

July 19, 2019

Elizabeth Callahan Massachusetts Department of Environmental Protection One Winter Street Boston, MA 02108

Submitted via e-mail to: bwsc.information@mass.gov

Re: Comments on Proposed MCP Standards for PFAS

Dear Ms. Callahan:

Sanborn Head has prepared this letter to transmit our comments on the proposed groundwater and soil standards for per- and polyfluoroalkyl substances (PFAS) specified within the proposed 2019 amendments to the Massachusetts Contingency Plan.

Sanborn Head is an environmental and engineering consulting firm with offices in Massachusetts and other states. Our staff comprises Massachusetts Licensed Site Professionals, Professional Engineers, environmental scientists, risk assessors, and staff with other related expertise. We believe we are well-qualified based on our PFAS knowledge and experience to provide constructive input on the proposed PFAS standards.

Our overall comments and recommendations are summarized in the following two points, with more detailed comments and explanation provided on the ensuing pages of this letter:

- 1. Based on our comprehensive review of the available health study data, the GW-1 groundwater standard would be protective of human health and the environment if set at 70 parts per trillion (ppt) consistent with the U.S.EPA's Lifetime Health Advisory (LHA) level. The LHA already contains a considerable degree of health protectiveness, and the U.S.EPA's position is that the LHA is set at a safe level. Importantly, the MassDEP's proposed lower level of 20 ppt is not based on scientific data demonstrating adverse health effects at 20 ppt, but it is instead the result of an additional safety factor that is not robustly evidence-based and goes beyond the already-protective assumptions used to reach the 70 ppt LHA level.
- 2. The proposed S-1/GW-1 soil standard of 0.2 parts per billion (ppb) for the sum of six PFAS compounds is likely lower than background conditions in soil. A study of background PFAS in Massachusetts soils would provide the necessary data to establish an appropriate level that accounts for anthropogenic background, but one has not been performed. In the meantime, based on a recent study of background PFAS in shallow soils in Vermont, the S-1/GW-1 soil standard could be set at 4.2 ppb, which is the 90th percentile value of the summed concentrations of six PFAS compounds measured in the Vermont study (please see our detailed comments attached). In addition, given the lack of a published and recognized method for

analyzing PFAS in soil, an analytical method should also be specified for PFAS in soil, and a study made of the ability of commercial laboratories to generate reliable data from the method.

We greatly appreciate the opportunity to comment and are happy to discuss our comments at greater length, so please do not hesitate to contact us with questions.

Thank you again for this opportunity to participate in this process.

Very truly yours, Sanborn, Head & Associates, Inc.

Stephen D. Jenbe

Stephen G. Zemba, Ph.D., P.E. *Project Director*

Harrison Roakes, P.E. *Project Manager*

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Russell H. Abell, LSP Vice President

Matthew P. Heil, P.E., LSP *Project Director*

Attachments: Comments on Proposed MCP Standards for PFAS (following pages) Excel spreadsheet "VTBackgroundSoilData.xlsx" with PFAS soil data

Comments on the proposed groundwater and soil standards for per- and polyfluoroalkyl substances (PFAS) specified within the proposed 2019 amendments to the Massachusetts Contingency Plan

Sanborn Head respectfully submits these comments to the Massachusetts Department of Environmental Protection (MassDEP) for its consideration regarding the establishment of Massachusetts Contingency Plan (MCP) Method 1 soil and groundwater standards for perand polyfluoroalkyl substances (PFAS). We recognize and support MassDEP's responsible actions to protect public health and the environment, and we applaud the focus and attention MassDEP has dedicated to this issue. We also recognize the concerns of the regulated community regarding the potentially very high costs of meeting extremely low concentration standards for PFAS, especially if these standards are more stringent than the levels necessary to protect public health, as supported by existing toxicological and epidemiological data. It is thus imperative, from our perspective, that MassDEP set MCP standards for PFAS at levels that reflect scientifically sound evaluation of adverse health effects based on a holistic analysis of available data.

COMMENT ON THE PROPOSED GW-1 GROUNDWATER STANDARD OF 20 PPT

Based on our review of available scientific studies and information related to PFAS, and considering this information in aggregate, insufficient scientific evidence has been developed to compel establishing a GW-1 standard for PFAS at 20 parts per trillion (ppt), equivalent to 20 nanograms per liter (ng/l), in place of using the U.S.EPA 70 ppt Lifetime Health Advisory (LHA) level. The LHA was established as MassDEP's Drinking Water Guideline and thus far MassDEP's *de facto* level of concern. Current, important, scientific evidence (some not available when U.S. EPA established its guideline of 70 ppt) demonstrates that concentrations this low pose no significant threat to public health. We urge MassDEP to carefully review and consider comments submitted by Green Toxicology that discuss this new evidence.

There is a considerable degree of health protectiveness built into the U.S.EPA's LHA that receives insufficient attention and acknowledgment. Recently, in announcing the PFAS Action Plan in February 2019, the U.S.EPA stated its position that the 70 ppt LHA is a safe level (<u>https://www.youtube.com/watch?v=xaRgWcwwmXc</u>), in direct response to a question on the lower levels being established by certain states such as New Jersey.

