An Assessment of Arsenic Concentrations in Upper Indian River Due to Mass Loading from the Burton Island Historical Ash Disposal Area, Millsboro, DE

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Introduction: A Remedial Investigation (RI) Report for the Indian River Generating Station Operable Unit No. 2 Burton Island Historical Ash Disposal Area was recently submitted to the Department (Shaw 2011). The RI report includes an estimate of the amount of arsenic released from the ash disposal area to adjacent surface water (i.e., upper Indian River and Island Creek) via groundwater discharge and overland flow. The methods used were technically sound, were based on site-specific data, and yielded conservative estimates overall. Releases from both pathways were expressed as mass per time, which is equivalent to mass loading rate. Mass loading for the groundwater to surface water flow pathway was expressed as a range between 0.067 pounds per day and 0.366 pounds per day. Mass loading for the overland flow pathway was provided as a single value of 0.09 pounds per year, which is the same as 0.000246 pounds per day. Hence, groundwater loading is far greater than overland flow, representing between 99.6% to 99.9% of the estimated arsenic loading to surrounding surface water (not accounting for former breaches in berms known to have occurred and since corrected).

The RI report indicates that the lower end of the groundwater to surface water loading range is considered more representative, and I would agree for several technical reasons, including but not limited to the fact that arsenic is strongly removed from solution via sorption and coprecipitation, especially by iron and especially at redox boundaries such as the sediment - surface water interface (e.g., Johnstone et.al., 2011). Hence, although arsenic may be released from the ash pile via groundwater discharge, a significant fraction may become sequestered at the sediment-water interface, thereby reducing the amount of arsenic that actually enters, mixes, and circulates in the surface water environment. Fate issues aside, it is important to place the arsenic loading rates from the RI report into perspective in terms of potential ***increases*** in ambient arsenic concentrations in the upper Indian River and provide comparisons to applicable water quality criteria for the protection of human health and aquatic life. This was not done as a part of the RI report but rather is presented in this spreadsheet assessment to provide DNREC decision makers with regulatory context for the loading rates.

Objectives: The purpose of this assessment is to determine whether arsenic loading from the Burton Island historical ash disposal area is expected to cause exceedances of applicable water quality criteria in upper Indian River, and if so, how frequently and under what circumstances those exceeedances are expected to occur. This objective is accomplished through a simple steady-state, tidally-averaged mass balance model along with proper consideration of the water quality criteria. The modeling framework and underlying assumptions are described below as are the applicable water quality criteria.

Methods: The tidally averaged, steady-state concentration of arsenic in Indian River and Island Creek adjacent to Burton Island was calculated by dividing the arsenic mass loading from Burton Island (via groundwater + overland flow) by the net advective freshwater flow expected at Burton Island. Two scenarios were considered: first, that the long-term groundwater loading of arsenic equals the low end of the range provided by Shaw (2011); and second, that the long-term groundwater loading equals the high end of the range provided by Shaw (2011). The single overland flow loading of 0.09 pounds per year was added to the groundwater loading in both scenarios. The net advective freshwater flow at Burton Island is the measured flow at the Millsboro Pond outlet (USGS gage 01484525, drainage area = 61.7 sq mi), plus the estimated flow from the Iron Branch watershed (15.43 sq mi), plus the estimated flow from the Swan Creek watershed (10.54 sq mi). The flows for Iron Branch and Swan Creek were estimated by multiplying the flow at Millsboro Pond by the ratio of the ungaged drainage area to the area upstream of the Millboro Pond gage. For example, the flow for Iron Branch was estimated by multiplying the flow at Millsboro Pond by 0.25 (i.e., 15.43 sq mi divided by 61.7 sq mi). The daily flow values for Millsboro Pond were downloaded from the USGS web site (USGS, 2011). Daily flow values were available for the period 5/1/1986 through 9/30/1988 and 3/16/1991 through the present. Only values approved for publication by the USGS were used in this analysis and so provisional data beginning 2/1/2011 and ending on 3/17/2011 were not used. In all, this resulted in 8146 daily flow values that were used, representing over 22 years of flow data. Note that the published daily flow for 8/30/1998 was zero. To allow mass balance calculations for this particular day, a flow of 0.5 cfs was assigned, which represents one-half of the lowest non-zero flow in the record. The published flows at the Millsboro Pond outlet (including the modified value of 0.5 cfs on 8/30/1998), appear on the tab 'Arsenic Mass Balance Calcs'. The estimated flows for Iron Branch and Swan Creek also appear on that tab.

