SUPREME COURT OF THE STATE OF NEW YORK
COUNTY OF STEUBEN

In the Matter of the Application of

SIERRA CLUB, CONCERNED CITIZENS OF ALLEGANY COUNTY, PEOPLE FOR A HEALTHY ENVIRONMENT, INC., JOHN CULVER, and BRIAN and MARYALICE LITTLE,

Petitioners,

For a Judgment Pursuant to Article 78 of the Civil Practice Law and Rules,

–against–

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION, BASIL SEGGOS, COMMISSIONER, AND HAKES C&D DISPOSAL INC.,

Respondents.

AFFIDAVIT OF DUSTIN M. MAY IN SUPPORT OF THE VERIFIED PETITION

Index No. E2017-1384CV

State of Iowa,
County of Johnson, ss.:

DUSTIN M. MAY, being duly sworn, deposes and says:

1. I am a professional chemist and current Ph.D. candidate in Human Toxicology. I received a Bachelor of Science (B.S.) degree in chemistry from the University of Iowa in 2006. I possess substantial experience regarding the analysis of samples for radioactive materials, the properties of radioactive materials (i.e. radioactive decay, radioactive particles, radiation interactions with matter, etc.), and the chemical behavior of radionuclides in the environment. I also possess considerable experience in laboratory operations, accreditation compliance, review and interpretation of laboratory results. I have acquired this knowledge through my employment with the State Hygienic Laboratory at the University of Iowa, the state of Iowa's public health laboratory, in the radiochemistry department for the last eight years, first as an analyst and more recently as department supervisor.

2. Additionally, I, along with colleagues, have published a number of peer-reviewed papers studying drilling wastes, including so-called "hydraulic fracturing flow-black fluids", drilling "bit" cuttings, and environmental impacts downstream from coal-waste processing facilities.

3. All opinions expressed here are solely my own and do not express the views or opinions of my employer or academic institution.

**Overview**

4. As part of this review I have examined and evaluated several documents related to the Hakes landfill. Specifically, I reviewed the (a) Hakes Landfill Management Plan, (b) Hakes Environmental Monitoring Plan, (c) Hakes Operation and Maintenance Manual, (d) Hakes Landfill Leachate Radiological Analysis Results, and (e) Hakes Annual Operations Reports.

5. Based on this review, I have concluded that: (a) the measured concentrations for radium in the leachate samples are likely correct, and represent the soluble fraction of radium-226 and radium-228 under method conditions, (b) there exists sporadic and extreme disequilibrium between radium-226 and its radioactive daughter radon-222, and (c) radon-222 gas, as well as its radioactive daughters, may be present in and around the leachate at levels of concern.

**Background**

6. Terrestrial naturally occurring radioactive material (NORM) is ubiquitous in the environment and is primarily the result of two decay series, the so-called Thorium and Uranium Series. Both series begin with long-lived parent radionuclides, thorium-232 and uranium-238, that have been present on Earth since the planet's formation. Isotopes of radium, specifically the long-lived radium-226 and radium-228 have been found of be of particular concern due to their

potentially carcinogenic health impact and their motility in the environment and are thus regulated in drinking water under the Safe Drinking Water Act (SDWA).

7. Analytical methods for the quantification of radium-226 and radium-228 employ principles of radioactive equilibrium. These principles state that when the half-life (i.e. the time taken for half of the atoms of a radioactive isotope to disintegrate/decay) of a parent radionuclide is longer (more than ten times) than the half-life of its radioactive daughter and they not physically separated, the radioactive parent and daughter will reach so-called "secular equilibrium." This means that both the parent and daughter will exist at the same rate of decay and will decay with the half-life of the parent radionuclide.

8. Radium-226 is routinely quantified by measuring the alpha particle emission of its daughter product radon-222 after chemical purification or after sealing by the measurement of the gamma-ray emissions of its more distant decay products, lead-214 and bismuth-214. Both of these measurements require an ingrowth period where the sample is sealed and the radioactive daughters are allowed to reach equilibrium. Radium-228 is also routinely quantified by utilizing its radioactive daughter, actinium-228, either after chemical purification by measuring the beta particle emission or by measuring actinium-228's many gamma-ray emissions.

9. With the regard to drill cuttings and other solid waste materials from the Marcellus Shale, higher concentration of NORM are generally present in these materieals than in typical soil or waste. In a recent study conducted by myself and other co-authors, drill cuttings from Marcellus shale were found to contain between 5 and 8 pCi/g each of thorium-230, uranium-238, uranium-234, radium-226, lead-210, and polonium-210[1]. These concentrations are substantially higher, 2-3 times, than the average concentration found in soil in the eastern United

[1] Eitrheim, E. S., May, D., Forbes, T. Z., & Nelson, A. W. (2016). Disequilibrium of Naturally Occurring Radioactive Materials (NORM) in Drill Cuttings from a Horizontal Drilling Operation. *Environ Sci Technol Lett, 3*(12), 425-429. A copy of this article is attached as Exhibit A.

