Appendix E.4

Supplemental Artificial Turf Field Materials Analysis – Exponent (February 2023)

E X T E R N A L   M E M O R A N D U M

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DATE:	February 16, 2023
PROJECT:	2209255.000
SUBJECT:	Supplemental memo re: River Park Project Artificial Turf Field Materials Analysis

At your request, Exponent, Inc. (Exponent) authored a technical memo dated December 21, 2022 ("the Exponent 2022 memo"),[1] in which we assessed the material components proposed for use in the artificial turf fields of the Harvard-Westlake River Park Project, specifically the Vertex CORE 2.5 synthetic turf carpet and Cryogenic Rubber 14-30 crumb rubber infill. This analysis included an evaluation of material composition and the potential to release certain chemical substances under the conditions of intended use, based on the chemical and physical principles related to the materials, as well as data reported by several sources, including a chemical analysis of artificial turf materials commissioned by the City of Portsmouth, New Hampshire. You have now requested that Exponent supplement the Exponent 2022 memo with an analysis of certain specific claims and information included in an August 3, 2022 article titled "'Our community has been deceived': Turf wars mount over PFAS" ("the Greenwire article"),[2] published in the E&E News publication Greenwire, related to per- and polyfluorinated alkyl substances (PFAS) in the context of artificial turf fields located in Portsmouth, New Hampshire.

The Greenwire article makes claims that relate to testing of the artificial turf components for fluorine-containing substances. Specifically, the article describes "high levels of organic fluorine" in the turf materials (but does not provide the measurements associated with this claim) and a generalized interpretation of the test results. Other claims relate to properties of specific PFAS,

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[1] Parker, S. December 21, 2022. *River Park Project Artificial Turf Field Materials Analysis* [Memorandum]. Exponent, Inc.

[2] Crunden, E.A. and Wittenberg, A. (2022). 'Our community has been deceived': Turf wars mount over PFAS. E&E News: Greenwire. Available at: https://www.eenews.net/articles/our-community-has-been-deceived-turf-wars-mount-over-pfas/, accessed February 7, 2023.

including fluoropolymer processing aids used in the manufacturing of grass fibers for artificial turf, and their degradation pathways. A description of the nature and purpose of fluorinated substances that are used in artificial turf materials as well as the types and capabilities of test methods used to describe fluorinated substances were addressed broadly in the Exponent 2022 memo, and this supplemental memo provides a specific, concise discussion relating these topics to the claims in the Greenwire article. Additional information about the Harvard-Westlake River Park Project, as well as a description of my qualifications and relevant background information related to artificial turf systems, PFAS, testing methods for PFAS including total organic fluorine (TOF) and total organic precursors (TOP) methods, limitations of PFAS composition information in relation to PFAS exposure evaluations, and other topics, is provided in the Exponent 2022 memo.

The Greenwire article references the results of analytical testing conducted on the turf materials, including testing by the TOF and TOP methods, as evidence of "PFAS" in the turf materials. As described in Exponent's 2022 memo, these methods provide useful information but have specific limitations.[3] For example, the TOF method can be a useful screening tool to assess whether a sample may contain PFAS substances, but cannot identify specific PFAS compounds present or distinguish between polymeric substances (such as a fluoropolymer processing aid) and small-molecule PFAS (e.g., PFOS and PFOA). This distinction is important because organic fluorine is not a direct measurement of PFAS (in fact, TOF may overestimate PFAS content) and, to the extent that PFAS are present, the specific chemistry, size, and mobility of specific substances are important factors that influence their properties and behavior in environmental and biological systems. The Greenwire article implies that "high levels of organic fluorine"[4] detected during TOF testing of Portsmouth's artificial turf demonstrates an environmental and health risk. However, because both the amount and nature of the substances present in the turf will influence the risks associated with the material, it is crucial to understand the identity of the PFAS that may be present in the materials when conducting a risk assessment. As described in Exponent's 2022 memo, analysis of the specific PFAS chemistries present is especially important for artificial turf materials, because fluoropolymer processing aids used in the manufacturing of these materials are considered to be of low concern for PFAS exposure compared to other PFAS (such as perfluorooctanoic acid, "PFOA" or perfluorooctane sulfonate, "PFOS") that could also contribute to the level of "organic fluorine" detected by the TOF method.[5]

[3] For a description of the Total Organic Fluorine and Total Organic Precursors methods and their known limitations, see Exponent's 2022 memo (section titled "Experimental Test Methods for PFAS Identification and Quantification: Nontargeted Analysis")

