

Executive Summary; Contaminant Characterization of Effluent from Pennsylvania Brine Treatment Inc., Josephine Facility Being Released into Blacklick Creek, Indiana County, Pennsylvania

Implications for Disposal of Oil and Gas Flowback Fluids from Brine Treatment Plants

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Executive Summary

This report contains results from sampling and analysis of wastewater effluent entering Blacklick Creek, Indiana County Pennsylvania from the Pennsylvania Brine Treatment (PBT) Josephine Facility conducted by the Center for Healthy Environments and Communities (CHEC) of the University of Pittsburgh, Graduate School of Public Health. The PBT-Josephine Facility accepts only wastewater from the oil and gas industry, including flowback water from Marcellus Shale gas extraction operations. This report describes the concentrations of selected analyzed contaminants in the effluent water and compares the contaminant effluent concentrations to standards, guidelines and criteria set by federal and state regulatory and investigative agencies for the protection of human and aquatic health. In particular and where applicable, it compares effluent concentrations to Agency for Toxic Substance and Disease Registry (ATSDR) minimal risk levels (MRL). MRL's are screening levels used as an estimate of "daily human exposure to a hazardous substance that is not likely to pose an appreciable risk of adverse noncancerous health effects."

This report is being widely disseminated to local, state and federal public health and regulatory authorities, municipal water authorities, and policymakers, because there is sufficient evidence that recreationalists and private well water users may reasonably be exposed to identified contaminants in the effluent discharge, and that downstream water intakes be made aware of potential impacts to water sources from these discharges, and act accordingly.

Sampling Methodology and Concentrations of Contaminants in Effluent Water from Pennsylvania Brine Treatment Facility, Josephine Plant

CHEC conducted sampling of wastewater as it was discharged into Blacklick Creek, Indiana County, Pennsylvania from the PBT-Josephine Facility on December 10, 2010. Samples were taken at 3-hour intervals over the course of one 24-hour period. These samples were analyzed for listed inorganic and organic species by R. J. Lee Inc, a PA State Certified Laboratory (Certificate # 006).

The concentrations of analyzed contaminants in this effluent of primary environmental public health importance, which may also stress aquatic life, include: barium (Ba) [mean, 27.3 ppm; maximum, 37.0 ppm]; bromides (Br) [mean, 1068.8 ppm; maximum, 1100.0 ppm; strontium (Sr) [mean, 2983.1 ppm, maximum 3120.0 ppm]; benzene [mean 0.012 ppm; maximum 0.013 ppm] and 2

butoxyethanol (2-BE) [mean 59ppm; maximum 66 ppm]. Contaminant concentrations of ecological and secondary drinking water importance include: chlorides (Cl) [mean 117,625 ppm, maximum 125,000 ppm]; magnesium (Mg) [mean 1247.5 ppm; maximum 1300.0 ppm]; total dissolved solids (TDS) [mean 186,625 ppm; maximum 190,000 ppm]; sulfate (SO₄) [mean 560 ppm; maximum 585 ppm], and pH [mean 9.58 units; maximum 10 units].

Comparisons of Effluent Contaminant Concentrations to Standards, Guidelines and Criteria set by Federal and State Regulatory and Investigative Agencies for the Protection of Human and Aquatic Health

Levels of contaminants in effluent from the PBT- Josephine Facility were interpreted according to comparisons with applicable federal and state standards and recommended guidelines for both human and aquatic health. Refer to Table 3, Federal and State Recommendations and Standards for Concentrations of the Analytes Sampled in PA Brine Josephine Effluent and Table 4, Derived Minimum Risk Levels (MRL's) for Ingestion of Contaminants through Drinking Water Sources for a complete list of comparison values by contaminant.

Barium - Barium had a mean concentration in effluent of 27.3 ppm (maximum of 37 ppm); this is approximately 14 times the United States Environmental Protection Agency (EPA) maximum concentration limit (MCL) of Ba in drinking water of 2 ppm. The EPA consumption concentrations 'water and organism' and 'organism alone' for barium are both 1 ppm. The levels of barium in the effluent are over 27 times these consumption concentrations. The U.S. EPA criteria maximum concentration (CMC) and the EPA criteria continuous concentration (CCC), both for protection of aquatic health, are 21 ppm and 4.1 ppm, respectively; the mean level of barium in effluent exceeds these criteria by 1.3 and 6.7 times, respectively. The mean concentration of barium in PBT-Josephine effluent water (27.3 ppm) is 3.96 times the derived drinking water MRL for intermediate and chronic exposures for adult men; 4.73 times the derived drinking water MRL for intermediate and chronic exposures for adult women; and 8.98 times the derived drinking water MRL for intermediate and chronic exposures for children.

