

June 13, 2005

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Subject: Preliminary Comments on “*Arsenic Concentrations in Groundwater in the Vicinity of Koppers and Murphree Wellfield*” by Dr. Thomas Pichler, May 2005

Dear Mr. Goodman:

On behalf of Beazer East Inc. (Beazer), included with this letter are GeoTrans, Inc. and Roman Z. Pyrih & Assoc., Inc. comments on Dr. Thomas Pichler’s May 2005 report entitled: “*Arsenic Concentrations in Groundwater in the Vicinity of Koppers and Murphree Wellfield*”. Elevated concentrations of arsenic (As) were detected in GRU wells MWTP-MW1 and MWTP-MW2, shortly after these wells were installed in October 2003. Multiple conceptual models were hypothesized by the Gainesville Regional Utility (GRU) to explain the presence of elevated As concentrations including: 1) The As is naturally occurring, and 2) Historical, wood-treating operations at the Koppers Inc. site (Site) resulted in impacts to the Upper Floridan (UF) Aquifer. Dr. Pichler was contracted by GRU to perform an independent analysis of potential sources of As detected in UF Aquifer wells within the Gainesville area. The results of this analysis are contained in Dr. Pichler’s May 2005 report.

The report provides additional geochemical data that may be useful in determining the origin of As detected in wells completed in the UF Aquifer. However, this evaluation appears to be a cursory examination of the data, with limited analyses in support of the conclusions.

The primary conclusion of the Pichler (May 2005) report is that As “*in the Upper Floridan aquifer beneath the Cabot/Koppers Superfund Site must be the result of vertical As movement through the Hawthorn Group*”. This conclusion is based solely on the observation of elevated concentrations in the Surficial Aquifer, and low concentrations in the UF Aquifer upgradient of the Site. It neglects the facts that:

- a. Concentrations in the intervening Hawthorn Group (HG) are considerably lower than measured in the UF Aquifer. Data are available for many more HG well samples than are listed in the report. The majority of these samples did not contain As concentrations above the reporting limit. The samples with measurable As contained concentrations in the range of approximately 2 to 4 $\mu\text{g/L}$. On the other hand, FW-3 and FW-7 had reported concentrations as high as 50 and 197 $\mu\text{g/L}$, respectively.
- b. Concentrations in FW-7 and FW-3 have continued to decline. The As concentration in FW-7 has decreased from 197 $\mu\text{g/L}$ in November 2004 to 83 $\mu\text{g/L}$ in March 2005. Similarly, concentrations in FW-3 have decreased from 50 to 17 $\mu\text{g/L}$. These observations are similar to observations of declining concentrations in MWTP-MW1 (from 19 $\mu\text{g/L}$ in April 2004 to a value of 7.3 $\mu\text{g/L}$ in November 2004).
- c. Elevated As concentrations are associated with the recovery of oxygenated water that had been injected into the UF Aquifer (a practice known as Aquifer Storage and Retrieval, ASR). Price and Pichler (Price, R.E. and Pichler, T., 2005, Abundance and mineralogical associations of naturally occurring arsenic in the Suwannee Limestone (Florida): implications for arsenic release during water-rock interaction (draft for publication); Price, R.E. and Pichler, T., undated poster, Arsenic and ASR in Southwest Florida: Source, Abundance, and Mobilization Mechanism, Suwannee Limestone, Upper Floridan Aquifer [<http://www.dep.state.fl.us/geology/geologictopics/asr4/posters/Price.pdf>]) performed a study of this phenomenon and determined that microscopic, As-bearing pyrite was dissolved by oxygenated water, releasing As into the water at concentrations as high as 130 $\mu\text{g/L}$. [This mechanism is mentioned in the current report as a possible explanation for As observed in MWTP-MW1 and MWTP -MW2, but not for the concentrations observed in FW-3 and FW-7. It is not clear why the conclusions from this ASR study were not considered to be pertinent to this investigation and report.]
- d. Elevated As concentrations were also observed in F-6F, which is located to the west of the Murphree Wellfield and outside of any potential impacts from the Site. Thus, another source or mechanism is needed to explain concentrations observed in F-6F, and as suggested by Dr. Pichler, may also be pertinent to the source of the As observed in MWTP-MW1.

