From: Nehs, Janelle M - DNR
Sent: Wednesday, October 16, 2019 11:00 AM
To: Krueger, Sarah E - DNR
Subject: RE: Question regarding bis(2-ethylhexl)phthalate
Attachments: wa1011.pdf

Categories: Tracking

Hi Sarah,

I think I can help.

If it is an issue of lab contamination, you would expect to see hits in your blanks as well. Do you know if the method blanks (field blanks, trip blanks, etc) have been passing? You could always try sending a duplicate to a different lab.

That being said, I think the issue is the PVC. bis(2-ethylhexl)phthalate is a plasticizer commonly used in PVC.

See the attached paper I found from the WI DNR circa 2002 that details the exact situation you are in and how to deal with it.

I hope that is helpful! Let me know if you have any other questions. ☺

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From: Krueger, Sarah E - DNR <sarah.krueger@wisconsin.gov>
Sent: Wednesday, October 16, 2019 8:53 AM
To: Nehs, Janelle M - DNR <janelle.nehs@wisconsin.gov>
Subject: Question regarding bis(2-ethylhexl)phthalate

Janelle –

I have a question about bis(2-ethylhexl)phthalate in several monitoring wells at a RR site of mine. I am wondering if the bailers, tubing, or even the PVC pipe that the well is made of might be a source for this particular contaminant. Might this be a lab contaminant? There are no other SVOCs detected in the wells, and I am trying to understand why it is showing up in these wells even in areas that are considered clean relative to the source of contamination.

If you have any ideas or input let me know.
Thank you,
Sarah

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Problems Associated with bis(2-ethylhexyl)phthalate Detections in Groundwater Monitoring Wells

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Description: This document provides guidance for investigating whether phthalate detections in monitoring wells are false exceedances or real groundwater contaminants, and the application of NR 50716, NR 507.17, NR 507.28(3), NR 508.05, NR 140.16 in these situations.

Guidance manager/Contact: Jack Connelly, Solid Waste Program Coordinator

Applicability: This guidance primarily is intended for evaluating the need for assessment monitoring when di-(2-ethylhexyl)phthalate is detected in monitoring wells at landfills regulated under NR 507 Wis. Adm. Code. In addition, it may be applicable to landfills for which corrective action is necessary or cases where NR 507 and NR 716 may both be applicable. The recommendations contained in this guidance may have general applicability to site investigations, brownfields, or remediation sites; however, it is not intended to supersede Superfund guidance or existing guidance in the Remediation and Redevelopment program related to acceptable levels of contamination.

Problem Statement:

Consultants, facilities, and staff have had questions about the validity of bis(2-ethylhexyl)phthalate in landfill monitoring wells, particularly when it is the only contaminant detected.

Bis(2-ethylhexyl)phthalate is a semi-volatile organic compound (SVOC) that is also known as di-(2-ethylhexyl)phthalate, and **D**EHP. Some DNR programs refer to this compound as BEHP; however, this is not a recognized synonym in many chemical databases. Using this acronym can cause confusion because in scientific literature, **B**EHP usually refers to butyl(2-ethylhexyl)phthalate (cas number 85-69-8). Although DEHP has been identified as a common laboratory contaminant, phthalates are prevalent in the environment because of their use in plastics like PVC. Groundwater monitoring plans may include SVOCs when facilities investigate elevated indicator parameter concentrations, leachate results indicate possible problems, special circumstances at a landfill raise concerns or a general site investigation is being performed by the Department or others. Data in GEMS indicates that most detection limits reported are at or above the NR 140 Groundwater Quality Preventive Action Limit (PAL) of 0.6 ug/L, so almost every quantifiable result is a PAL exceedance. This guidance attempts to lay out the problems and appropriate approaches to assessing whether with phthalates are really present in the groundwater or an artifact of the sampling and analysis procedures (in other words, a false exceedance). We have reviewed a number of reports for Wisconsin sites and queried other states for their experience with this problem.

Recommendations

Whether DEHP is detected during assessment monitoring or in conjunction with other monitoring done at a site, staff should ask the facility to investigate whether the DEHP is a false exceedance attributable to sampling or laboratory procedures.