Strontium - The EPA recommended MCL for Sr in finished municipal drinking water is 4 ppm. The mean concentration of Sr in PBT-Josephine effluent water is 2,981.1 ppm (over 745 times the recommended MCL). The strontium ATSDR MRL for oral route, intermediate exposure is 2 mg/kg of body mass/day, for

musculoskeletal endpoints. The derived minimum risk levels for strontium in drinking water for intermediate exposure for adult men, adult women, and children are 68.87 mg/L/day, 57.67 mg/L/day, and 30.45 mg/L/day, respectively. The mean concentration of strontium in PBT-Josephine effluent water (2,981.1 ppm) is 43.29, 51.68 and 97.90 times the derived strontium drinking water MRL's for intermediate exposures for adult men, adult women, and children, respectively. The maximum level of strontium leaving the outfall into Blacklick Creek was 3,120 ppm; this concentration is 45.30, 54.10, and 102.46 times the derived strontium drinking water MRL's for adult men, adult women, and children, respectively.

Strontium is not listed on the PBT-Josephine Facility NPDES permit but the facility is required to notify the PA DEP if they routinely discharge 100 ppb of a toxic pollutant or nonroutinely discharge 500 ppb of a toxic pollutant. The mean concentration of Sr in effluent water of 2,981.1 ppm is 29,811 and 5,962 times the lower and upper notification levels required by the PA DEP NPDES permit, respectively. Searches of the PA DEP file for December, 2010, which is contained in Appendix A shows no such notification to the DEP.

Bromide - Bromide in water is of concern because of its ability to form brominated analogs of drinking water disinfection by-products (DBP). Specifically, bromide can be involved in reactions between chlorine and naturally occurring organic matter in drinking-water, forming brominated and mixed chloro-bromo byproducts, such as trihalomethanes or halogenated acetic acids. Several DBPs have been linked to cancer in laboratory animals, and as a result the U.S. EPA has regulated some DBP's. There is general agreement that bromide levels in fresh-water sources be kept below about 100 ppb (.1 ppm) so that formation of brominated DBP's are minimized, therefore regulatory authorities and water treatment plant operators become concerned when there are sources of bromides in a surface water system adding to this level. The PBT- Josephine facility discharged effluent into Blacklick Creek with a measured mean concentration of bromide of 1,068.8 ppm, which is 1,068,800 ppb. This is 10,688 times the 100 ppb level at which authorities become concerned.

Bromide is not listed on the PBT-Josephine Facility NPDES permit but the facility is required to notify the PA DEP if they routinely discharge 100 ppb of a toxic pollutant or nonroutinely discharge 500 ppb of a toxic pollutant. The mean concentration of Br in effluent water 1,068.8. ppm is 10,688 and 2,138 times the

lower and upper notification levels required by the PA DEP NPDES permit, respectively. Searches of the PA DEP file for December, 2010, which is contained in Appendix A shows no such notification to the DEP.

Benzene - The mean level of benzene, a known carcinogen, in outfall effluent from PBT-Josephine was 0.012 ppm or 12 ppb. The drinking water MCL for benzene is 5 ppb, thus effluent levels were above twice the drinking water MCL. The EPA consumption, water and organism risk level for benzene is 2.2 ppb in water, the mean level of benzene in PBT-Josephine effluent water is almost 6X this criteria; the organism only risk level for benzene is 50 ppb in water, the mean level of benzene in effluent water is 24% of this guideline. The benzene ATSDR MRL for oral route, chronic exposure is 0.0005 mg/kg of body mass/day, for immunological endpoints. The derived minimum risk levels for benzene in drinking water for chronic exposure for adult men, adult women, and children are 0.017 mg/L/day, 0.014 mg/L/day, and 0.008 mg/L/day, respectively. The mean concentration of benzene in PBT-Josephine effluent water (0.012 ppm) is 70% of, 86% of, and 1.5 times the derived chronic drinking water MRL for benzene for adult men, adult women, and children, respectively.

2-butoxyethanol - 2-butoxyethanol is a glycol ether and is used as an anti-foaming and anti-corrosion agent, as well as an emulsifier in slick-water formulations for Marcellus Shale gas extraction. The mean and maximum levels of 2-BE found in the PBT – Josephine effluent were 59 ppm and 66 ppm, respectively. The 2-BE ATSDR MRL for oral route, acute exposures is 0.4 mg/kg/day based on hematological effects, with an uncertainty factor of 90; the 2-BE MRL for oral route, intermediate exposure is 0.07 mg/kg/day and it is based on hepatic health endpoints with an uncertainty factor of 1000. The derived minimum risk levels for 2-BE in drinking water for acute exposure for adult men, adult women, and children are 13.77 mg/L/day, 11.53 mg/L/day, and 6.09 mg/L/day, respectively; the derived MRL's for 2-BE in drinking water for intermediate exposure for adult men, adult women, and children are 2.41 mg/L/day, 2.02 mg/L/day, and 1.07 mg/L/day, respectively.