The U.S.EPA has not been compelled to recommend lower advisory levels for PFAS. A principal reason to believe that 70 ppt is a "safe level" stems from the safety factor of 300 built into the underlying reference dose (RfD) of 20 nanograms per kilogram body weight per day (ng/kg-d). The combined safety factor of 300 is based on (i) the most sensitive effect identified, in (ii) the most sensitive test species (laboratory mice), and (iii) includes a safety factor of 3 to account for the possibility that people are more sensitive than laboratory rodents to effects from PFAS exposure. While this is a common standard "default" assumption for deriving reference doses, evidence related to PFAS effects mediated via the PPAR- alpha receptor (which effects include actions on the liver and on development) indicates precisely the opposite from the default. PFOA is now known to be much more toxic to

mice and rats than it is even to other rodents, such as guinea pigs and hamsters, let alone to monkeys and, importantly, humans.¹ It would thus be scientifically justifiable, and based on the evidence more technically correct, to either remove this safety factor of 3 or to apply the factor in the opposite sense (and by doing so *increase* the LHA by a factor of about 10).

There are additional degrees of protectiveness built into the U.S. EPA's 20 ng/kg-d reference dose that MassDEP should clearly communicate to the public and consider in their own standard development process. The safety factor of 300 also includes a factor of 10 to protect sensitive subpopulations. This factor is arguably unnecessary because the subpopulation thought to be most sensitive to PFAS – developing infants – is explicitly accounted for in the derivation of the LHA from the RfD – which is designed to protect the developing fetus and nursing infant, via the child's nursing mother. The assumed drinking water ingestion rate of 0.054 liters per kilogram body weight per day (L/kg-d) for a nursing mother is almost twice as large as the 0.029 L/kg-d ingestion rate typically used to derive Maximum Contaminant Levels (MCLs) and health advisories.²

The final safety factor of 10 that contributes to the overall safety factor of 300 is used to extrapolate the Lowest Observed Adverse Effects Level (LOAEL) to an assumed No Observed Adverse Effects Level (NOAEL) because effects on the mice offspring were observed in the lowest dose group tested in the toxicity study. This is again standard default procedure in RfD derivation, but is arguably over protective in the case of PFAS because the observed effects in the toxicity study were transient in nature, *i.e.*, the observations of delayed ossification of phalanges in the offspring and hastened puberty in male pups did not permanently affect the health of the baby mice and prevent them from developing into normal adults.³ Many toxicologists would argue that more serious and permanent effects, such as cellular damage, should serve as the basis of RfDs used for regulatory purposes. By basing its RfD on transient effects, the U.S.EPA has incorporated yet another health protective safety factor.

We also note that the U.S.EPA chose a developmental toxicity study in laboratory mice as the basis of its RfD even though no developmental health effects were linked to PFOA in the C8 Studies⁴ (the most comprehensive epidemiological studies conducted to date on people exposed to high levels of PFOA in their drinking water with approximately 70,000 respondents). Specifically, these studies found no associations between exposures to PFOA (whether measured in water or assessed according to concentrations in people's blood) and rates of birth defects, miscarriages, stillbirths, and/or preterm/low birth weight.

As correctly noted by MassDEP, there is yet another factor of safety built into the procedural basis of deriving GW-1 standards. The target hazard quotient of 0.2 that serves as the basis

¹ See for example: Tyagi S, Gupta P, Saini AS, Kaushal C, Sharma S. The peroxisome proliferator-activated receptor: A family of nuclear receptors role in various diseases. J Adv Pharm Technol Res. 2011 Oct;2(4):236-40

² 0.029 l/kg-d = 2 L/d of water consumption by a 70 kg individual.

³ Lau, C., J.R. Thibodeaux, R.G. Hanson, M.G. Narotsky, J.M. Rogers, A.B. Lindstrom, and M.J. Strynar. 2006. Effects of perfluorooctanoic acid exposure during pregnancy in the mouse. Toxicological Science 90:510– 518.

⁴ <u>http://www.c8sciencepanel.org/</u>

of GW-1 standards allows for background exposure (from pathways other than drinking water) to contribute up to 80% of the safe exposure level. But recent blood serum data collected by the Center for Disease Control indicate that current background exposure to PFAS is much smaller than 16 ng/kg-d (80% of the RfD). Our calculations, which are based on serum levels of several PFAS in human subpopulations over time and are described in Appendix A, indicate that current background exposure to four of the PFAS compounds of interest to MassDEP is only about 1 ng/kg-d, meaning that almost all the 80% assumed exposure via background is unnecessary (and hence highly protective) for a typical person. In other words, because PFOA and PFOS have not been manufactured and used in the U.S. for almost two decades now, our body burdens of these compounds are much smaller than they were even as recently as the year 2000. To the extent that PFOA and PFOS pose a potential threat to public health, that threat is already far smaller than it once was, both here in Massachusetts and throughout the U.S. These recent data and evidence-based trends should also be taken into account by MassDEP in development of their standards.

MassDEP has proposed to add another safety factor of 4 to the U.S. EPA's RfD to reduce the level from 20 ng/kg-d to 5 ng/kg-d to account for potential immunotoxicity effects. Based on the protective factors described above, the extra factor of 4 is not necessary, and MassDEP should simply adopt the U.S.EPA's 70 ppt LHA as the GW-1 standard and await further change (if any) from the U.S.EPA to re-evaluate the merits of such change. We note that the U.S.EPA also considered immunotoxicity effects in establishing its RfD and LHA, and a relevant discussion is provided in the Drinking Water Health Advisory for PFOA document.⁵ At present, the U.S. EPA does not find consistent evidence to warrant any additional factor to account for possible immunotoxicity effects of PFOA or related compounds.