If sampling procedures or field conditions are identified as contamination sources, the facility should be instructed to change their sampling procedures to eliminate the contamination source. This may mean changing sampling equipment, materials or collection method. Although some have proposed filtering as a means of excluding DEHP particulates from sampling, there is a general consensus that **filtering samples is not an appropriate option.**

If the source of DEHP is attributed to laboratory contamination, the facility should be directed to obtain additional analyses for which laboratory contamination is controlled. The facility may need to switch laboratories if their laboratory is unable to control contamination adequately.

If the facility is requesting the cessation of assessment monitoring and DEHP is the only substance detected above the NR 140 PAL and the facility has demonstrated that DEHP is a false exceedance as per 508.05(1), then staff may allow the facility to discontinue assessment monitoring. If the concentrations of DEHP cannot be fully attributed to a false exceedance, staff should consider whether it is more appropriate to discontinue assessment monitoring or to propose alternate assessment monitoring as provided in NR 508.05(2) and (3)(a).

If the facility has not begun assessment monitoring, DEHP is the only substance detected above the PAL and there are no other reasons for assessment monitoring, then it would not be necessary for the facility to initiate assessment monitoring.

Suggested Approach to Determine the Credibility of DEHP Detects

Given the prevalence of DEHP in the environment and the high potential for contaminating samples, the source of DEHP in groundwater cannot be dismissed automatically as sampling or laboratory error. It may be necessary to modify sampling plans to incorporate additional blanks and to change sampling protocols. Ultimately, any corrective action or requirements for assessment monitoring will need to be based on evaluation of all available information and the applicable rules.

Assess Blank Results

Method blanks are useful for determining whether laboratory procedures introduced any contamination into the analysis. Although facilities are supposed to flag data when a contaminant is detected in the method blank, you should not rely solely on the flag in assessing the source. Experience has taught us that data is not flagged reliably and even when flags are present, the concentration of the contaminant in the method blank may not be reported or available in GEMS. If method blank results are available and the concentration of the blank is less than 5% of the sample concentration, the DEHP concentrations in the sample may be biased high, but cannot be attributed entirely to laboratory contamination. If the concentration of the sample is in the same range as the method blank, sample results may be the result of laboratory contamination. If the concentration of the method blank is near the detection limit or less than the limit of quantitation and sample results are in the same range, we suggest that sample results could be attributed to contamination. If method blank results exceed the LOQ, the facility should take steps to obtain sample results under circumstances in which laboratory contamination is better controlled.

Field blanks may be quite useful in determining whether sampling is contributing contamination. You should be clear about how these blanks were collected and what they represent. To the extent possible, field blanks should be collected in the same manner as the samples, i.e. be exposed to the same equipment and materials as the samples. In evaluating these results, you may need to consider what water was used for a field blank. If the water in the blank is from the same container as was used to clean equipment and without additional information, it may not be possible to determine whether the water or the sampling equipment is the source of contamination.

Rinsate blanks may also be useful indicators that sampling is the source of DEHP. As with field blanks, investigators should be clear about what rinsate blanks represent. Typically, these blanks are collected after equipment is cleaned and represent potential carry-over between sampling stations. These blanks may also provide an indication of rinse water contamination if this blank is from the same source as the rinse water.

Trip blanks are not generally collected or used for semi-volatiles and may have limited use in evaluating the source of the contamination because DEHP does not volatilize at an appreciable rate. These blanks typically are supplied by the laboratory and accompany samples without direct exposure to field conditions.

Change Sampling Procedures

Although evaluating blanks is an important first step in investigating sources of contamination, not all procedural problems result in contaminated blanks. The History section below highlights possible sampling artifacts that are not easily proven or addressed. Obviously, any equipment or supplies that are plastic or are in contact with plastics should be carefully evaluated. It may be necessary to choose another sampling procedure and compare results. For instance, if investigators believe that bailing is causing abrasion to the well casing or that the well casing is flaking, it may be wise to sample using a pumping procedure. Because DEHP adheres strongly to any particulates, filtering the samples is not an acceptable modification to sampling procedures nor can it be used to “prove” that the source of DEHP is the well casing.

Other Considerations

In addition to evaluating blank results, facility or staff investigations of DEHP detections should include the following considerations:

- What about well construction materials?
  Is the piping or casing PVC or other plastic?
  Is the piping or casing steel?