The increase in arsenic concentration due to the loading from Burton Island was predicted (i.e., hindcasted) for each day that had an approved daily flow value at Millboro Pond. Hence, this provided 8146 arsenic concentrations in upper Indian River near Burton Island over the period 5/1/1986 through 1/31/2011 using the low end loading estimate provided by Shaw (2011). It provided an additional 8146 arsenic concentrations using the upper end loading estimate provided by Shaw (2011). The actual calculations for the low end and high end loading scenarios appear on the tab 'Arsenic Mass Balance Calcs'. The strength of this approach is that it provides a distribution of concentrations which can then be assessed in terms of magnitude, duration, and frequency of occurrence. The weakness is that we are forced to make several assumptions. First, it is assumed that the mass loading from Burton Island is and has been constant over time (either at the low end or at the high end of the range, depending on the scenario). Surely loading is a dynamic, non-constant process but there is insufficient information to fully characterize time variable loading. Although we have predicted variability in the concentrations of arsenic in upper Indian River, that variability is due entirely to daily variation in net advective flow. In fact, based on the modeling framework used, in-stream concentrations of arsenic are predicted to vary linearly and inversely with net advective flow (Chapra, 1997) and nothing else. So, no other fate processes that would act to reduce the concentration of arsenic in the water column (e.g., coprecipitation at the sediment-water interface and subsequent sediment-water interactions) are considered. In this regard, the hindcasted arsenic concentrations should be considered conservative (protective), provided we accept that the mass loading estimates are also conservative. The other key point that should be kept in mind is that the modeling framework used in this analys predicts the ***increase*** in arsenic concentration in Indian River due soley to the Burton Island loading, independent of any other sources and independent of background. This is not a flaw but rather a strength since it allows us to determine whether the specific source of interest, namely Burton Island, has a reasonable potential to cause exceeedances of applicable water quality criteria in-and-of-itself, without any confounding issues. In situations where one or more sources cause exceedances of applicable water quality criteria, DNREC lists the affected waters on Delaware's Clean Water Act 303(d) list and schedules those waters for Total Maximum Daily Loads (TMDLs). Delaware's most recent (2010) CWA 303(d) list does not identify arsenic as a contaminant of concern in any segment of the Inland Bays. That position is not likely to change based upon a comprehensive review ambient concentrations of arsenic in the water, sediment, biota, and air within the Inland Bays (Greene, 2010).

The applicable water quality criteria considered in this assessment are taken from Delaware's Surface Water Quality Standards (DNREC, 2004). Specifically, the applicable human health criterion for arsenic is 10 ug/L. This is interpreted as a long-term average concentration since it relates to long-term, chronic exposure in the human population. The applicable aquatic life criteria are 36 ug/L to protect marine organisms from chronic toxicity and 69 ug/L to protect marine organisms from acute toxicity. Both of these criteria are expressed on a dissolved basis and strictly speaking, both apply only to trivalent arsenic. Further, chronic aquatic life criteria are 4-day average concentrations not to be exceeded more than once in any 3 year period, while acute aquatic life criteria are 1-hour average concentrations not to be exceeded more than once in any 3 years. To properly account for the 4-day averaging period associated with the chronic aquatic life criteria, moving 4-day average concentrations were calculated from the predicted daily arsenic concentrations. Those calculations appear on the tab 'Arsenic Mass Balance Calcs'). The individual daily values were compared to the acute aquatic life criteria. Finally, for the aquatic life criteria comparison, the conservative assumptions are made that all of the arsenic released from Burton Island remains in the dissolved phase and further that all of the arsenic is in the trivalent oxidation state. Although conservative, the first assumption is reasonable in that standard equilibrium partitioning (EqP) equations (Chapra, 1997) predict that between 96% and 72% of arsenic in the water column is expected to be dissolved for typical suspended solids concentrations between 5 mg/L and 50 mg/L, respectively. These percentages assume a partition coefficient (log K_d) of 3.9 L/kg for arsenic, which represents the mean ratio of sorbed to dissolved arsenic based upon data compiled from the literature (EPA, 2005). The second assumption (that all the arsenic is trivalent) is somewhat more conservative based upon research performed in the nearby Patuxent Estuary (Nice et.al., 2008). Measurements there indicate that the ratio of dissolved arsenate, As(V), to dissolved arsenite, As(III), vary as a function of space and time and range between approximately 20:1 to 1:1. Hence, at most, 50% of the dissolved arsenic in the Patuxent Estuary is trivalent. If a similar maximum percentage occurs in the upper Indian River, then clearly, assuming 100% for purposes of this analysis is conservative, essentially introducing a safety factor of 2 as it relates specifically to compliance with the applicable aquatic life criteria.

