\%$. All above samples will be measured for PFAS. TOPA will be conducted for all contaminated and biosolids samples. Both aqueous and solid phases will be measured for all samples. The PFAS spikes will be from a perfluoroalkyl acid standard mix from Wellington Laboratories and will contain no precursor compounds (see PFAS Analyses section). The spike concentration (1000 - 2000 ng L⁻¹) is the concentration of each compound before anion concentration correction.

Subtask 2.5: pH

- Partitioning can be impacted by pH. Therefore, a pH range relevant to NH precipitation and groundwater will be evaluated (Table 5) using the same batch experiment setup as described above. pH may need to be adjusted throughout the experiment, as the soil will likely change the starting pH.

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Table 5.

Two different pH concentrations					
Initial Aqueous Spike Concentration (ng/L)*	Control Reactors; No Solids	Uncontaminated Soil, Spiked	Contaminated Soil, no additional PFAS spike	Biosolids, Spiked	Sum at Each Concentration
0	3	3*1 soil	3*1 soil	3*1 soil	12 Aq. / 12 Solid
1000	3	3*1 soil	0	3*1 soil	9 Aq. / 9 Solid
2000	3	3*1 soil	0	3*1 soil	9 Aq. / 9 Solid
Total	9	9	3	9	30 Aq. / 30 Solid
Total for 2 pH Values	18 Aq. / 18 Solid	18 Aq. / 18 Solid	6 Aq. / 6 Solid 6 Aq. / 6 Solid (TOPA)	18 Aq. / 18 Solid 18 Aq. / 18 Solid (TOPA)	30 Aq. / 30 Solid 24 Aq. / 24 Solid (TOPA)

*Methanol content of each reactor will be $\leq 0.1\%$. All above samples will be measured for PFAS. TOPA will be conducted for all contaminated and biosolids samples. Both aqueous and solid phases will be measured for all samples. The PFAS spikes will be from a perfluoroalkyl acid standard mix from Wellington Laboratories and will contain no precursor compounds (see PFAS Analyses section). The spike concentration (1000 – 2000 ng L⁻¹) is the concentration of each compound before anion concentration correction.

Subtask 2.6: Column Experiments

11. Select column experiments will be run, since batch experiments are not always ideal due to unrealistic soil:water ratios and potential for accumulation at the air-water interface. Column experiments allow for dynamic conditions, have a more realistic soil:water ratio, and don't suffer from potential interference from accumulation of PFAS at the air-water interfaces (as some PFAS are surfactants). While column experiments typically require large numbers of samples and are often flow-dependent, a closed-loop column would reduce the sample numbers and would not be flow-dependent. Sampling would be similar to the kinetics experiment. The proposed experimental design is outlined in Table 6.

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Table 6.

Sample Time (days)	Contaminated Soil, no additional PFAS spike	Uncontaminated Soil	Biosolids, no additional PFAS spike	Sum at each time point
0 (measure Initial aqueous phases/soil concentration)	3*5 soil	3*1 soil	3*1 biosolid	21 Aq.
1	3*5 soil	3*1 soil	3*1 biosolid	21 Aq.
2	3*5 soil	3*1 soil	3*1 biosolid	21 Aq.
4	3*5 soil	3*1 soil	3*1 biosolid	21 Aq.
6	3*5 soil	3*1 soil	3*1 biosolid	21 Aq.
10	3*5 soil	3*1 soil	3*1 biosolid	21 Aq.
16	3*5 soil	3*1 soil	3*1 biosolid	21 Aq./ 7 solid
Total	105 Aq. / 5 Solid (PFAS) 105 Aq. / 5 Solid (TOPA)	21 Aq. / 1 Solid 1 aq / 1 solid (TOPA)	21 Aq. / 1 Solid 21 Aq. / 1 Solid (TOPA)	147 Aq. / 7 solid (PFAS) 126 Aq. / 3 Solid (TOPA)

Columns will be prepared in triplicate. *Methanol content of each reactor will be $\leq 0.1\%$. All above samples will be measured for PFAS. PFAA precursor analysis will be conducted for all contaminated and biosolids samples. Aqueous phase will be measured for all samples. Solid phase will be measured at the end of the column experiment.

Objective 3. Conduct a field-scale investigation of PFAS leaching.

The goal of this objective is to investigate PFAS transport from contaminated soils at a field site (dynamic system) and from contaminated biosolids at a field site, if an appropriate location can be identified. NHDES may be interested in collaborating by developing a SESOIL model to directly compare modeled results (using Objective 2 batch experiment input K_d values) to the field results. The site will be chosen based on ease of access, monitoring well availability, shallow depth to water table, knowledge of site hydrology and biogeochemical characteristics, and whether it is representative of other sites in New Hampshire. K_d values from batch experiments would ideally have already been performed for this particular site or soil type. Monitoring wells will be installed manually by the USGS using a direct push technology and will be periodically tested for PFAS. Well sampling will include monitoring for turbidity, pH, DO, temperature, and specific conductivity. Sampling will take place in response to hydrologic events including high and low precipitation. Water levels will be taken during each sample collection. Monitoring wells will be screened immediately below the water table (with some depth variation) to capture the highest concentrations of PFAS (before mixing/dilution with the underlying groundwater). Ideally a line of wells perpendicular to the direction of groundwater flow will be constructed to capture any variability from the source area. We will implement 1-2

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lysimeters for the collection of unsaturated zone samples (to the extent possible) and evaluate the quality of the data. At least one vertical soil profile will be sampled to determine the depth-dependent distribution of PFAS concentrations. Table 7 contains an upper limit on sample numbers.

