Appendix H MDE Sediment Analysis Memorandum



MARYLAND DEPARTMENT OF THE ENVIRONMENT

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Anthony G. Brown Lieutenant Governor

MEMORANDUM

To: Christopher H. Ralston, Administrator, MDE/OCP

From: Edward M. Dexter, P.G., Administrator, MDE/LMA/SWP

Subject: Sediment Sample 11712 SerenePT Sediment - CV Citgo

Date: Wednesday, November 20, 2013

This memorandum sets forth my observations and opinions with regard to my physical examination and review of analytical data of a small sample of sediment identified as "11712 SerenePT Sediment" (the "Sediment") The Sediment was collected by Lara Bennett and Sean Daniel of Chesapeake GeoSciences on 3/12/2013, and transferred under chain-of-custody to me by Mr. Chris Ralston, Administrator of the Oil Control Program on 3/27/2013. On 4/16 and 17/2013, I was provided with additional information regarding the origin and chemical content of the Sediment. This memorandum sets forth my conclusions of the physical and optical examination of the Sediment and conclusions following my review of the information subsequently provided regarding the location from which the Sediment was collected and the geological setting from which it derived.

I. Examination of 11712 SerenePT Sediment.

On 3/27/2013 I received a glass sample jar with a Phase Separation Science sample label on it, accompanied by a Chain of Custody form, from Mr. Chris Ralston of MDE's Oil Control Program (OCP). The sample jar contained a small quantity (a few grams) of a dark sediment. The lid and label indicated that it was sample number "11712 SerenePT Sediment", and the label and form indicated that it was collected by Lara Bennett and Sean Daniel of Chesapeake GeoSciences on 3/12/2013, and transferred under chain-of-custody to me from Mr. Chris Ralston on 3/27/2013. I took the sample home with me and kept it locked up in my fire safe until I examined it. I live alone and the sample was secure during this time.

On the evening of April 15, 2013 I conducted a physical and optical examination of the Sediment. At 7:50 pm I opened the jar, and smelled it to see if there was any perceptible odor. I detected no odor from the material inside, which had been kept closed in the jar since I received it three weeks previously. Then, using a clean stainless steel spatula, I place a gram or two on a clean, new glass microscope slide. The material in the jar was surprisingly cohesive for a sandy material, and tended to cling together in clumps and had to be physically spread out on the slide, although it didn't seem to be moist or sticky.

Christopher H. Ralston Page two

On inspection with a low-powered hand lens, the sample appeared to be sediment consisting largely of a dark sandy material, with a small percentage of lighter colored grains. On inspection with a higher-powered hand lens, the sample appeared to be composed largely of medium to coarse sand-sized dark particles, although a finer fraction of very fine sand-to-silt-sized particles were now observable. The grains all appeared to be sharply angular, and a small percentage were lighter colored grains that had the appearance of quartz sand. Some of the darker gains appeared to have a tabular shape.

I then examined the sample using an optical microscope (Ernst Leitz Wetzler #3146389). I used the 25 mm lens (lowest power), and started with direct observation lit from above with white light from a Tensor lamp.

The darker grains were dark slate grey to black, with a vitreous to greasy luster, and a very finely irregular fracture surface on the grain faces; some exhibited rusty red spots in places, like rust or garnet inclusions. The lighter grains appeared to be largely clear or reddish quartz, with a vitreous luster and conchoidal fracture. There also appeared to be some accessory orange grains that looked like a feldspar. A few of the tabular grains appeared to be a little less dark, and to have a slightly greenishgrey hue. When viewed when lit from below the stage (e.g., with light from below instead of above) the dark grains were uniformly opaque. Given the very high percentage of opaque grains (over 90%) I didn't proceed to an examination with polarized light.

However, I wished to explore the strange cohesiveness exhibited by the material, so I undertook a further physical examination. Exposure of the sample to a strong hand magnet revealed that a very high percentage of the dark grains were attracted to the magnet. Exposure to iron indicated that they were, however, not intrinsically magnetic themselves, at least significantly, although it is possible that there is some small percentage of magnetite in the sample, which would account for the cohesiveness. The grains would stick to each other when under the influence of magnetized iron, so they are not paramagnetic, and so are not likely chromium dioxide (CrO₂) or a similar mineral.

Based on these observations, the Sediment appears to largely be a ferric oxide or hydroxide of some kind (there are several - see http://en.wikipedia.org/wiki/Iron_oxide), with an accessory amount of natural quartz sand of a similar size. Given the fairly well-sorted particle distribution and the unrounded nature of the particles, this suggests that there was an efficient transport-based sorting mechanism at work here that eliminated both coarser and finer particles outside of the observed fine-to-coarse sand range. The dark color with patches of red suggests dominantly reducing conditions (e.g., "black rust" as opposed to "red rust"), and rust staining could also account for the reddish discoloration of some of the sand grains.

