

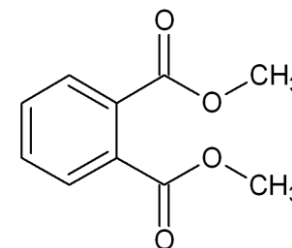
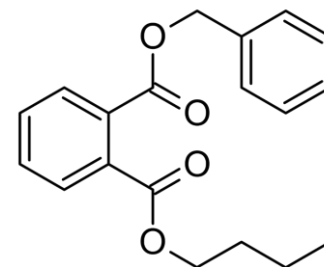
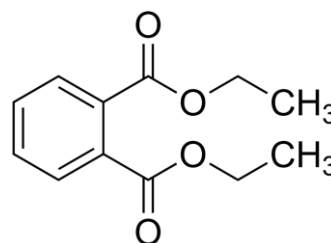
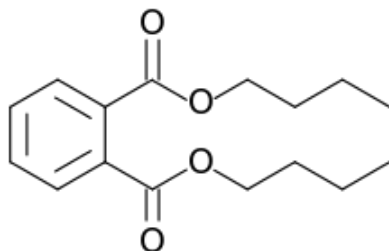
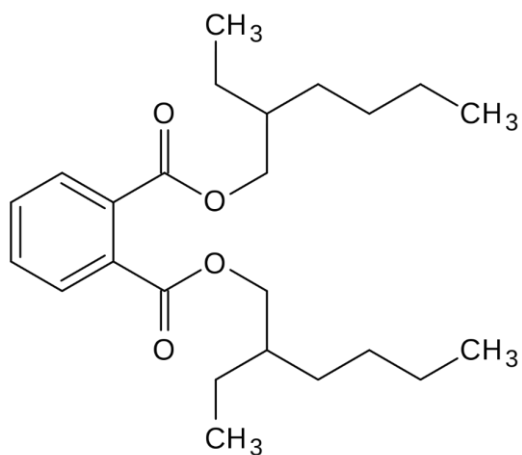
Northwest Green Chemistry (NGC) Report on Alternatives to Five Phthalates of Concern to Puget Sound



Northwest
Green Chemistry

Amelia Nestler,
Ph.D.

Lauren Heine, Ph.D.

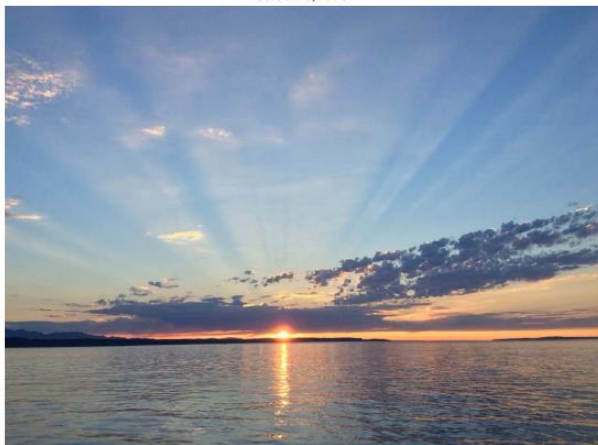


Enhancing human and
environmental health and
fostering business innovation
with sustainable and green
chemistry and engineering

*Northwest Green Chemistry is a project of
Social and Environmental Entrepreneurs
(SEE), a non-profit public charity exempt
from federal income tax under Section
501(c)3 of the Internal Revenue Code.*

Alternatives to Five Phthalates of Concern to Puget Sound

FINAL REPORT
October 8, 2018

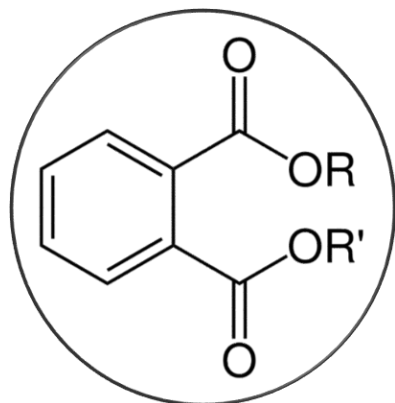


This project has been funded wholly or in part by the U.S. Environmental Protection Agency under a National Estuary Program (NEP) cooperative agreement with the Washington State Department of Ecology.