[4] Although the testing data are not provided in the Greenwire article, the advocacy group described to have commissioned these tests, Non Toxic Portsmouth, separately published a test report that is consistent with the description in the Greenwire article, which found between 16 and 119 parts-per-million (ppm) of organic fluorine in the sample, consistent with the level of fluoropolymer processing aid that is expected to be used during the manufacturing of the turf carpet. See "Tests Detect Dangerous Pfas Chemicals in Portsmouth's New Synthetic Turf Field." Tests Detect Dangerous PFAS Chemicals in Portsmouth's New Synthetic Turf Field, Non Toxic Dover, New Hampshire, 2 Oct. 2021, https://nontoxicdovernh.wordpress.com/2021/09/15/tests-detect-dangerous-pfas-chemicals-in-portsmouths-new-synthetic-turf-field/.

[5] For a discussion of properties and characteristics that contribute to behavior of fluoropolymers and small-molecule fluorosurfactants (such as PFOS and PFOA), see Exponent's 2022 memo (section titled "PFAS in the Environment")

In a second example from the Greenwire article, the testing commissioned by the City of Portsmouth did not identify the targeted PFAS[6] in the as-received turf carpet samples, as the article claimed. As described in Exponent's 2022 memo, the TOP method assesses the levels of a number of specific PFAS in two experiments, before and after the sample is chemically treated with oxidizing agents, that are intended to mimic the type of oxidative degradation that could take place during a product's lifetime of use. Importantly, although the method identifies potential degradation products, it does not identify the precursors to these products that existed in the original sample. The Greenwire article claims that TOP testing commissioned by the City of Portsmouth "found multiple compounds" in the turf carpet, including 135 parts-per-trillion (ppt) of PFOS, when in fact, the testing did not detect any of the targeted PFAS compounds in the unaltered, pre-treatment analysis of the carpet. Indeed, the 135 ppt of PFOS was only detected in the carpet sample after the sample was oxidized, which does <u>not</u> indicate that the sample contained the detected PFAS as manufactured (if it did, the pre-oxidation analysis would be expected to detect it).[7] Instead, the data indicate that another substance(s) in the sample may (or may not) degrade over time to generate the amount of these compounds detected post-oxidation.[8] It is also important to note that the precursor to the PFOS detected in the post-oxidation sample cannot be identified based on the available information,[9] and the precursor is unlikely to be the fluoropolymer processing aid because the fluoropolymers described for use in this application[10] do not contain sulfur or precursors to sulfonates (a sulfonate group is present in PFOS) and because the degradation of these fluoropolymer materials is well understood (discussed in more detail below).

Health and environmental risks related to the presence of certain PFAS, including the PFOS detected in the post-oxidation TOP sample, are informed by screening levels and allowable limits set by government agencies. As noted by the Greenwire article, the EPA advisory limit for PFOS in drinking water is 20 parts-per-quadrillion (ppq), while the EPA screening level for residential

[6] As described in Exponent's 2022 memo, targeted PFAS analysis detects and quantifies the amount of specific targeted substances in the sample. In the TRC testing commissioned by the City of Portsmouth, 70 specific PFAS were targeted in the pre- and post-oxidation TOP testing. TRC Technical Memorandum, "Evaluation of PFAS in Synthetic Turf," dated June 7, 2022.

[7] Note that the pre-oxidation TOP analysis involves an extraction step prior to analysis. As described in the Exponent 2022 memo, extraction conditions can vary, and the specific conditions used may influence the PFAS identified by the method and levels of these substances detected. See Exponent's 2022 memo (section titled "Experimental Test Methods for PFAS Identification and Quantification").

[8] The TOP method attempts to accelerate the oxidative degradation that may occur as a result of in-service conditions experienced by a product during its lifetime of use. All such attempts at accelerated testing require simplification and modification of actual in-service conditions, and as a result, the extent to which TOP results will accurately predict product degradation mechanisms, and the rate at which they occur, is expected to differ depending on the specific product and application. For artificial turf, the anticipated use conditions have not been correlated to the TOP conditions and may be milder than those predicted by this generalized method.

[9] As described in the Exponent 2022 memo, a limitation of the TOP method is that it cannot identify specific PFAS precursors. Because the conditions used in TOP reduce numerous potential precursors to a common set of perfluorinated carboxylic acids (*e.g.*, PFOA) via oxidative conversion, there is inherent ambiguity surrounding the source of PFAS present within the sample.