Moreover, MassDEP's stated basis of the additional factor of 4 reflects concern over potential immunotoxicity effects, which differs from the developmental basis of the U.S.EPA RfD. This is a non-standard and unjustified approach for RfD derivation. If MassDEP wishes to base its RfD on immunotoxicity, then a toxicological study based on immunotoxicity should be used as the basis of the RfD derivation. If instead no scientifically reliable immunotoxicity study can be identified, as is apparently the case here, then no "accounting" for "immunotoxicity" can or should be offered. In the absence of a scientifically reliable study, the additional safety factor of 4 is entirely arbitrary.

In summary, the 70 ppt LHA that remains supported by the U.S.EPA contains a systematic series of protective assumptions and biases that, when considered in aggregate, impart a high degree of health protectiveness. There is no reliable scientific evidence that these, yet alone lower levels of exposure, actually harm human health. We therefore recommend that MassDEP adopt the 70 ppt concentration as the PFAS GW-1 standard (and subsequently as the state MCL) subject to reevaluation if there is any further modification by the U.S.EPA.

COMMENT ON THE PROPOSED S-1/GW-1 SOIL STANDARD OF 0.2 PPB

We believe that MassDEP's proposed S-1/GW-1 standard is both impractical and unnecessarily low because the underlying assumptions in its selection do not consider or

⁵ <u>https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final-plain.pdf</u>

account for key information. Specifically, our comments below support an increase in the proposed standard because: (1) the proposed standard is less than likely background levels in shallow soils, (2) the proposed standard, set at the MassDEP's proposed reporting limits for the six PFAS, is less than common commercial laboratory reporting limits for those six PFAS, and (3) the proposed standard should be based on the already-protective concentration of 70 ppt in groundwater.

Because the proposed S-1/GW-1 PFAS soil standard is unnecessarily low and PFAS occurrence in background soils is potentially widespread, the proposed standard could result in reportable conditions at any site in the state where soil is sampled for PFAS, leading to unnecessary groundwater sampling and remedial actions throughout the state.

The MassDEP proposed Method 1 Soil Standard is 0.0002 micrograms per gram (μ g/g) Σ PFAS for S-1 Soils, where Σ PFAS is the sum of six PFAS (PFHpA, PFOA, PFNA, PFDA, PFHxS, and PFOS). The 0.0002 μ g/g value is equivalent to 0.2 ppb in soil. This value is based on the anticipated reporting limit (RL) for the six PFAS rather than a leaching-based value, because MassDEP's calculated leaching-based value is less than the anticipated RL. It should be noted that we refer to the "anticipated RL" since this is based on MassDEP conversations with several commercial laboratories who stated that they could meet an RL of 0.2 ppb but this is not the current practice at these same laboratories where the RLs are currently higher than 0.2 ppb. From documentation provided in MassDEP's 2019 MCP Revision Spreadsheets, we understand the following methodologies were used for calculating a leaching-based value and then selecting the anticipated RL.

- The leaching-based value is based on the proposed GW-1 standard and a dilution attenuation factor (DAF). The ∑PFAS leaching-based value was calculated from an assumed/default dilution attenuation factor (DAF) of 1 and the target GW-1 standard of 20 ppt, resulting in a value of 0.02 ppb based strictly on leaching from soil. Documentation of the DAF is unclear. The MassDEP apparently did not model the DAF for ∑PFAS or the DAFs for individual PFAS using its standard MCP approach. Further comments on the DAF are provided below.
- A RL of 0.2 ppb was selected by the MassDEP for ∑PFAS and for individual PFAS, in soil, and in the spreadsheet documentation, the MassDEP noted that the RL for the individual PFAS were based on a "Reporting Limit (RL) from MassDEP Wall Experiment Station recommendation". In the summary of the proposed revision, MassDEP indicated the RL, was "based on a survey of several laboratories currently conducting PFAS analysis". Technical documentation supporting the anticipated RL has not been provided for review and comment.

The proposed S-1/GW-1 standard for \sum PFAS appears to be based solely on the reported analytical capabilities of laboratories; neither chemical-specific fate and transport information nor toxicological information (e.g., via the proposed GW-1 standard) are the basis. Although not noted in the documentation, the approach suggests that the MassDEP has insufficient fate and transport information for PFAS to model leaching from soil to derive chemical-specific DAFs, or perhaps, the MassDEP believes the model would not sufficiently describe PFAS leaching. While the science regarding PFAS is rapidly evolving and may

sometimes be uncertain, we urge the MassDEP to consider the available information on PFAS in soil and to modify the proposed PFAS standard accordingly.

Background Levels

Published studies indicate detectable concentrations of PFAS in surface soils collected around the world, including the Northeast United States. One global study (n=60, Strynar et al. 2012⁶) estimated global median "background" concentrations of 0.124 ppb and 0.472 ppb for PFOA and PFOS, respectively. Another study (n=62, Rankin et al. 2016⁷) included "background" samples from across the US and across the globe, including Antarctica (0.048 ppb PFOA and 0.007 ppb PFOS) and the Arctic Circle in Canada (0.270 ppb PFOA and 0.018 ppb PFOS). Every soil sample had quantifiable concentrations of PFAS, with PFOA and PFOS being the most prevalent. The reported mean concentrations for North America were 1.82 ppb for the sum of perfluoroalkyl carboxylic acids (which includes PFHpA, PFOA, PFNA, and PFDA) and 0.410 ppb for the sum of perfluoalkyl sulfonic acids (which includes PFHxS and PFOS). These studies indicate a global background distribution of PFAS in soils, with mean and median concentrations of summed PFAS in North America likely exceeding the proposed S-1/GW-1 standard.

