# Toxics Use Reduction Institute Science Advisory Board Meeting Minutes January 19, 2024 Virtual Zoom Meeting 10:00 AM

*Members Present:* Robin Dodson (Chair), Christine Rioux (Vice Chair), Heather Lynch, Lisa Cashins, Christy Foran, Wendy Heiger-Bernays, Rich Gurney, Helen Poynton, Denise Kmetzo, Ryan Bouldin

# Members not present: Alicia Timme-Laragy

**Program staff present:** Liz Harriman (TURI), Heather Tenney (TURI), Karen Thomas (TURI), Hayley Hudson (TURI), John Raschko (OTA), Nicole Moody (MassDEP), Kari Sasportas (OTA), Caredwen Foley (OTA), Sandra Baird (MassDEP)

**Others present:** Katherine Robertson (MCTA), Owen Jappen (ACC), Allie McGerigle (Serlin Haley LLP), Carrie Brown, Tom Hmiel (Teknor Apex), Erin DeSantis (ACC), Elizabeth Healy (Serlin Haley LLP)

# Welcome & Introductions

The chair noted that this meeting is being conducted remotely, consistent with *An Act Relative to Extending Certain State of Emergency Accommodations* signed by Governor Baker on June 16<sup>th</sup>, 2022. This allows the extension of the remote meetings under the Open Meeting Law until March 31, 2025. Board members and program staff were introduced, and visitors were asked to put their name and affiliation in the chat.

### Approve November Meeting Minutes

A motion was made to approve the November meeting minutes, and there was a second. A roll call vote was conducted, and the minutes were unanimously approved by the eight members present.

# Flame Retardant Law

TURI presented information on the MA Flame Retardant Law, beginning with an overview of the law and highlighting the key differences between this law and TURA. The biggest differences are that the MA Flame Retardant Law is a ban of the 11 named chemicals and their chemical analogues, and it pertains to certain products.

Per the MA Flame Retardant Law, MassDEP is to consult with TURI and the SAB. The first questions that DEP has asked for advice on pertain to CAS numbers, isomers, and analogues of the 11 named chemicals, including similarities in toxic hazard between the named chemicals and their chemical analogues. The board reviewed the summary statements on several sub-classes from the September and November meetings. This meeting agenda covered two subclasses: polyhalogenated bisphenol aliphatics (TBBPA) and polyhalogenated phthalates (TBPH).

# Polyhalogenated Bisphenol Aliphatics

The base structure of the Bisphenols is Bisphenol A (BPA), and the chemical named in the FR law is TBBPA, which is the result of adding four bromines to BPA. TURI identified four closely related structural analogues believed to be used in products covered under the law.

TURI reviewed the structures and why they were chosen to be included as analogues. Analogues 1,3, and 4 are "derivatives" or precursors of TBBPA and can degrade into BPA. TURI provided an EHS summary for TBBPA and the analogues focusing on endpoints of highest concern which include: Persistence, Bioaccumulation, and Toxicity (PBT) properties, and endocrine, developmental and reproductive toxicity.

The board was reminded that they had already concluded that these substances were analogues of TBBPA by examining their structures. At this meeting the question they were asked to advise DEP on: *Is each proposed Polyhalogenated Bisphenol Aliphatic analogue (specifically, the analogues on the screen and listed in* Updated Proposed FR CAS Numbers, isomers, and Analogues for SAB *) sufficiently similar to the included FR (TBBPA) that it would be reasonably anticipated to have similar concerns re toxic hazard, persistence, or bioaccumulation?* 

A board member stated that the data are very compelling for developmental and neurotoxicity endpoints. All analogues degrade to BPA and good aquatic toxicity data exists. The outstanding question is whether there is sufficient information to include analogue #4. The precursors are the same and the data we have for the others suggest that persistence would be similar.

Aquatic toxicity is a factor as three of the analogues break down to TBBPA, which has very high aquatic toxicity. Members expressed their support for considering the analogues similar to TBBPA as they will break down to TBBPA.

### Visitor Comments/Questions

There was an opportunity for visitor comments and there were none.

### Summary Statement

A board member provided a summary statement to start with and the board discussed it thoroughly. They came up with the following bullet points:

- Given the structural homology of "analogue 1, 3 & 4" with TBBPA, and the fact they are
  precursors to TBBPA via environmental degradation and metabolism, and therefore are likely to
  exert similar effects as TBBPA including, endocrine, developmental, reproductive effects, and
  environmental persistence. There is evidence of aquatic toxicity for these analogues in multiple
  test systems.
- While there is a paucity of data for "Analogue #4", the structural homology and the small difference introduction of a methyl group preserves the physical and chemical properties of the original structure and therefore can reasonably be included in this group of similar substances.
- Analogues that have TBBPA as a metabolite are justified to be included in the law.