[10] Lauria, M. Z., Naim, A., Plassmann, M., Fäldt, J., Sühring, R., and Benskin, J. P. (2022). Widespread Occurrence of Non-Extractable Fluorine in Artificial Turfs from Stockholm, Sweden. *Environmental Science & Technology Letters* 9(8), 666-672, at p. 669.

soil is 130 parts-per-billion (ppb). These levels differ because of the way the substance may be encountered in drinking water (*e.g.*, daily consumption over a lifetime) compared to in soil (a lower frequency exposure with minimal ingestion, inhalation, or absorption).[11] The Greenwire article confused these guidance levels by comparing the concentration of PFOS found in the post-oxidation turf carpet sample (135 ppt) to EPA health advisories for PFOS in drinking water (20 ppq) instead of the PFOS soil screening level (130 ppb).[12] Notably, when EPA performs risk assessments of artificial turf materials, the EPA uses soil screening levels to assess environmental and health risks.[13] In fact, the turf carpet's post-oxidation PFOS level as determined by the City of Portsmouth's testing is three orders of magnitude lower than the soil screening level, and was determined by the study authors not to represent a human health risk to those using the synthetic turf fields.[14]

With respect to potential degradation, the Greenwire article makes misleading statements that are not supported by the peer-reviewed literature about two fluoropolymer materials that are used as additives in artificial turf manufacturing, polyvinylidene fluoride (PVDF) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). For example, the article states that "[t]esting meant to imitate the impact of decades of use on turf has shown other PFAS compounds present, which some scientists say could mean that PVDF-HFP can break down into more concerning compounds, like the PFOS found in Portsmouth's field." The degradation pathways of these polymeric materials have been studied by multiple authors and data are available in the peer-reviewed scientific literature that describe how PVDF, PVDF-HFP, and other fluoropolymer materials are likely to break down under different conditions. However, the article does not cite a source for this assertion, and the peer-reviewed literature (including Lohmann *et al.*[15] and Marshall *et al.,*[16] cited elsewhere in the Greenwire article) do not substantiate this claim. In fact, the peer-reviewed literature demonstrates the opposite – that PVDF materials are durable under typical environmental conditions,[17] such as environmentally relevant temperatures and pH

[11] For a discussion related to the use of soil screening levels to assess the potential risks associated with artificial turf materials, see the Exponent 2022 memo (section titled "Established Guidelines and Systems for Evaluating Environmental and Health Risk from PFAS").

[12] US EPA. Regional Screening Level (RSL) Summary Table (TR=1E-06, HQ=1) November 2022. Accessed at https://semspub.epa.gov/work/HQ/403628.pdf.

[13] Exponent 2022 memo (section titled "Established Guidelines and Systems for Evaluating Environmental and Health Risk from PFAS").

[14] TRC Technical Memorandum, "Evaluation of PFAS in Synthetic Turf," dated June 7, 2022.

[15] Lohmann, R., Cousins, I. T., DeWitt, J. C., Gluge, J., Goldenman, G., Herzke, D., ... & Wang, Z. (2020). Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS?. Environmental science & technology, 54(20), 12820-12828.

[16] Marshall, J. E., Zhenova, A., Roberts, S., Petchey, T., Zhu, P., Dancer, C. E., ... & Goodship, V. (2021). On the solubility and stability of polyvinylidene fluoride. Polymers, 13(9), 1354.

[17] For example, PVDF has been described as having high "stability under harsh environmental conditions" and "outstanding resistance to sunlight/UV exposure." *See* Korzeniowski, S. H., Buck, R. C., Newkold, R. M., Kassmi, A. E., Laganis, E., Matsuoka, Y., ... & Musio, S. (2022). A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers. *Integrated Environmental Assessment and Management.*

ranges.[18] And further, these references show that when degradation of PVDF materials does take place under relatively extreme conditions, such as when exposed to high temperatures (>440 °C), harsh chemical environments (pH >11), or high levels of UV radiation (identified by the Greenwire article as a potential concern), the dominant degradation pathways are unlikely to produce small molecule perfluorinated materials such as PFOS and the other PFAS detected in the TOP testing.[19,20,21] Overall, the implication by the Greenwire article that PVDF and related fluoropolymer materials are likely to decompose to form small molecule fluorosurfactants is unsupported by the current state of knowledge about these materials. Further, as mentioned above, PVDF and PVDF-HFP do not contain sulfur or sulfonate precursors, which would be needed to form PFOS,[22] specifically, as a degradation product.