The mean concentration of 2-BE in PBT-Josephine effluent water (59 ppm) is 4.28, 5.12, and 9.69 times the derived 2-BE drinking water MRL's for acute exposure to adult males, adult females, and children, respectively. The mean concentration of 2-BE in PBT-Josephine effluent water is 24.48, 29.21, and 55.14

times the derived 2-BE drinking water MRL's for intermediate exposure to adult males, adult females, and children, respectively.

2-BE is not listed on the PBT-Josephine Facility NPDES permit but the facility is required to notify the PA DEP if they routinely discharge 100 ppb of a toxic pollutant or nonroutinely discharge 500 ppb of a toxic pollutant. The mean concentration of 2-BE in effluent water is 590 and 118 times the lower and upper notification levels, required by the PA DEP NPDES permit, respectively. Searches of the PA DEP file for December, 2010, which is contained in Appendix A shows no such notification to the DEP.

Other Contaminants - Contaminants with secondary MCL's (SMCL) and aquatic receptor effects that were measured in the PBT-Josephine Facility effluent include magnesium, manganese, chlorides, sulfates, and total dissolved solids (TDS). Magnesium was found in the effluent with a mean concentration of 1,247.5 mg/L, which is 24,950 times the EPA Mg SMCL of .05 mg/L. The mean concentration of Manganese in the effluent was .08 mg/L, and the SMCL for Manganese concentration in drinking water is .05 mg/L, which is 62.5% lower than the concentration in the effluent. The mean concentration of chlorides in the sample analysis was 117,625 mg/L, which is 470.5 times the SMCL for chlorides in drinking water of 250 mg/L. To protect aquatic communities, the criteria maximum concentration (CMC) for chlorides in surface water is 860 mg/L, and the criteria continuous concentration (CCC) for chlorides in surface water is 230 mg/L. The mean concentration of chlorides measured in samples was 138 times the CMC and 511 times the CCC. The mean concentration of sulfates in the sample analysis was 560 mg/L - 2.2 times the SMCL for sulfates in drinking water (250 mg/L). The SMCL for total dissolved solids (TDS) in drinking water is 500 mg/L, and the mean concentration of TDS measured in samples was 186,625 mg/L, 373 times the SMCL.

Masses of Contaminants Entering Blacklick Creek

CHEC has information from the Pennsylvania, Department of Environmental Protection (DEP) that the PBT – Josephine Facility treated 15,728,241 gallons of oil and gas wastewater in the 6 month period from July 1, 2010 to December 31, 2010. Using this figure as the amount of effluent wastewater exiting the Josephine outfall and using the mean level of each contaminant found in the effluent over the sampling period of the study, the masses of contaminants with important human and ecological consequences discharged from the PBT,

Josephine Facility into Blacklick Creek in the last 6 months of 2010 are projected to be: barium - 1627 kg (3588 pounds); strontium - 177,712 kg (391,856 pounds; 196 tons); bromides -63,708 kg (140,476 pounds; 70.2 tons); chloride – 7,011,631 kg (15, 460,646 pounds; 7,730 tons); sulfate – 33,382 kg (73,607 pounds; 36.8 tons); 2 butoxyethanol – 3517 kg (7,755 pounds; 3.88 tons); and total dissolved solids – 11,124,733 kg (24,530,036 pounds; 12,265 tons).

Potentially Exposed Populations

Recreationalists are at high risk of being exposed to outfall contaminants through ingestion, inhalation and through dermal exposure. While the pH of outfall water will not cause irreversible eye damage at the maximum observed level of 10 pH units, irritation of the eyes and mucous membranes may occur. The outfall of the Josephine Facility is easily accessible to users of nearby rails-to-trails pathways, and there are indications that anglers frequent the area.¹ Additionally, children wade and swim in the creek during warmer weather, and regional watershed websites indicate that paddlers use the creek for canoeing and kayaking. 2 BE released into Blacklick Creek may be ingested by swimmers in the creek. This pollutant can become airborne and present an inhalation hazard to anglers, swimmers and boaters. It is also taken in to the body via dermal absorption. Anglers catching and eating fish from upstream or downstream of the effluent outfall are at risk for exposure to multiple contaminants that were sampled in this study.

CHEC has developed maps showing numerous private water wells in the immediate vicinity of Blacklick Creek downstream from the effluent discharge. Private well water users are at risk of exposure to contaminants in effluent being released into Blacklick Creek because these private wells may capture water from the creek when the well pump rate is sufficiently high. High pump rates can occur especially during peak usage by residents.