In addition to the global studies, a study of PFAS concentrations in Vermont shallow soils was recently published by the Vermont Department of Environmental Conservation (VTDEC).⁸ The study was conducted by the University of Vermont and Sanborn Head with partial funding and support provided by VTDEC. Soil samples were collected from 66 properties with no known potential sources of PFAS (primarily municipal or state-owned parks, forests, greens, or lawns). Because PFAS is anthropogenically sourced, it is reasonable to suspect that background data collected from largely-rural Vermont may be indicative of, or perhaps underpredict, background concentrations that may be detected in Massachusetts.⁹ The VT Background Soil Study data for the six PFAS included in the proposed MCL standards are provided with these comments as an excel spreadsheet named "VTBackgroundSoilData.xlsx".

Several PFAS were detected in greater than 50% of the soil samples collected in Vermont, including the six PFAS proposed to be included in the S-1/GW-1 standard. A summary of the

⁶ Mark J. Strynar, Andrew B. Lindstrom, Shoji F. Nakayama, Peter P. Egeghy, Laurence J. Helfant. (2012). Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils. Chemosphere, 86, 252-257.

⁷ Rankin, K., Mabury, S. A., Jenkins, T. M., & Washington, J. W. (2016). A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence. Chemosphere, 161, 333–341.

⁸ Badireddy, A.R, Zhu, W., Zemba, S. G., Roakes, H. (2019). PFAS Background in Vermont Shallow Soils. Available for download: <u>https://anrweb.vt.gov/PubDocs/DEC/PFOA/Soil-Background/PFAS-Background-Vermont-Shallow-Soils-03-24-19.pdf</u>

⁹ Vermont is known to have a "point" source that released PFOA and impacted groundwater wells in and near Bennington via atmospheric deposition. Studies of the area indicate facility-related impacts to soil and water extending several miles from the point of PFOA emissions. While it is likely that emissions from this facility have deposited to soils at some levels at greater distances, the speciation and distribution of PFAS suggest atmospheric deposition from other (probably multiple) sources have more greatly affected the shallow soils sampled in the VT background soil study. The other cited background soil studies corroborate the significance of longer-range transport of PFAS from multiple sources to the environment.

data is provided in Exhibit 1, below. The proposed S-1/GW-1 standard of 0.2 ppb, or 200 ng/kg, is plotted on the exhibit for reference.



Exhibit 1. Summary of Vermont Shallow Soil PFAS Data

Note: Estimated values are used for the data detected above the method detection limit but below the laboratory reporting limit.

The detected background concentrations of individual PFAS compounds often exceed the proposed S-1/GW-1 standard. For example, over 95% of the samples had PFOS concentrations greater than 0.2 ppb. The sum of the six PFAS exceeds the proposed S-1/GW-1 standard in all samples. Clearly, we do not present the comparison to suggest that all soil in Vermont presents a potential leaching concern because it is greater than MassDEP's, or other, proposed soil screening values for the protection of groundwater. On the contrary, the comparison provides evidence that the proposed S-1/GW-1 standard is inconsistent with environmental occurrence data and that "below detection" is not a reasonable threshold for assessing the leaching potential of PFAS in soils.

Thus, MassDEP should either use available data to assign background levels to PFAS in soils or engage in a state-specific study of background levels in Massachusetts. Consistent with MassDEP policies under the MCP, background levels should be set at upper percentile levels (e.g., 90th percentile) and should also consider potential differences in urban and rural areas.

Finally, the implication of the proposed 0.2 ppb S-1/GW-1 standard is that, if background PFAS levels are considerably greater than the 0.2 ppb value proposed by MassDEP as an S-1/GW-1 standard, as suggested by the Vermont soil study results, then one might expect PFAS levels in groundwater should be ubiquitously greater statewide than the 20 ppt level of concern as proposed by MassDEP. This is because the leaching models used by MassDEP, based on the 20 ppt GW-1 standard, resulted in a target soil value of 0.02 ppb. The proposed 0.2 ppb soil standard, based on the anticipated RL, is ten-times greater than the modeled soil value; through application of the same leaching model, the proposed 0.2 ppb soil standard would be associated with 200 ppt in groundwater (i.e., ten-times greater than the 20 ppt GW-1 standard). Because anthropogenic background is likely much higher than the proposed 0.2 ppb standard, the model suggests PFAS in background groundwater should be above even 200 ppt. Although paired groundwater data was not collected as part of the Vermont soil study, the implied, ubiquitous, elevated concentrations of PFAS in groundwater are inconsistent with our understanding of PFAS occurrence in background groundwater based on sampling at multiple sites in VT, NH, and MA.

In addition to considering the occurrence of PFAS in background soils, the MassDEP should consider the proposed S-1/GW-1 standard in the context of empirical relationships between PFAS in soil and groundwater. PFAS leaching from soil to groundwater is difficult to generically model due to complex interactions and sorption processes, including an affinity for the air-water interface in vadose zone soil. Proposed standards should be compared with actual soil and groundwater data, including background studies, to support the feasibility and appropriateness.