- Is there other evidence that the landfill is leaking?
  Are indicator parameters elevated or do they show a trend?
  Are VOCs present? (VOCs may increase DEHP solubility)
  Are petroleum contaminants present? (As with VOCs, gasoline and other petroleum products can act as a solvent for DEHP)

- Is there a pattern to the detected values?
  Is it detected in the leachate?
  Was it detected in background or up-gradient wells in the "same" concentration range?
  Has it been detected historically in the affected wells?
  Are detected concentrations consistent over time? Are they erratic?
  Were affected wells constructed in the same time period?

Evaluating whether the detected concentrations in the down-gradient wells are the "same" as background wells can be somewhat subjective. Usually there is only one result per sample, so investigators may not be able to determine the variability associated with sampling and laboratory analysis adequately. Absent other information and as a rule of thumb, down-gradient results two to five times the concentration in the background well may be considered to be in the same concentration range. This evaluation can easily be complicated if blanks also show contamination. Frequently, there are insufficient data to apply statistical techniques to determine whether differences are significant. For instance, to understand and assess the variability in various data points, multiple analyses of the same samples may be necessary. Before using a statistical approach, it is important to consider the underlying principles and assumptions of the statistical tool proposed to assure that it can be applied appropriately to the data set.

History – Sites Where DEHP is Attributed to Sampling

After detecting DEHP in groundwater monitoring wells at concentrations in excess of the NR 140 PAL, a number of consultants and laboratories performed investigations to determine whether the source was sample contamination. The investigations generally ruled out laboratory contamination as the source because method blanks were either free of contamination or the concentrations of DEHP in the method blanks were much lower than concentrations in the samples. The investigators have attributed detects in the wells to degradation (aging) of the well casing, microbial action (iron bacteria) on sample tubing and abrasion on well casing, bailer and rope associated with bailing procedures.

At this point, contamination from sampling cannot be attributed to any single sampling technique. At one facility using bailers, the field collection personnel reported that visually turbid samples seemed to be a predictor of phthalate concentrations. Subsequent analyses of scrapings from the bailer and ropes indicated the presence of DEHP. They proposed filtering samples as a means to more accurately assess the true DEHP concentrations in the wells. At another facility where sample crews used low-flow pumping and collected field blanks, investigators visually examined tubing that had been dedicated to sampling an affected monitoring well and noted the presence of black mucilaginous material on the walls. Field blanks collected through new tubing did not contain detectable DEHP concentrations; however, blanks prepared using the tubing dedicated to the well contained significant concentrations of DEHP.

During Superfund Site Inspections in Northeast Region, DNR staff found phthalates both in groundwater and rinsate samples, regardless of the site under investigation. The investigators traced the phthalates to contaminated rinse water. They tested water directly from the still and found that it, too, contained high phthalates so contamination could not be attributed solely to storing the rinse water in plastic carboys. There are sites, however, for which phthalate concentrations cannot be attributed to sampling or laboratory analysis.

Additional Chemical Information and Environmental Fate of Bis(2-ethylhexyl)phthalate

Bis(2-ethylhexyl)phthalate (CAS Number 117-81-7) is one of several common names for 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester. DEHP is common in the environment because of its use in plastics. Sampling and laboratory equipment, monitoring wells, and waste disposed in landfills may contain or be constructed of plastics. In addition to its use in plastics, DEHP is also used in inks, adhesives, coatings, pesticides, cosmetics, vacuum pump oil and as a dielectric fluid in ballast capacitors and other electrical equipment (e.g., transformers).

DEHP has low solubility in water (300 - 400 μg/L), is soluble in most organic solvents, and evaporates slowly into the air. In the environment, DEHP will attach strongly to soil particles or humic material. Although DEHP may biodegrade under aerobic conditions (e.g. in lakes or rivers), DEHP has not been shown to degrade in anaerobic conditions, such as landfill leachate. Additional information on DEHP, its environmental fate and toxicity can be obtained through EPA's Substance Registry System (SRS) by searching for the compound and following the Related Links at the end of the compound listing (http://ofmpub.epa.gov/sor_internet/registry/substreg/home/overview/home.do). The TOXNET web site accesses several chemical databases and is also good source of information. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?TOXLINE

Contact 608/266-2111 or DNRWasteMaterials@Wisconsin.gov for further information.