- Analogue #2 is also structurally homologous and has compelling evidence in multiple species for reproductive toxicity, developmental toxicity, and endocrine disruption.
- Carbon chlorine bonds are more easily broken in the environment (to form BPA). While all four analogues (and TBBPA) have the potential to break down to BPA, analogue #2 may be the most likely to.

### Polyhalogenated Phthalates

TURI reviewed the analogues for subclass #4. The base of TBPH is DEHP. TURI reviewed the different structures and similarities between subclass #4 (polyhalogenated phthalates) and subclass #5 (polyhalogenated bisphenol aliphatics).

The question the board was asked to advise DEP on was : *Is each proposed polyhalogenated Phthalate analogue (specifically, analogues on screen and listed in* Updated Proposed FR CAS Numbers, isomers, and Analogues for SAB*) sufficiently similar to the included FRs (TBPH) that it would be reasonably anticipated to have similar concerns re toxic hazard, persistence, bioaccumulation?* 

A board member asked a few questions about the differences in the log Kow and BCF and how the log Kow can be so different. It was noted that those values are predicted rather than measured. There was discussion around the modeled data and predicted values.

A board member discussed the structure of analogues and how they will break down in a fire. All the analogues will hydrolyze the same way and break down to phthalic acid. Also, the stomach's pH will allow this to happen in the human body. This is supported by the growing evidence of biomonitoring data that concludes they are getting into our bodies. Additionally, analogue #4 might have some acute ecotoxicity.

A board member stated they would like to know more about analogue #4, and whether it is included in the biomonitoring data.

There was discussion around the structure and the predicted effects we would expect to see. It was noted that the REACH decision of vPvB was that based on the fact they are finding TBPH and isomers everywhere and they are persistent.

A board member asked if the persistence designation is based on the half-life in soil. There is indication in reports that it is persistent, but a lack of studies that support that. However, they all share a common metabolite, tetrabromophthalic acid, and it is persistent.

### Visitor Comments/Questions

There was an opportunity for visitor comments and there were none.

### Draft Summary Statement

Given the structural homology of "analogue 1, 2, 3 & 4" with TBPH, and that TBPH has a common metabolite of "analog 1, 2, 3 & 4" and the data predicted thus far for the endocrine disruption,

developmental, reproductive, aquatic toxicity of "analogue 1, 2, 3 & 4"; these structures are and in fact analogs of TBPH in their "free form".

Polymerized applications on reacted versions of analogue 4 will likely have much slower rates of degradation due to lower bioavailability and higher steric and hydrophobicity in polymeric form.

While conclusions are based upon chemical structure, as toxicity data on analogues are lacking. The paucity of data for individual analogues 1, 2, 3 & 4 is not a concern as the structural homology is compelling and the change in each structure does not substantially change the degradation processes of these analogs into the common metabolites of TBPH.

It may be particularly important to note that at the high temperatures, high pH, and highly aqueous environments occurring during use as in extinguishing fires the rate of conversion of "analog 1, 2, 3 & 4" into tetrabromophthalic acid is in fact highly accelerated, and tetrabromophthalic acid is persistent.

Further, carboxylesterases are widely distributed in the environment and catalyze the ester bond cleavage in various conditions. Carboxylesterases are often the first line of defense to metabolize drugs, xenobiotics, pesticides, insecticides, and ester-based plastics.

The draft summary statement will be put in the minutes, and we can devote a small amount of time at our next meeting reviewing and finalizing the statement.

#### Next Meeting

Heather will put out a When2Meet for the last couple weeks of February.

There was a motion to adjourn and there was a second.

#### Handouts:

November Meeting Minutes Updated Proposed FR CAS Numbers, isomers, and Analogues for SAB FR Questions and Definitions Brominated Phthalates EHS Summary Cheminformatics Data for Phthalates Physical and Bioactivity for Phthalates Bisphenols EHS Summary Cheminformatics Data for Bisphenols Physical and Bioactivity for Bisphenols Summary of Literature on TBBPA and Analogues ACC-NAFRA Comments MA TURA SAB

### Visitor Comment (inserted with [one edit] from Chat)

Owen Jappen 10:05 AM Owen Jappen, American Chemistry Council Allie McGerigle to Everyone 10:05 AM Allie McGerigle, Serlin Haley LLP

Katherine to Everyone 10:05 AM Katherine Robertson, MCTA

John Raschko to Everyone 10:06 AM John Raschko, Mass. Office of Technical Assistance

Denise Kmetzo, DABT to Everyone 10:12 AM Denise Kmetzo, Collaborative Risk Solutions

#### Rich Gurney (Simmons U) to Everyone 10:39 AM

Given the structural homology of "analog 1, 2, 3 & 4" with TBBPA, that TBBPA is a metabolite of "analog 1, 3 & 4" and the data collected thus far for the endocrine disruption, developmental, reproductive, aquatic toxicology "analog 1, 3 & 4" I argue that these structures are regrettable substitutions and in fact analogs of TBBPA. The paucity of data for Analog #4 does not trouble me at all or persuade me to not include it in this grouping as the structural homology is compelling and the small change - introduction of a methyl group - is perhaps the most minor structural change that can be made while keeping the physical and chemical properties the same as the original structure.