Dilution Attenuation Factor Determination for PFAS

MassDEP elected not to use its leaching model of PFAS from soils because the model predictions were much lower than detectable concentrations of PFAS in soil. Hence the proposed S-1 standard of 0.2 ppb represents the analytical reporting limit that MassDEP believes is reliably achievable. MassDEP can and should explore more realistic leaching models in developing S-1/GW-1 standards. While we recognize that the use of MassDEP's standard leaching model likely does not account for the complexities of PFAS fate and transport, MassDEP should at a minimum apply its standard modeling approach as described in its the Background Documentation for the Development of the MCP Numerical Standards (April 1994) technical guidance to estimate a Dilution Attenuation Factor (DAF).

The only chemical-specific data provided in the guidance was for PFOS. Henry's Law Constant (K_H^{pc}) and soil organic carbon-water partitioning coefficient (K_{oc}) were reported for PFOS as $0.011 \frac{atm-m^3}{mol}$ and 370 $\frac{ml-aqueous}{g-soil}$, respectively. References for these values were not provided. Per a relatively simple MassDEP guidance model, these values correspond to a DAF of 130.¹⁰ Applying this DAF of 130 would result in a leaching-based soil standard of 2.6 ppb. We note that chemical-specific data are also available for the other PFAS (*e.g.*, see the ITRC PFAS fact sheets). While chemical-specific data may not be available for the typical

¹⁰ Estimated from DAF = 6207*H + 0.166*Koc, as provided in MassDEP's 1994 documentation.

model used by MassDEP for DAF calculation, sufficient information is available to calculate DAF from the more simple MassDEP model.

We also suggest that MassDEP could modify and improve its standard approach to account for the unusual properties of PFAS. Shortcomings of MassDEP's model with respect to PFAS will likely lie in the difficulty of estimating partitioning to the air-water interface and the inadequacy of using K_{oc} alone to model PFAS partitioning to solids. As described in a recent paper by Anderson et al. 2016,¹¹ PFAS partitioning in soil depends on additional factors not included in MassDEP's model. We suggest that MassDEP review the available literature and propose a different model to estimate PFAS leaching potential. Similar to models used for some metals, it may be more practical and appropriate to estimate DAFs from soil-water distribution coefficients based on empirical factors and data.

MassDEP's assumed DAF of 1 is inconsistent with reasonable models for PFAS in the environment. A DAF of 1 has been used by MassDEP as a lower limit for chemicals that, based on modeling by MassDEP, are highly soluble and tend not to partition to solids (e.g. K_{oc} values less than 40 $\frac{ml-aqueous}{g-soil}$), and therefore, flush through soils. The six PFAS are the only chemicals in the MassDEP spreadsheets for which a DAF of 1 was assumed without modeling. The K_{oc} values reported in the ITRC PFAS fact sheets range on the order of 40 to 5,000 $\frac{ml-aqueous}{g-soil}$ across the six PFAS, so the broad assumption that there is very little adsorption of the six PFAS to soil is not appropriate. In addition to neglecting sorption of the PFAS to soil, the DAF of 1 does not include dilution that can be anticipated from groundwater dilution and flow within a typical aquifer system. The result is an unrealistic leaching scenario that is not based on any chemical-specific information or hydrogeologic model.

Reporting Limit (RL) Selection

In the MassDEP's 2019 MCP Revision Spreadsheets, the MassDEP referenced the "reporting Limit (RL) from MassDEP Wall Experiment Station recommendation" as the basis for the proposed selection of the RL for PFAS. Further, in the MassDEP's "Summary of Proposed MCP Method 1 Standards Revision, March 2019," it was described that the RL "was established by [the MassDEP] based on a survey of several laboratories currently conducting PFAS analysis." However, as summarized in Exhibit 2 below, the selected RL is less than common laboratory reporting limits for soil, as reported in laboratory reports prepared by reputable commercial laboratories and provided in reports to us.

Laboratory	Report Date	Method	RL (minmax.) (ppb)		
Commercial Lab A	2019 QAPP		1		
Commercial Lab A	Spring 2019	Modified EDA 527 with	0.976 - 2.00		
Commercial Lab B	2019 QAPP	Modified EPA 537 with	2		
Commercial Lab B	Fall 2018	isotope Dilution	2.00		
Commercial Lab C	2019 QAPP		0.2 – 0.5		

Exhibit 2. Summary of Common Laboratory Reporting Limits (RLs)

¹¹ R. Hunter Anderson, Dave T. Adamson, Hans F. Stroo. (2019). Partitioning of poly- and perfluoroalkyl substances from soil to groundwater within aqueous film-forming foam source zones. Journal of Contaminant Hydrology, 220, 59-65.

Commercial Lab C	Summer 2018	0.21 - 0.60
Commercial Lab D	Fall 2017	~0.1 - 5

Results at the lowest ends of the RL spectrum may be less reliable, lack precision, be more subject to cross contamination, and more commonly result in false positive detections or qualified, estimated values. False positive detections, whether from cross-contamination or laboratory methods, are especially problematic when laboratory reporting limits are at or near the S-1 standard. This concern is amplified by the lack of standard laboratory methodologies for PFAS in soil analysis and the great potential from cross-contamination issues where PFAS are present in many consumer products.

MassDEP has thus not determined that commercial laboratories can reliably detect PFAS at levels as low as 0.2 ppb. There is, to our knowledge, no commonly accepted analytical method for determining PFAS levels in soils. We suggest that MassDEP provide a recommended analytical method for determining PFAS in soils, and then engage in a multilab study to determine whether commercial labs are reliably able to quantify PFAS concentrations at the S-1/GW-1 level proposed by MassDEP. Further, MassDEP should also provide guidance on handling combinations of detections, non-detections, and estimated values with respect to calculating the sum of six PFAS compounds and comparing the result to the proposed standard.