To the extent that the Greenwire article attempts to imply that the detection of PFOS in the City of Portsmouth's post-oxidation TOP analysis of turf carpet samples is due to the degradation of PVDF processing aids, it is important to consider that 1) PVDF and similar fluoropolymer processing aids do not contain sulfur or sulfonate precursors, and 2) the TOP assay does not identify the precursors to the PFAS identified in the post-oxidation analysis. As described in the Exponent 2022 memo and above, unless a precursor is detected in the pre-oxidation analysis (which, in this example, was not the case), the TOP assay identifies only the *products* of oxidative degradation, not the *precursors* that generated them. Due to the large number of PFAS that can be present at trace levels in a wide variety of materials and substances that may contact a product

[18] Thermal decomposition of PVDF does not start until 440 °C producing an initial weight loss and a resulting residue that is stable above this temperature. Additionally, when exposed to alkaline conditions at pH of 11or greater PVDF will undergoes base-mediated degradation, see Marshall, J. E., Zhenova, A., Roberts, S., Petchey, T., Zhu, P., Dancer, C. E., ... & Goodship, V. (2021). On the solubility and stability of polyvinylidene fluoride. Polymers, 13(9), 1354.

[19] Indeed, PVDF, which contains alternating carbon-hydrogen and carbon-fluorine bonds, primarily degrades by losing inorganic fluoride, typically in the form of hydrofluoric acid (HF), and *increasing* the size of the polymeric chain by creating carbon-carbon double bonds and/or increasing the crosslinking between polymer chains.

[20] Similarly, PVDF-HFP was shown to be durable to relevant environmental conditions, and only to degrade under relatively severe conditions such as high temperatures or high levels of UV radiation. When degradation did occur, these processes were observed to produced crosslinked and/or chain scission degradation products, neither of which were described as small-molecule perfluorinated material. *See* Julienne, F., & Richaud, E. (2022). Degradation of PVDF-HFP Matrix. *Macromolecular Symposia* (Vol. 405, No. 1, p. 2100223); *see also,* Radwan, A. B., El-Hout, S. I., Ibrahim, M. A. M., Ismail, E. H., & Abdullah, A. M. (2022). Superior Corrosion and UV-resistant Highly Porous Poly (vinylidene fluoride-co-hexafluoropropylene)/alumina Superhydrophobic Coating. ACS Applied Polymer Materials, 4(2), 1358-1367.

[21] Hexafluoropropylene oxide-dimer acid (HFPO-DA), which was detected at low levels in the post-oxidation TOP testing (levels more than 400 times lower than residential soil screening values for this chemical), is used as a surfactant in fluoropolymer production and as a consequence, residual amounts of HFPO-DA may be present in fluoropolymer processing aids. However, fluoropolymers such as PVDF are not expected to form additional HFPO-DA through degradation of the polymer chains, and therefore, the HFPO-DA detected in this testing may have a different precursor in the tested materials.

[22] The currently available literature suggests that PFAS degradation under environmental conditions typically form products that contain the elements already present in the PFAS, or may add oxygen and/or hydrogen (but not sulfur). *See, e.g.,* Patch, D., O'Connor, N., Koch, I., Cresswell, T., Hughes, C., Davies, J. B., ... & Weber, K. (2022). Elucidating degradation mechanisms for a range of per-and polyfluoroalkyl substances (PFAS) via controlled irradiation studies. *Science of The Total Environment,* 832, 154941.

during manufacturing, transport, installation, and use, the introduction of trace levels of PFOS precursors is possible at various points throughout a product's lifetime. The available information does not support the degradation of PVDF as the source of PFOS in the post-oxidation TOP analysis described above.

Limitations

This memo is based on publicly available literature; the materials cited in this memo; and my education, training, and experience. In the analysis, Exponent has relied on provided information and has not independently assessed the underlying accuracy and rigor by which the information was collected (including, but not limited to, professional standards and care exercised by independent laboratories in the investigation of the aforementioned chemicals and compounds).

The guidance formulated during this assessment is based on observations and information available at the time of the investigation. Exponent's role is advisory in nature, and the opinions, analysis, conclusions, results, recommendations, and the like will be assessed by ESA with respect to its products, processes, or services. As such, no guarantee or warranty as to future life or performance of the reviewed artificial turf systems is expressed or implied. The scope of services performed during this investigation may not adequately address the needs of other users of this memo, and any reuse of this memo or its findings, conclusions, or recommendations presented herein are at the sole risk of the user.