States[2]. Sludge from flowback waste impoundment may contain even more NORM, with one recent study showing a "range from 10 pCi/g to several hundred pCi/g depending on age"[3].

**Collection and Method Selection**

10. Analytical results for leachate provided in reports from On-Site Technical Services, Inc. for gamma emitters, radium-226, radium-228, and uranium on a semi-annual basis from 2012 to 2017. Additionally, leachate characterization results were reviewed from the Hakes C & D, Inc. Annual Operations Reports for the combined leachate. According to the sample collection forms, samples were collected from the cell discharge pipes in 5 gallon buckets. Field measurements of pH, conductivity, turbidity, temperature, and oxygen reducing potential were collected. None of these field measurements appear to be unusual for landfill leachate.

11. Pace Analytical Services LLC performed the analyses for radionuclides. According to Pace Analytical's reports, leachate samples were analyzed for radium-226 EPA 903.1, radium-228 by EPA 904.0, gamma emitters by EPA 901.1, and uranium by EPA 908.0 or ASTM D5174-97. The methods utilized are generally appropriate for aqueous samples, but chemical separations can potentially be susceptible to chemical interferences. According to the provided documents and reports Pace Analytical analyzed samples as received and after filtration in the laboratory. Samples were preserved in accordance with method specifications to a pH of less than 2 with nitric acid.

12. It is important to note that in the process of analysis by both EPA 903.1 and EPA 904.0, solids are removed from the analyzed aliquot by either centrifugation or filtration. This means that only the fractions of radium-226 and radium-228 that are soluble in samples that have

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[2] Shacklette, H.T., Boerngen, J.G. Element Concentrations in Soils and Other Surficial Materials of the Conterminous Untied States. USGS Professional Paper 1270.

[3] Zhang, T., Hammack, R. W., & Vidic, R. D. (2015). Fate of Radium in Marcellus Shale Flowback Water Impoundments and Assessment of Associated Health Risks. *Environmental Science & Technology, 49*(15), 9347-9354.

been preserved to a pH of less than two with nitric acid or in a 10M sodium hydroxide solution (used to dissolve insoluble sulfates) utilized in both methods. It is also important to understand that these methods were developed to analyze drinking water; they may be applied to wastewater, but the initial validations for these methods were focused on drinking water. The leachate samples analyzed are much higher in dissolved solids, with measured conductivities ranging from 2000 to 20,000 μS/cm. These high conductivity readings indicate substantial dissolved solids present in the leachate sample. High concentrations of barium can interfere with these methods, as observed with hydraulic fracturing flowback fluid[4] Characterization results for the combined leachate indicate that these solids are primarily calcium, magnesium, and sodium salts present in the leachate.

**Radium Results**

13. Across all leachate samples taken from 2012 to 2017, radium-226 and radium-228 concentrations were found to be very low. The concentrations of radium-226 and radium-228 were generally less than 10 pCi/L combined in these samples across all cells. The results reports from Pace Analytical do not contain any notes regarding method deviations or quality control related issues with these analyses. Additionally, the reports state that all quality control parameters meet method-specified limits.

14. Beginning with the 2nd Quarter of 2014 results, Pace began reporting carrier and tracer yields with these results. As part of EPA 903.1 and 904.0 stable barium is utilized to separate radium from the bulk matrix. This known quantity of barium is then measured at the end of the analysis to correct the result for recovery. In EPA 904.0, yttrium is utilized to separate the

[4] Nelson, A. W., et al. (2014). Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale. *Environmental Science & Technology Letters, 1*(3), 204-208. doi:10.1021/ez5000379

actinium-228 daughter from the radium-228 parent. This known quantity of yttrium is also measured at the end of analysis to correct the radium-228 result for recovery. The reported carrier yields are generally high and reasonable for all analyses for which they are reported. As neither the samples, nor the general radium concentrations, nor the analysis methods changed during the sampling period, it can be reasonably assumed that the carrier and tracer yields were similar for samples analyzed before these parameters were reported.

15. From review of other stable metal results provided in the Hakes C & D, Inc. Annual Operations Reports, it was also found that concentrations of barium were not found to be substantially elevated in combined leachate samples taken from 2012 through 2017. This indicates that stable barium, a potentially important interferent in both EPA 903.1 and EPA 904.0, is not likely to cause any serious issues with analysis for radium-226 and radium-228 by these methods. Additionally, in review of the reported tracer and carrier yields, no yields greater than 100% were reported. The lack of extremely high carrier yields (>100%) provides additional evidence that stable barium is not present in the leachate samples at concentrations that would cause serious interference with these methods.