Closing Comments for the Proposed S-1/GW-1 Soil Standard

In consideration of the above information, MassDEP should reconsider the 0.2 ppb proposed S-1/GW-1 Soil Standard for Σ PFAS. The table below demonstrates that the 0.2 ppb value for Σ PFAS is not practical given expected background levels of PFAS in soil (based on the Vermont shallow soils study) and typical commercial laboratory reporting limits for PFAS.

PFAS	Leaching-Based Value Based on Modeling or Empirical Data	90 th Percentile from VT Background Soil Study	Typical Commercial Laboratory Reporting Limit
PFHpA		0.53 ppb	1 ppb
PFOA		0.75 ppb	1 ppb
PFNA		0.36 ppb	1 ppb
PFDA	Not Calculated	0.32 ppb	1 ppb
PFHxS		0.30 ppb	1 ppb
PFOS		2.1 ppb	1 ppb
∑six PFAS		4.2 ppb ¹²	6 ppb

Based on the above, MassDEP should at least consider background soil concentrations and common laboratory reporting limits in establishing the PFAS standard for soil. Further, MassDEP should consider development of leaching-based values using modeling and/or empirical data. Because modeling may not account for the complexities of PFAS fate and

¹² The 90th percentile of the sum of six PFAS does not equal the sum of the 90th percentile values of the individual PFAS as the PFAS concentrations do not correlate perfectly between samples.

transport, we urge that a proposed standard based on modeling be made available for public comment prior to finalizing.

A soil background study should be completed in Massachusetts to understand anthropogenic background of PFAS in soil and to develop soil standards that are protective of human health and the environment, but that are also more likely indicative of leaching potential of PFAS to groundwater. MassDEP could consider using the VT Background Soil Study results to develop interim S-1/GW-1 standards. The table above suggests that a S-1/GW-1 standard of 4.2 ppb for the sum of six PFAS could be used as an interim standard until a background study can be completed in Massachusetts. The accompanying spreadsheet file "VTBackgroundSoilData.xlsx" contains the individual sample results and derivation of the 90th percentile value.

APPENDIX A ESTIMATION OF PFAS BACKGROUND EXPOSURE

By regulation, MCP standards based on non-cancer health endpoints correspond to a Hazard Quotient of 0.2, meaning that the allowable exposure is only 20% of the safe reference dose, thereby allowing up to 80% additional exposure from other exposure pathways. MassDEP states that, in the case of PFAS, this is likely a conservative/protective allowance as typical background exposure is likely smaller than 80% of the reference dose. MassDEP's observation is indeed supported by a, time trend analysis of the PFAS serum concentration data collected by the Center for Disease Control (CDC) under the National Health and Nutrition Examination Survey (NHANES). The NHANES data indicate that Americans are at present excreting more PFOA, PFOS, PFHxS, and PFNA than they are taking in. Better estimates of PFAS Relative Source Contributions (RSCs) can be calculated using the NHANES time trend data and other parameters documented by New Hampshire Department of Environmental Services (NH DES)¹³ in their recently proposed Maximum Contaminant Levels.

The draft Toxicological Profile for Perfluoroalkyls issued by the Agency for Toxic Substances and Disease Registry (ATSDR) provides a framework for estimating background exposure to PFAS based on the observation that concentrations of many PFAS have been decreasing in blood in the general U.S. population.¹⁴ Heuristically:

Rate change in PFAS body burden = Background intake rate of PFAS – PFAS excretion rate

Adapting the nomenclature in Appendix A of the ATSDR Toxicological Profile, and assuming (as does ATSDR) 100% absorption of PFAS intake exposure:

$$\frac{d}{dt}(C_b V_d) = D_{back} - k_e C_b V_d$$
$$k_e = \frac{\ln(2)}{t_{1/2}}$$

where the terms are:

- *C*_b Arithmetic average concentration of PFAS in serum (blood) (ng/l);
- V_d Apparent volume of PFAS distribution (l/kg);
- *D*_{back} Background exposure to PFAS (ng/kg-d);
- k_e PFAS elimination constant (d⁻¹); and
- $t_{1/2}$ PFAS half-life in the body (d).

¹³ <u>https://www.des.nh.gov/organization/commissioner/pip/publications/documents/r-wd-19-01.pdf</u>

¹⁴ <u>https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf</u> The fact that serum levels of many PFAS are decreasing in the general U.S. population is an important point worthy of greater emphasis in the face of growing concerns over adverse health effects. We recommend the incorporation of graphics similar to Figure 1 and Figure 2 within the ATSDR report, along with additional discussion of the declining trends.

PFAS concentrations have been measured in blood in the general U.S. population over several periods as part of the NHANES, the earliest in 1999, and the latest in 2013 (https://www.atsdr.cdc.gov/pfas/pfas-blood-testing.html). Assuming (1) PFAS concentrations in blood of C_{b1999} and C_{b2013} in the earliest and latest periods, (2) independence between the variables C_b and V_d , and (3) constant background exposure to PFAS over the period of exposure (T = 14 yrs = 5133.5 d),¹⁵ the differential equation can be solved and rearranged to yield the following expression for estimating the background exposure D_{back} :

$$D_{back} = \frac{k_e V_d (C_{b2013} - C_{b1999} e^{-k_e T})}{1 - e^{-k_e T}}$$

We apply this equation to four of the six PFAS that MassDEP includes in its PFAS sum (PFOA, PFOS, PFHxS, and PFNA). Arithmetic average serum PFAS concentrations, which are appropriate for the model, are not directly available from ATSDR in the draft toxicity profile. As such, the values of the 50th, 75th, 90th, and 95th percentile levels have been extracted from CDC¹⁶, curve-fit to estimate parameters for assumed log-normal distributions, and the parameters have been used to estimate arithmetic means. A spreadsheet with the calculations to estimate these values is provided as an attachment to our comments.