The first identified municipal drinking water intake downstream of this discharge is at Freeport, Pennsylvania on the Allegheny River. Populations served by the Freeport authority and water authorities downstream of Freeport are at potential risk for exposure to contaminants identified in effluent, as well as other contaminants in Marcellus Shale flowback water that were not sampled for in this study.

¹ Blacklick Creek is classified as a ‘trout stocking’ stream.

Implications of Effluent Discharge from the PBT – Josephine Facility Discharge for Exposures to Other Contaminants Known to be Present in Marcellus Shale Flowback Fluids and a Regional Appreciation of These Results

Of particular environmental public health significance is that Marcellus Shale flowback water contains other contaminants, in addition to those analyzed for in this study, which have health consequences if ingested, inhaled, and/or absorbed through the skin. While we make no statements regarding the presence of other contaminants in this effluent water being discharged into Blacklick Creek, it is imperative that additional testing be conducted immediately by federal and state health and enforcement agencies to determine if other contaminants of public health significance are entering this watershed.

Additionally, oil and gas wastewater and Marcellus shale flowback fluids are being disposed of in “brine treatment” facilities and at Publically Owned Treatment Works (POTW’s) throughout the Commonwealth of Pennsylvania and in Ohio, West Virginia, and New York. The ramifications of disposal of large quantities of oil and gas wastewater through ineffectual brine treatment plants and POTW’s needs further evaluation throughout the region to determine its impact on stream and river systems and public drinking water supplies, as well as to recreationalists and private well water users.

Recommendations

- The Pennsylvania Brine Treatment – Josephine Facility is discharging up to 60 ppm of 2-BE into Blacklick Creek, which is not listed in its NPDES discharge permit. Other contaminants of human health importance found in effluent but not present on the permit also include bromide, benzene and strontium. Operations at this plant should be halted until all contaminants of human and aquatic health concern in accepted oil and gas fluids are known and it can be determined that the treatment processes used at the plant effectively remove these contaminants from the fluids being treated. The PA DEP should reevaluate the permit given to this operator as it clearly allows for chlorides and total dissolved solids to be discharged at levels exceeding aquatic health criteria.
- All approaches to the effluent discharge area and a reasonable distance downstream (at least 100 meters) from streamside and landside should be posted with warning signs. These signs should discourage any use of and/or contact with stream water.

- An advisory to all anglers should be issued stating that fish taken from this stream, both up and down stream may be contaminated in order to discourage fish take and consumption.
- Studies to determine the levels of all potential Marcellus Shale flowback fluid contaminants in downstream water, sediments and pore water should be undertaken immediately. These should include sampling upstream of the effluent discharge point and at short, intermediate and longer distances downstream from the effluent discharge point. The number of samples (n) of surface water, sediments and pore water upstream and at the various distances downstream should be sufficient so that statistically significant differences of contaminant concentrations can be inferred.
- Residential and other private well water users downstream of the effluent outfall of the PBT-Josephine Facility should be advised that there may be contaminants in their well water and discouraged from using it for drinking, cooking or bathing until such water is tested for continuous safe use. Therefore, it is imperative that well water from wells in close proximity to Blacklick Creek should be tested to assure that contaminants in Marcellus Shale flowback fluids and other oil and gas waste fluids are not present in concentrations that may affect human health.
- Municipal water authorities downstream of this outfall should be notified of the contaminants found in effluent from the PBT- Josephine Facility, of other possible contaminants in Marcellus Shale flowback fluids and oil and gas wastewater, and that there are other treatment facilities and POTW's in the Blacklick, Conemaugh, and Kiskikiminetas drainages that accept and discharge oil and gas waste fluids into surface water. Downstream municipal water authorities should test raw unfinished intake water and finished drinking water for these contaminants that have been identified in effluent from the PBT- Josephine Facility, and other contaminants known to be present in Marcellus Shale flowback fluids and oil and gas wastewater.
- All municipal water authorities at reasonable distances downstream of "brine treatment" and POTW's accepting Marcellus Shale flowback fluids and other oil and gas wastewater in the region extending eastward across Ohio, Pennsylvania and West Virginia and New York should be notified of these results. It is important that they initiate sampling of raw, unfinished inflow water and finished drinking water immediately to ensure that their systems are capable of handling all potential contaminants, without breakthrough above specific drinking water MCL's or ATSDR derived MRL's.

- The PA DEP and other state and federal regulatory authorities should immediately review all surface water discharge permits granted to brine treatment facilities and POTW's that accept Marcellus Shale flowback fluids and oil and gas wastewater, to ensure that 2-BE concentrations being discharged are below all applicable standards, guidelines and criteria. This review should be informed by results of this report but should be extended to all known contaminants in flowback and other oil and gas wastewater.

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