II. Review of Analytical Data related to 11712 SerenePT Sediment .

Following my initial physical examination of the Sediment in April 2013, I returned the sample with a preliminary memorandum to Mr. Ralston in Oil Control Program. In April 2013 I was provided additional analytical information regarding the origin of the Sediment and in October 2013 was asked to supplement or revise my initial conclusions, as appropriate.

I learned that the Sediment had derived from a domestic well water supply pressure tank in the Monrovia area of eastern Frederick County, and that the area was underlain by Marburg Formation phyllites. This is significant, as transportation of the water through a piping system at a given pressure, or subject to agitation and perturbation in a tank, provides a mechanism for sorting the material – coarser material would not be transported, and finer material would be carried away, so only material in a given size and density range would be left in the tank. I also learned that although the case involved a release of petroleum, there had been concern expressed that the treatment system had caused the mobilization of certain metals including lead and chromium into the surrounding groundwater flow regime. Mr. Ralston also provided me with some analytical data of both water from the affected well, and the sediment.

I am familiar with the phyllites of the Marburg Schist and surrounding similar formations from previous work at several sites in this geological setting (e.g., the Keystone Landfill in Pennsylvania just north of Silver Run, Carroll County, which is located in the Marburg, and the Reich's Ford Road landfill and the Linthicum/Spectrum Development Dump in Frederick County, which are in the similar Ijamsville Phyllite). The Marburg Schist is a bluish grey to green schist with accessory quartz among other minerals. Analyses of rock cuttings from 9 monitoring wells placed by the State of Maryland in the Marburg along the Carroll County/Pennsylvania line back in the mid-1980s revealed the presence of lead and chromium at around 50 ppm (parts per million) for lead (Pb) and 80 to 100 ppm for chromium (Cr) (e.g., see the report entitled *Keystone Landfill – Maryland Monitoring System Investigation and Report*, dated June 1986, self-published by the Maryland State Department of Health and Mental Hygiene, Waste Management Administration, Appendix VII – "Geochemical Analysis of Maryland Monitoring Well Drill Cuttings", which were performed by the Geology Department of the University of Maryland on samples obtained from 9 monitoring wells installed to monitor water entering Maryland from the vicinity of the Keystone Landfill, located in Pennsylvania).

The solution and transport of naturally-occurring metals in groundwater, derived from the geologic materials through which the groundwater moves, is a widely recognized phenomenon that is not doubted by the scientific community (see for example *Groundwater*, 1rst ed., by R.A. Freeze and J.A. Cherry, Prentice Hall, Englewood Cliffs, NJ:1979, pages 520-521, and numerous other texts on hydrogeology). The solution of metals from domestic plumbing systems is also a widely recognized occurrence (see for example the United States Environmental Protection Agency's website at http://water.epa.gov/drink/info/lead/, accessed on 10/16/2013, for a discussion of this widespread problem, and links to a variety of documents related to this topic). The acidic groundwaters common to most of the siliceous metamorphic rocks in Central Maryland are well known to cause corrosion and leaching of metals including iron, copper and lead from plumbing. Therefore, the presence of low concentrations of lead or chromium in the groundwater in Central Maryland is natural and to be expected. Moreover, this is expected to be exacerbated in a pressure tank where water is in contact with metal-bearing sediments – whether natural or derived from the plumbing system – for a prolonged residence time.

Fresh schist can have a dark coloration, particularly when damp; but as the majority of the particles I observed in the Sediment were dry and responded to a magnet, I interpret this to indicate that most of the particles were not residual particles of the formation derived from the drilling of the well. The grey color is similar to that commonly observed in goethite, hematite, and other iron-bearing minerals – although not the bright yellow and red of strongly oxidized hematite. Also, it is not surprising that an accumulation of iron-rich sediment in a pressure tank would be under dominantly reducing conditions.

The analytical data summary provided by Mr. Ralston supports this interpretation. According the summary (I did not review the original data sheets), the constituency of the particles was reported as being 430,000 parts per million Fe, or 43% iron with a suite of other elements at much lower concentrations. The progressive decrease in concentration shown for the parameters in the water in the tank as it was purged also supports the views expressed above concerning the local water quality.

III. Conclusion. Based on my physical examination of the Sediment, review of the analytical data for the Sediment, and an understanding of the origin of the Sediment, it is my opinion that the dark metallic particles that make up most of the sample examined are largely rust from the well casing, piping or water tank.

Questions concerning this report can be directed to me at X3376 or ed.dexter@maryland.gov.

Edward M. Dexter, P.G.

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