Applying the following parameters for PFOA:

<i>Cb</i> 1999	5,625 ng/l (estimated arithmetic mean, U.S. residents, 1999-2000);
Cb2013	2,337 ng/l (estimated arithmetic mean, U.S. residents, 2013-2014);
V_d	0.17 l/kg (NH DES) ¹³ ;
$t_{1/2}$	2.7 yr = 985.5 d (NH DES) ¹³ ; and
Т	5133.5 d (14 years)

yields a background PFOA dose estimate of 0.268 ng/kg-d.

Applying the following parameters for PFOS:

C _{b1999}	33,405 ng/l (estimated arithmetic mean, U.S. residents, 1999-2000);
Cb2013	6,408 ng/l (estimated arithmetic mean, U.S. residents, 2013-2014);
V_d	0.23 l/kg (NH DES) ¹³ ;
<i>t</i> _{1/2}	$3.4 \text{ yr} = 1,241 \text{ d} (\text{NH DES})^{13}$; and
Т	5133.5 d (14 years)

yields a background PFOS dose-estimate of 0.612 ng/kg-d.

¹⁵ The pattern of serum PFNA does not indicate a steady decline since 1999, but rather an increase from 1999 through 2009, followed by a subsequent decline. The equation to consider background is thus considered over the period from 2009 to 2013 for PFNA.

¹⁶ <u>https://www.cdc.gov/exposurereport/</u>

Added together, PFOA and PFOS background exposure are predicted to be 0.88 ng/kg-d, or 4.4% of EPA's reference dose of 20 ng/kg-d for the sum of PFOA and PFOS.

Similar estimates can be developed for PFHxS and PFNA using the blood serum data and parameters reported by ATSDR. However, unlike PFOA and PFOS, concentrations of PFHxS and PFNA (Figure 1) have not declined as rapidly in blood as those of PFOA and PFOS (Figure 2). In fact, from 1999 to 2009, concentrations of PFNA increased (Figure 1).

Applying the following parameters for PFHxS:

C b1999	2,645 ng/l (estimated arithmetic mean, U.S. residents, 1999-2000);
Cb2013	1,350 ng/l (estimated arithmetic mean, U.S. residents, 2013-2014);
V_d	0. 287 l/kg (NH DES) ¹³ ;
<i>t</i> _{1/2}	5.3 yr = 1934.5 d (NH DES) ¹³ ; and
Т	5133.5 d (14 years)

yields a background PFHxS dose estimate of 0.167 ng/kg-d.

Applying the following parameters for PFNA, but adjusting the equation to cover only the recent decay period from 2009 to 2013:

Cb2009	1,418 ng/l (estimated arithmetic mean, U.S. residents, 2009-2010);
Сь2013	801 ng/l (estimated arithmetic mean, U.S. residents, 2013-2014);
V_d	0. 2 l/kg (NH DES) ¹³ ;
$t_{1/2}$	$2.5 \text{ yr} = 912.5 \text{ d} (\text{NH DES})^{13}$; and
Т	1461 d (4 years)

yields a background PFNA dose estimate of 0.0757 ng/kg-d.

The total background dose estimate for the sum of the four PFAS is:

0.268 ng/kg-d + 0.612 ng/kg-d + 0.167 ng/kg-d + 0.0757 ng/kg-d = 1.1 ng/kg-d,

which represents 5.6% of the U.S. EPA' reference dose of 20 ng/kg-d, a value far less than the default allowance of 80% under the MCP regulatory formula.

A more complex analysis that considers time-varying background and other factors, or a sensitivity study could be constructed to test the variability introduced by different parameter choices. But barring extreme changes in parameter values, large differences in estimated background exposure estimates are not likely.







Figure 2 Geometric mean concentrations of serum PFOA and PFOS reported for the U.S. population, from Table 5-21 of the draft ATSDR Toxicity Profile. Bars represent the 5th and 95th percentile concentrations, obtained from the more detailed NHANES data available online.