#### Heather Lynch to Everyone 10:51 AM

I think we could take Rich's statement and re-jigger, and then add what you have on aquatic toxicity. How about "Given the structural homology of "analogue 1, 2, 3 & 4" with TBBPA; that TBBPA is a metabolite [IN human bodies and the environment???] of "analogue 1, 3 & 4"; and the data collected thus far for the endocrine, developmental, reproductive effects, "analogue 1, 3 & 4" are likely to exert similar effects. While there is a paucity of data for "Analogue #4", the structural homology and the small difference - introduction of a methyl group - preserves the physical and chemical properties of the original structure and therefore can reasonably be included in this group of similar substances. Additionally, .... evidence of aquatic toxicity in multiple test systems blah blah...."

Elizabeth Healy to Everyone 11:04 AM Hi all. This is Liz Healy from Serlin Haley LLP

#### Rich Gurney (Simmons U) to Everyone 11:46 AM

Given the structural homology of "analog 1, 2, 3 & 4" with TBPH, that TBPH is a metabolite of and precursor for "analog 1, 2, 3 & 4" and the data collected thus far for the endocrine disruption, developmental, reproductive, aquatic toxicity of "analog 1, 2, 3 & 4"; these structures are and in fact analogs of TBPH. The paucity of data for individual analogues 1, 2, 3 & 4 is not a concern or persuade "us" to not include all four in this grouping as the structural homology is compelling and the change in each structure does not substantially change the degradation processes of these analogs into TBPH. It may be particularly important to note that at the high temperatures, high pH, and highly aqueous environments occurring during use as in extinguishing fires the rate of conversion of "analog 1, 2, 3 & 4" into [edit: replaced TBPH with tetrabromophthalic acid] is in fact highly accelerated.

Further, carboxylesterases are widely distributed in the environment and catalyze the ester bond cleavage in a variety of conditions. Carboxylesterases are often the first line of defense to metabolize drugs, xenobiotics, pesticides, insecticides and ester-based plastics.

Heather Lynch to Everyone 12:13 PM

Ryan - to the extent it is helpful, I found some decent data on the tetrabromophthalic anhydride, it seems less toxic than TBPH....

https://ntp.niehs.nih.gov/sites/default/files/ntp/htdocs/chem\_background/exsumpdf/tetrabromophtha lic\_508.pdf

Ryan Bouldin (he/him) - Bentley University to Everyone 12:16 PM

From the report that Heather posted: "Tetrabromophthalic anhydride is expected to be persistent in soils. Its bioaccumulation potential, however, in aquatic environments is low."

Heather Lynch to Everyone 12:20 PM

https://www.epa.gov/sites/default/files/2015-

09/documents/bpc\_data\_needs\_assessment\_technical\_supplement\_p\_chem\_and\_fate\_assessment.pdf "There are no experimental data for 3,4,5,6-tetrabromo-1,2-benzenedicarboxylic acid, mixed esters with diethylene glycol and propylene glycol (CASRNs 77098-07-8 and 20566-35-2), but based on chemical structure and estimated BCF and BAF (Table 1-3), bioaccumulation potential is considered low (B1) for the parent substance. Bioaccumulation potential is also judged to be low for all potential hydrolysis products."

Liz Harriman to Everyone 12:31 PM https://pubs.acs.org/doi/full/10.1021/es034746j

Karen\_Thomas1 to Everyone 12:34 PM https://echa.europa.eu/documents/10162/170b9b2f-a1d0-9661-d36d-faf0846f6763

Ryan Bouldin (he/him) - Bentley University to Everyone 12:44 PM One study is available for tetrabromophthalic anhydride (CASRN 632-79-1), which would be quickly hydrolyzed to tetrabromophthalic acid (CASRN 13810-83-8) in the environment, and it showed no degradation in 28 days (Butz, 1979)

John Raschko to Everyone 1:00 PM Should the common metabolite(s) be mentioned in the first paragraph?

Sandra Baird (MassDEP) 1:01 PM Thank you all for your work!!