Table 7a. Soil sampling for Objective 3.

SOIL SAMPLING	PFAS Analysis	TOPA	Sediment Organic Carbon	Soil pH	% Solids	Grain Size	Protein Content
Site 1 soil samples (including vertical profiles)	40	40	40	40	40	40	40
Site 1 field duplicate soil samples	4	4	4	4	4	4	4
Site 1 soil blanks (equipment blanks, field blanks)	10	10	10	N/A	N/A	N/A	N/A
Site 2 biosolid samples (including vertical profiles)	40	40	40	40	40	40	40
Site 2 field duplicate biosolid samples	4	4	4	4	4	4	4
Site 2 biosolid blanks (equipment blanks, field blanks)	10	10	10	N/A	N/A	N/A	N/A
Total Sample Numbers	108	108	108	88	88	88	88

Table 7b. Water sampling for Objective 3.

WATER SAMPLING	PFAS Analysis	TOPA	Anions	Cations	pH	DOC
Site 1 Water samples	50	20	50	50	50	50
Site 1 field duplicate water samples	5	2	5	5	5	5
Site 1 water blanks (equipment blanks, field blanks)	10	8	10	10	N/A	10
Site 2 Water samples	50	20	50	50	50	50
Site 2 field duplicate water samples	5	2	5	5	5	5
Site 2 water blanks (equipment blanks, field blanks)	10	8	10	10	N/A	10
Total Sample Numbers	130	60	130	130	110	130

PFAS Analyses

All spikes performed in Objective 2 will include the following perfluoroalkyl acid (PFAA) compounds at a minimum:

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Table 8. PFAA Compounds.

Perfluoroalkyl Carboxylates	Perfluoroalkyl Sulfonates
PFBA	PFBS
PFPeA	PFPeS
PFHxA	PFHxS
PFHpA	PFHpS
PFOA	PFOS
PFNA	PFNS
PFDA	PFDS
PFUnDA	
PFDoDA	
PFTTrDA	
PFTeDA	

PFAA compounds necessary for NHDES (PFHxS, PFNA, PFOA, and PFOS) will be included in all PFAS analyses completed by the contract laboratory. TOPA analysis will be employed selectively throughout the project to estimate PFAA precursor concentrations. NHDES will contract out PFAS analyses, including TOPA analysis.

Non-PFAS Analyses

The anticipated breakdown of non-PFAS characterization of soils, biosolids, and water throughout the proposal is outlined in Table 10.

Table 10.

USGS	NHDES Subcontracted Laboratory
Soil pH	Sediment Organic Carbon (Solid Phase)
Anions (Aq. Phase)	Protein Content (Solid Phase, if laboratory capacity is available)
Cations (Aq. Phase)	Percent Solids
pH (Aq. Phase)	Iron Content (Solid Phase)
DOC (Aq. Phase)	Aluminum Content (Solid Phase)
Grain size (% sand, % silt, % clay)	Cation Exchange Capacity (Solid Phase)
	Anion Exchange Capacity (Solid Phase)

Relevance and Benefits

The results of the sampling outlined in Objective 1 will enable a broader understanding of PFAS concentrations in New Hampshire shallow surface soils. Partitioning experiments in Objective 2 will provide a range of K_d values for representative soils and biosolids, providing a necessary foundation for modelling and risk assessment studies. The combination of desorption and adsorption partitioning experiments will result in a more comprehensive understanding of the potential for PFAS migration from soils and biosolids. Finally, Objective 3 will provide data on

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measured PFAS concentrations in the shallow aquifer and enable comparison to laboratory partitioning data.

The results of this study will provide the NHDES with reliable and impartial data that can be used to evaluate the risk posed by PFAS contamination in soils and biosolids. Both the USGS and the public will gain an extensive data set on soil concentrations in New Hampshire, and partitioning coefficients for future modelling efforts. This project aligns with the following goals of the USGS Strategic Science Directions⁹:

- *"Advancing our understanding of processes that determine water availability"*
- *"Anticipating and responding to water-related emergencies and conflicts"*

While this proposal is focused on soils, biosolids, and partitioning, this work has direct applications to water quality. Currently (2020) there is substantial widespread concern from citizens, scientists, and regulators over PFAS in the environment. The data set from this study will contribute to national needs to better understand the occurrence, distribution, and transport of PFAS in the environment.