Further, the report provides several hypotheses (“scenarios”) for why As concentrations are declining in MWTP-MW1, without providing any supporting analyses or data. In our view, a careful evaluation of the chemical data is needed before

conclusions should be reached about the presence of As in the UF Aquifer. If the As is determined to be of natural origin, the hypotheses pertaining to a hydrologic shifting of an As plume, pulse-like releases of As, or fractures opening and closing are moot. However, brief discussions of the proposed hypotheses are warranted:

1. *“The migration of As in the Floridan aquifer could be periodic or pulse-like and thus we may have sampled the tail end of a passing plume.”* An explanation of the mechanism is not provided. It would appear that this hypothesis is unlikely given the continued observation of elevated concentrations in the Surficial Aquifer in parts of the Site, the low hydraulic conductivity of the HG, and the sorptive nature of As.
2. *“The As plume varies in position due to pumping patterns at the Murphree well field and thus we may have sampled its left or right boundary.”* Changes in pumping rates can cause shifts in the movement of plumes, especially if the constituent of interest does not tend to sorb. However, As does tend to sorb, and release of As during changing of flow directions will retard shifting of the plume. This mechanism also does not explain the observed decline in concentrations in FW-3 and FW-7. In addition, it is highly unlikely that a significant hydrologic shift in the plume location can occur at a distance of approximately 2 miles from the pumping source.
3. *“The installation of the monitoring wells itself caused the introduction of oxygen into the Floridan aquifer and caused the oxidation of pyrite and subsequent release of As to groundwater in the vicinity of MWTP-MW-1.”* This mechanism is similar to that described by Price and Pichler (2005, and undated poster) for the release of As observed with the ARS operations. We believe that this is the most likely explanation for the elevated As concentrations, as well as the observed decline on concentrations. This explanation also is consistent with the elevated DO and antimony (Sb) observed in MWTP-MW-1. As pointed out by Dr. Pichler, similar to As, Sb is also elevated in pyrite and thus Sb can be used as a proxy for As.
4. *“Microbial activity (influenced by the well installation) may cause the oxidation of pyrite and thus the release of As.”* Sulfur-oxidizing microbes often catalyze the oxidation of pyrite, and may be associated with the oxidation process. The reaction can probably proceed abiotically at the alkaline pH of the UF Aquifer groundwater, so that sulfur-oxidizing microbes could be absent without preventing pyrite oxidation from occurring.

5. *“Dilution of Floridan groundwater in the vicinity of well MWTP-MW-1 due to enhanced recharge through the confining Hawthorn Group, i.e., activation of fractures after rainfall, etc.”* We consider significant increases in the leakage rate through the HG to be extremely unlikely. The hydraulic conductivity of the HG lower-clay unit is quite low, as evidenced by the high hydraulic gradient across it. The increase in hydraulic head at the top of the HG is limited to the measured effects of recharge on Surficial Aquifer water-levels, which are less than 10 feet. Opening of fractures would require increases in pore pressure within the HG much greater than physically possible under natural conditions in either the Surficial Aquifer or HG.

The new data could have been evaluated to estimate mixing ratios of Surficial Aquifer and UF Aquifer waters, based on major-ion chemistry and isotopic ratios, to determine whether mixing of Surficial Aquifer and upgradient UF Aquifer waters could produce the observed concentrations at and downgradient of the Site. At a minimum, Piper or Durov diagrams should have been prepared to provide insight into the differences and similarities in the compositions. In order to evaluate mixing, reaction-path modeling would have been required, because of solid/liquid reactions that are likely to be occurring.

Additional QA of the reported data appears to be needed. For example, Table 2b lists one of the sampling dates as November 2005. Also, the sulfide and sulfate concentrations measured in the field in November are much different than reported for the July samples. Comparison of the laboratory and field data for sulfate concentrations measured on the November samples suggests that the sulfide and sulfate columns in Table 2b are switched. Because of the concern about transformation of sulfide and sulfate, sulfur mass-balance calculations would have been useful to determine if the field analyses for sulfur species are reliable. It would also have been useful to perform charge-balance calculations, perhaps using a speciation code given the high pHs measured in some samples.

In summary, although it appears that there was an earnest attempt at collecting data to provide answers pertaining to the source of the elevated As concentrations measured in the UF Aquifer, the effort to interpret the data appears to be incomplete. The conclusion and hypotheses presented in the report are not carefully supported or developed.

Beazer intends to perform a detailed and comprehensive analysis of all arsenic data, including the data collected by Dr. Pichler. This analysis will include performing the analyses discussed above in addition to others. Beazer is committed to evaluating As geochemistry processes in the UF Aquifer and to develop technically defensible explanations for the observed concentrations.

Sincerely,



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