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Location	PFHpA	PFOA	PFNA	PFDA	PFHxS	PFOS	Σsix PFAS
A.1	[ng/kg or ppt]	[ng/kg or ppt]	[ng/kg or ppt]	[ng/kg or ppt]	[ng/kg or ppt]	[ng/kg or ppt]	[ng/kg or ppt]
A1	0 ND	520	140	96 20 I	300	1800	2,856
A3	150	240	82	38 J	63 J	330	903
A5	66U	290	310	170	87 0 ND	720	2,237
A7	110 510	150	170	95 72	0 ND	1600	2,125
A9 B2	510 410	140	1200	100	120	4400	1,712
B2 B4	410	1600	1200	100	180	4400 670	7,890
D4 P6	200 E40	0 <mdi< td=""><td>150</td><td>160</td><td>05 0 ND</td><td>070</td><td>1,300</td></mdi<>	150	160	05 0 ND	070	1,300
BQ	170	300 <mdf< td=""><td>78</td><td>22 I</td><td>0 ND</td><td>380</td><td>1,780</td></mdf<>	78	22 I	0 ND	380	1,780
D0 C1+	140	430	150	80	195	675	1,000
C1 1	110	140	78	45	89	340	802
C5	340	160	54	76	140	590	1 360
C7	390	690	230	77	40 I	860	2 287
C9	120	190	110	51	25 I	380	876
0) D1	410	500	260	210	440	940	2,760
D3	120	140	100	65	89	360	874
D4	650	1400	230	330	62 I	1200	3.872
D6	210	270	33 I	0 ND	0 ND	310	823
D8	46	160	51	110	42 I	1800	2.209
E1	52	0 <mdl< td=""><td>120</td><td>87</td><td>0 ND</td><td>290</td><td>549</td></mdl<>	120	87	0 ND	290	549
E1a	160	260	290	210	0 ND	1400	2,320
E1c	210	430	400	250	0 ND	3700	4,990
E1d	290	470	190	430	120	3200	4,700
E1e	0 ND	0 ND	370	360	0 ND	3800	4,530
E1f	0 ND	82	340	400	0 ND	2000	2,822
E3	230	410	160	95	0 ND	650	1,545
E5	900	4900	330	66 J	94	1000	7,290
E7	87	330	96	49	430	690	1,682
E9	80	370	100	53	96	310	1,009
F2	110	470	290	81	0 ND	540	1,491
F4	280	690	300	280	130	2200	3,880
F6	78	200	110	69	40 J	310	807
G1	90	300	90	56 J	0 ND	380	916
G3	130	200	44 J	30 J	95	110	609
G5	180	590	180	75	55 J	1000	2,080
G7	89	450	180	28 J	29 J	320	1,096
H2	200	370	190	43	22 J	330	1,155
H4	320	1000	150	81	0 <mdl< td=""><td>630</td><td>2,181</td></mdl<>	630	2,181
I1	190	610	160	55	35 J	500	1,550
13	210	540	180	64	0 ND	800	1,794
15	410	550	210	110	32 J	990	2,302
17‡	86	385	190	89.5	52 J	505	1,308
J4	200	490	150	44	110	330	1,324
J6	830	2000	5000	7600	39 J	9700	25,169
K1	180	770	170	63	100	690	1,973
K3	150	590	220	97	100	470	1,627
K5	100	0 <mdl< td=""><td>38 J</td><td>44</td><td>0 ND</td><td>210</td><td>392</td></mdl<>	38 J	44	0 ND	210	392
K6	0 ND	0 <mdl< td=""><td>220</td><td>110</td><td>0 ND</td><td>620</td><td>950</td></mdl<>	220	110	0 ND	620	950
K6b	0 ND	0 ND	140	100	0 ND	680	920
KOC	4/0	420	390	310	U ND	1800	3,390
коа	U ND	52	430	410	U ND	1900	2,792
кое	500	/ 30	170	2000	U ND	1300	0,230
LZA	190	500	1/0	03 47	100	780	1,823
	250	4/0	150	4/	88U 76	570	2,347
L4 M1	200	300	130	97 110	70	/90	1,0/3
MD	700	70	120	110	390	04U 200	2,030
MIS ME	230	440	/ 3	30 J	0.0	300	1,104
мэ	140	210	120	120	40 J	1200	1,888

N2	44	120	160	65	140	230	759
01	150	660	160	97	0 ND	800	1,867
03	110	150	140	70	15 J	350	835
05	0 ND	120	80	150	290	720	1,360
P2	870	350	120	54	89 J	1200	2,683
Q1	160	990	220	140	320	2100	3,930
Q3	76	88	56 J	0 ND	280	160	660
Q5	130	110	66 J	110	360	330	1,106

	PFHpA	PFOA	PFNA	PFDA	PFHxS	PFOS	Σsix PFAS
	[ng/kg or ppt]						
90th Percentile	530	750	360	320	300	2,100	4,200

Notes:

1. See the report published by the VTDEC for additional notes. https://anrweb.vt.gov/PubDocs/DEC/PFOA/Soil-Background/PFAS-Background-Vermont-Shallow-Soils-03-24-19.pdf

2. Data are presented in nanograms per kilogram (ng/kg) on a dry basis, which are equivalent to parts-per-trillion (ppt).

2. "ND" indicates the analyte was not detected (ND). "<MDL" indicates the analyte was detected at a concentration less than the method detection limit (MDL). "J" indicate the analyte was qualitatively detected at a concentration greater than the MDL but less than the reporting limit (RL).

3. For the purposes of calculating percentiles, the value of "0" was used for "ND" and "<MDL" values.

4. Data were rounded to two significant digits.

5. "Σsix PFAS" is the sum of PFHpA, PFOA, PFNA, PFDA, PFHxS, and PFOS. "J"-flagged values were included in the sum.

6. The 90th Percentiles for this data set of 66 locations were calculated as the linear interpolation between the 59th and the 60th highest values. The values were then rounded to two significant figures.

7. "‡" indicates the data for locations C1 and I7 are the average of the duplicate samples collected at those locations. Data for the duplicate samples are provided below.

Duplicate sample data collected for locations C1 and I7:

Sample	PFHpA	PFOA	PFNA	PFDA	PFHxS	PFOS	Σsix PFAS
	[ng/kg or ppt]						
C1#1	150	430	160	89	230	660	1,719
C1#2	130	430	140	71	160	690	1,621
I7#1	79	410	210	100	36 J	540	1,339
17#2	93	360	170	79	68 J	470	1,172