16. As a result of the reasoning outlined in this section and the previous section these results likely represent the soluble and leachable fraction of radium-226 and radium-228 present in the leachate samples analyzed. The reported concentrations do not include any contribution from radium-226 and radium-228 that is not soluble in dilute nitric acid, as the preserved samples are stored, nor 10M sodium hydroxide.

**Gamma Results**

17. Analysis for gamma emissions of naturally occurring radioactive materials (NORM) at low concentrations is generally limited to measuring a small number of radionuclides in the uranium and thorium series and potassium-40. The most useful

radionuclides for these types of measurements are actinium-228, bismuth-212, lead-212 and thallium-208 in the thorium series and lead-214 and bismuth-214 in the uranium series due to their high probability of gamma emission upon decay and their short half-lives, leading to rapid radioactive ingrowth. Under most circumstances, following a period of ingrowth (usually at least 21 days) in a sealed container, actinium-228 is very useful for determining the concentration of radium-228 and lead-214 and bismuth-214 are very useful for determining the concentrations of radium-226 present in a sample as these radioactive daughter products will reach a secular equilibrium state with radium-228 and radium-226 during this period of ingrowth.

18. It should be noted that direct measurement of radium-226, radium-228, uranium-234, and uranium-238 by gamma spectrophotometry is not generally performed in environmental samples. This is due to the lack of useful gamma ray emissions by these radionuclides; gamma rays emitted by these radionuclides are either too rare, occur with energies that are too low to measure, or, as is the case with radium-226, overlap with other radionuclides. As a result of these limitations, the above radionuclides are generally measured by other methods or indirectly by the gamma ray emissions of their daughter products.

19. In some circumstances, secular equilibrium may not be reached in in 21 days. In situations where samples can be substantially enriched in radon-222 gas by physical processes, lead-214 and bismuth-214 may be present at concentrations much greater than that of radium-226. Enrichment can occur in situations where radium-226 is trapped in insoluble solid material, radon-222 escapes as a gas, and dissolves in surrounding water. This is widely seen in groundwater, as shown in the USGS Study, *Trace Elements and Radon in Groundwater Across the United States, 1992–2003,* where radon-222 gas can exist at orders of magnitude higher than radium-226 concentrations would typically exist in groundwater. In these situations, radon-222

gas dissolved in the sample may need to be purged by bubbling air through the sample or boiling the sample to drive out the radon gas prior to sealing to allow for determination of radium-226 concentration by the measurement of lead-214 and bismuth-214.

20. In the samples of leachate taken from 2012 to 2017, very few radionuclides were identified above the reported Minimum Detectable Concentrations (MDC), but some results are concerning. In nearly all of these samples, potassium-40 was found above the MDC, but not at particularly high concentrations. This is to be expected considering the detectable concentrations of potassium observed in the leachate characterization results from the Hakes landfill annual reports. Potassium-40 is generally not of major public or environmental health concern due to the tight regulation of potassium concentrations in biological systems[5]; the concentration of potassium-40 is maintained at more or less stable levels regardless of exposure.

21. Of major concern regarding these results are the concentrations of lead-214 and bismuth-214 found in some of the leachate samples analyzed. In 9 of the 79 leachate samples analyzed from 2012 to 2017, lead-214 and bismuth-214 concentrations exceeded 1000 pCi/L and all of these samples showed good agreement between lead-214 and bismuth 214, indicating that these are unlikely to be false positives as lead-214 decays directly to bismuth-214. These elevated lead-214 and bismuth-214 concentrations were found in samples from Cells 3, 4, 5, 6, and 8B, all cells receiving drilling wastes. The highest observed lead-214 and bismuth-214 concentration was approximately 6000 pCi/L from an unfiltered leachate sample taken from Cell 8B take in Q22017. Of the 9 samples found to be extremely high in lead-214 and bismuth-214 concentrations, 6 of these samples were filtered in the laboratory prior to analysis. In a number of other samples, a substantial disequilibrium was observed, with the concentration of lead-214 and

[5] ORAU Potassium-40 General Information, https://www.orau.org/ptp/collection/consumer%20products/potassiumgeneralinfo.htm

bismuth-214 greatly exceeding the concentration of radium-226 measured in the samples via EPA 903.1. These results indicate major potential enrichment of leachate with radon-222 gas; the half-lives of lead-214 and bismuth-214, 27 and 20 minutes, respectively, are too short for these radionuclides to exist independently during the time period between collection and analysis, they would have decayed away entirely. Thus, in order for these two radionuclides to be detectable in the samples weeks after collection, they would have to be supported and exist in an equilibrium state with radon-222 gas or radium-226.