Quality Assurance/Quality Control

Several Quality Control (QC) samples including appropriate blanks are included throughout Objectives 1 - 3 to ensure defensible data. Sample duplicates (triplicates for Objective 2) are included throughout the project and provide additional QC data. Outside labs contracted through the NHDES will be used as discussed herein. These labs will be evaluated in accordance with the Office of Water Quality Technical Memorandum 2014.01.

Products

Data releases will be published for all Objectives shortly after the collection of data. Dependent on study results, journal article(s) or USGS Scientific Investigations Reports will be prepared. Separate journal articles are anticipated for Objectives 1 and 2.

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Timeline

The proposed timeline is below, and may require modifications depending on circumstances.

Year	2020			2021										2022		
Month	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.
Project Setup	X															
Objective 1	X	X	X	X												
Objective 2		X	X	X	X	X	X	X								
Objective 3							X	X	X	X	X					
Reporting				X				X			X	X	X	X	X	X

Personnel

The below table summarizes the USGS personnel needs for this project. NHDES is a cooperating agency in this project. NHDES staff will collaboratively work with us throughout the project by providing information and existing data on sites. Further, NHDES will contract out the analyses described herein (Table 10).

Employee	Staff Location	Calendar Year		
		2020 Hours	2021 Hours	2022 Hours
GS-9 Hydrologist	NewEng WSC	965	1533	23
GS-11 Hydrologist	NewEng WSC	376	941	23
GS-12 Hydrologist	NewEng WSC	0	40	0
GS-13 Hydrologist	NewEng WSC	54	184	10
GS-14 Hydrologist	Menlo Park, CA	21	53	3
Data Management	NewEng WSC	75	149	0

Employee	Staff Location	Fiscal Year		
		2020 Hours	2021 Hours	2022 Hours
GS-9 Hydrologist	NewEng WSC	0	2430	90
GS-11 Hydrologist	NewEng WSC	0	1250	90
GS-12 Hydrologist	NewEng WSC	0	40	0
GS-13 Hydrologist	NewEng WSC	0	208	40
GS-14 Hydrologist	Menlo Park, CA	0	66	10
Data Management	NewEng WSC	0	224	0

Budget Summary

Objective	Description	Cost
1	Soil/Biosolids Sampling	\$158,452
2	Batch Experiments	\$268,992
3	Field Site Investigation	\$126,120
Reporting	Data release and interpretive report(s)	\$48,438
TOTAL		\$600,000*

* The New England WSC plans to contribute \$180,000 to the above total. The breakdown is \$180,000 from USGS and \$420,000 from NHDES.

NHDES Laboratory Analysis

NH DES will directly pay contract laboratories for the analyses described herein.

References

- Zhu, W.; Roakes, H.; Zemba, S. G.; Badireddy, A. R., PFAS Background in Vermont Shallow Soils. 2019.
- Li, F.; Fang, X.; Zhou, Z.; Liao, X.; Zou, J.; Yuan, B.; Sun, W., Adsorption of perfluorinated acids onto soils: Kinetics, isotherms, and influences of soil properties. *Science of The Total Environment* 2019, 649, 504-514.
- Belitz, K.; Jurgens, B.; Landon, M. K.; Fram, M. S.; Johnson, T., Estimation of aquifer scale proportion using equal area grids: Assessment of regional scale groundwater quality. *Water Resources Research* 2010, 46, (11).
- Sepulvado, J. G.; Blaine, A. C.; Hundal, L. S.; Higgins, C. P., Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids. *Environmental Science & Technology* 2011, 45, (19), 8106-8112.
- Roy, W. R.; Krapac, I. G.; Chou, S. F. J.; Griffin, R. A., Batch-Type Procedures for Estimating Soil Adsorption of Chemicals. In EPA, U. S., Ed. Washington, DC, 1992.
- Johnson, N. M.; Driscoll, C. T.; Eaton, J. S.; Likens, G. E.; McDowell, W. H., 'Acid rain', dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. *Geochimica et Cosmochimica Acta* 1981, 45, (9), 1421-1437.
- Berner, R. a.; Rao, J.-L.; Chang, S.; O'Brien, R.; Keller, C. K., Seasonal Variability of Adsorption and Exchange Equilibria in Soil Waters. *Aquatic Geochemistry* 1998, 4, (2), 273-290.
- Yavitt, J. B.; Fahey, T. J.; Long, R.; Driscoll, C. T., Solutes and soil in and around an in-stream wetland on the Hubbard Brook Experimental Forest, New Hampshire, USA. *Wetlands* 2006, 26, (2), 376-384.
- Evenson, E. J.; Orndorff, R. C.; Blome, C. D.; Böhlke, J. K.; Hershberger, P. K.; Langenheim, V. E.; McCabe, G. J.; Morlock, S. E.; Reeves, H. W.; Verdin, J. P.; Weyers, H. S.; Wood, T. M. *Strategic directions for U.S. Geological Survey water science, 2012-2022 - Observing, understanding, predicting, and delivering water science to the Nation*; 2012-1066; Reston, VA, 2012.