Findings: Based on the modeling framework, assumptions, and criteria described above, it is concluded that:

1. Under the low end groundwater loading scenario, the average increase in arsenic concentration in the Indian River near Burton Island over the 22+ year hindcast is 0.17 ug/L. The median (50th percentile) increase is 0.12 ug/L; the 99th percentile increase is 0.68 ug/L; and the maximum increase is 17.6 ug/L, which occurred on one day (8/30/1998) during an extreme low flow event. The second highest increase was 8.8 ug/L, which occurred the day after the maximum. Recall that 8/30/1998 is the day that the USGS recorded no flow over the spillway at Millsboro Pond and so a flow of 0.5 cfs was assigned as a part of this analysis in order to permit mass balance calculations. Hence, although we have calculated an arsenic concentration on that day, the value is highly uncertain and may have been higher. Even so, the arsenic concentration on the very next day when the flow was reported to be 1 cfs was 8.8 ug/L. By trial and error, it was determined that any flow less than 0.87cfs at Millsboro Pond would result in an increase in arsenic concentration at Burton Island greater than 10 ug/L. Based on an analysis of flow frequencies, a flow of 0.87 cfs is only expected to occur 0.0213% of the time, which is an extremely rare event. Viewed from another perspective, the net advective flow moving through upper Indian River is large enough to keep the increase in arsenic concentration from the Burton Island loading less than 10 ug/L 99.98% of the time. Since the human health criterion of 10 ug/L is interpreted as a long-term average, we conclude with a high degree of confidence that the arsenic loading from the ash pile (under the low end loading scenario) is not likely to exceed the criterion by itself. Likewise, the low end arsenic mass

loading from Burton Island was never large enough to cause an exceedance of the acute or chronic aquatic life criteria in Indian River near Burton Island. Of note, the maximum 4-day average concentration was predicted to be 6.8 ug/L (between 8/30/1998 and 9/2/1998). This is much less than the marine chronic aquatic life criterion of 36 ug/L, which is a 4-day average value not to be exceeded more than once in any 3 year period.

2. Under the high end groundwater loading scenario, the average increase in arsenic concentration in the Indian River near Burton Island over the 22+ year hindcast is 0.93 ug/L. The median (50th percentile) increase is 0.67 ug/L; the 99th percentile increase is 3.7 ug/L; and the maximum increase is 95.6 ug/L. Again, the maximum increase was predicted to occur on 8/30/98 during extreme low flow. And again, there is great uncertainty regarding what the actual flow was on that day and therefore there is associated uncertainty with the predicted increase in arsenic concentration. In addition to the high value predicted on 8/30/1998, the modeling indicates that the high end load may have been large enough to result in a concentration increase greater than 10 ug/L on 20 other days as well. That's 21 days out of 8,146 days or a frequency of 0.26%, which corresponds to days when the flow at Millsboro Pond falls below 4.78 cfs. This analysis also suggests that the net advective flow moving through upper Indian River is sufficient to keep the predicted increase less than 10 ug/L 99.74% of the time. Again, since the human health criterion of 10 ug/L is interpreted as a long-term average, we conclude that the mass loading from the Burton Island ash pile is not likely to exceed the human health criterion by itself, even under the high end groundwater loading scenario. For aquatic life, the predicted increase in arsenic was large enough (95.6 ug/L) on a single day (8/30/1998) to potentially exceed the acute criterion of 69 ug/L. Recall however that this criterion is actually for trivalent arsenic, which, based upon high quality measurements performed elsewhere, is expected to represent no more than one half of the dissolved arsenic present. So, a very rough estimate of the dissolved trivalent arsenic concentration present on 8/30/1998 is 47.8 ug/L (= 95.9/2), which is less than the acute criterion. Even if all of the arsenic present was in the trivalent oxidation state, the frequency of occurrence, 1 day out of 8,146 days (or 22.3 yrs) is far less than the allowable frequency of 1 in 3 years. Finally, the maximum 4-day average increase in arsenic concentration in Indian River due to the Burton Island ash pile loading under the high end loading scenario is 36.8 ug/L. Coincidentally, this is almost identical to the 4-day duration chronic aquatic life criterion of 36 ug/L. This criterion, like the acute criterion, applies to trivalent arsenic. If the predicted total dissolved concentration is divided by 2 to provide a worst case estimate of trivalent arsenic, then the maximum 4-day average concentration becomes 18.4 ug/L, which is less than the chronic criterion. Again, even if all of the arsenic present was dissolved trivalent arsenic, the frequency of occurrence is only once in 22.3 years which is far less frequent than the allowable exceedance frequency of once in 3 years.

3. Summarizing, this anlysis used the arsenic mass loading estimates provided by Shaw (2011) along with a conservative mass balance modeling framework to assess the likelihood that the loading has caused exceedances of applicable human health and aquatic life criteria in upper Indian River. It is concluded that exceedances due to the Burton Island loading are extremely unlikely.