22. On average, leachate samples were analyzed between two and three weeks following collection. This would allow for 3.6 to 5.5 half-lives of radon-222 to pass between collection and analysis. This period of decay means that approximately 92% to 98% of radon-222 (and due to the properties of radioactive decay, the same activity of lead-214 and bismuth-214) present at collection would have decayed away by the time of analysis. If we back calculate from analysis to collection with the in the sample from Cell 8B mentioned above, this would mean that, at the time of collection, the radon concentration of the sample was approximately 275,000 pCi/L.

23. There is also the potential that the radon-222 concentration in the sample source may be much higher than the concentrations found in the samples. Normally, to analyze for radon-222 in water samples, Standard Methods 7500 Rn-B, a commonly used method for this type of analysis, specifies that samples be taken in glass, septa-sealed vials are filled carefully to avoid loss of radon-222 gas at collection and the elimination of headspace to prevent loss during transport. Variability in the measured concentrations between the filtered and unfiltered samples taken at the same time, with one analysis showing extremely high concentrations of lead-214 and bismuth-214 and the other showing much less or no observable lead-214 and bismuth-214,

indicates the likely escape of radon-222 gas from the sample. This could have occurred at a number of different points between collection and analysis, including the initial filling of the sample bottles at collection or during handling at the laboratory. Vigorous handling of the samples, changes in temperature, and sample containers that do not seal well or have large headspaces could have lead to the escape of radon from the sample container.

24. This variability in lead-214 and bismuth-214 concentrations between filtered and unfiltered samples of the same leachate also indicates that the presence of these radionuclides are not likely the result of radium-226 decay occurring during the period between collection and analysis of the samples. If this were the case, results for the filtered and unfiltered samples would be the same or the unfiltered samples would contain more lead-214 and bismuth-214, as radium-226 is not likely to be lost during collection, handling, or analysis of these samples. In addition, the results of the analyses for radium-226 by EPA 903.1 do not support the extremely high concentrations that would be required for the lead-214 and bismuth-214 concentrations to be the result of radium-226 decay during the period between collection and analysis with these samples.

25. Without careful handling and direct measurement of radon-222 of samples from the leachate source it is impossible to know the true radon-222 concentration present, but it is likely higher than or equal to the measured lead-214 and bismuth-214 concentrations found in the sample already analyzed.

**Radon-222 and Lead-210**

26. As a result of the extremely high radon-222 concentration likely present in some of these leachate samples, there is also the potential for the long-lived decay products, specifically, lead-210, and polonium-210, to be present as well. In the above mentioned sample from Cell 8B, radon-222 gas present in the leachate at 275,000 pCi/L would result in lead-210 concentrations of approximately 130 pCi/L after 40 days. This radionuclide possesses a half-life

of 22.2 years and decays through bismuth-210 to polonium-210, with a half-life of 130 days. Once formed from radon-222, these radionuclides are persistent and take many years (generally 10 half-lives) to decay away to insignificant concentrations.

27. Additionally, lead-210 and polonium-210 are not regulated nor tested for in wastewater or drinking water and their environmental behavior is not well understood[6]. Complicating the issue further, lead-210 and polonium-210 do not emit any detectable gamma rays, making them difficult to screen for using *in situ* measurement equipment limiting the analysis to measurement via their beta and alpha emissions, respectively.

28. All of these factors indicate that lead-210 and polonium-210 could be present at levels of concern in the leachate from the Hakes landfill and should be characterized to prevent adverse environmental impacts.

**Conclusions**

29. In review of the provided data regarding the leachate analysis results, issues appear to exist regarding disequilibrium between radium-226 and radon-222. Radium-226 concentrations in the leachate are generally very low and do not appear to be questionable based on the information provided in the reports from Pace Analytical Services. Variable and extremely high concentrations of radon-222 daughter products, especially considering the low concentrations of radium-226 and the two to three week period between collection and counting, are very concerning.

30. The potentially high concentrations of radon-222 in and around the landfill leachate may pose risks to public health and the environment and thus should be characterized to evaluate its potential impact. Additionally, analyses for important radon-222 daughters, lead-210

[6] Seiler, R. L., and Wiemels, J. L. (2012) Occurrence of (210)Po and Biological Effects of Low-Level Exposure: The Need for Research. *Environ Health Perspect* 120, 1230-1237.

and polonium-210, should also be performed to evaluate the concentrations in the collected leachate solution, especially after the leachate has aged once exiting the landfill. These decay products must be considered when evaluating the potential environment and public health impact of these wastes.

31. Conclusions drawn in this statement are based solely on the information available at this time. If further information becomes available I reserve the right to alter or amend this statement.

Sworn to before me this 17th day of January 2018

Notary Public

NOTARIAL SEAL IOWA
MEGAN FITZGERALD
Commission Number 783103
My Commission Expires
3/13/20