Download from our website: <http://bit.ly/NGCPhth>

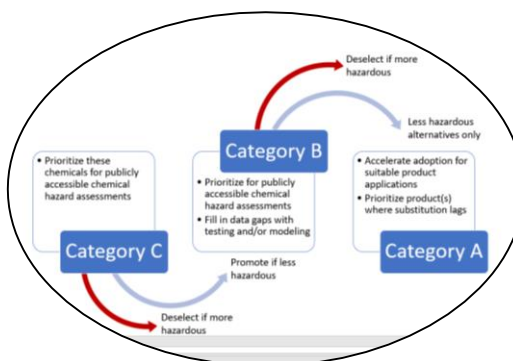
Or go to www.northwestgreenchemistry.org and go to the “Resources” heading, then “Publications”.



Phthalates: Chemicals of concern

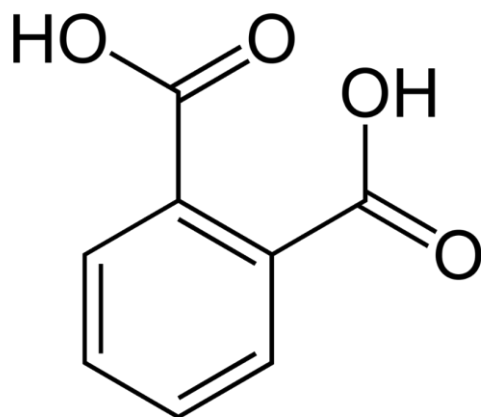


Alternatives to phthalates
as plasticizers / fast fusers

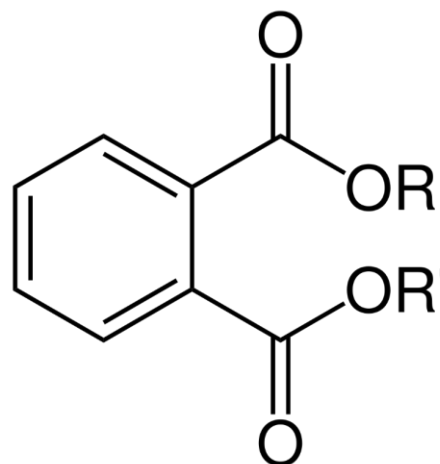


Next steps and
implementation

Introduction to phthalates

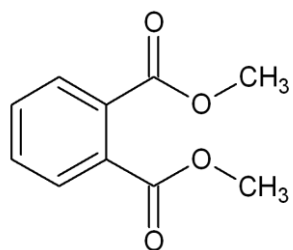


Phthalic Acid



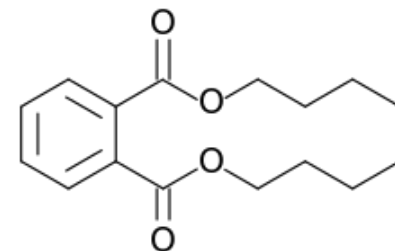
Phthalates

The Five Phthalates of Interest



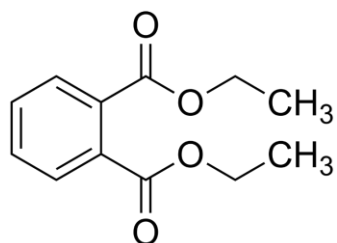
DMP

Dimethyl phthalate



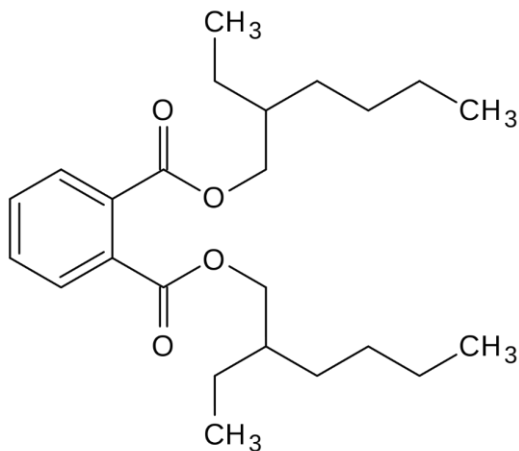
DBP

Dibutyl phthalate



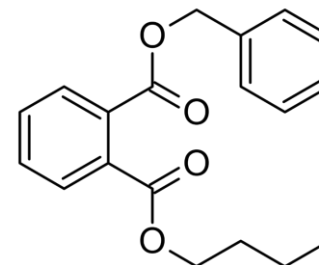
DEP

Diethyl phthalate



DEHP

Bis(2-ethylhexyl) phthalate



BBP

Butylbenzyl phthalate

Hazards of the five phthalates

(List Translator only)

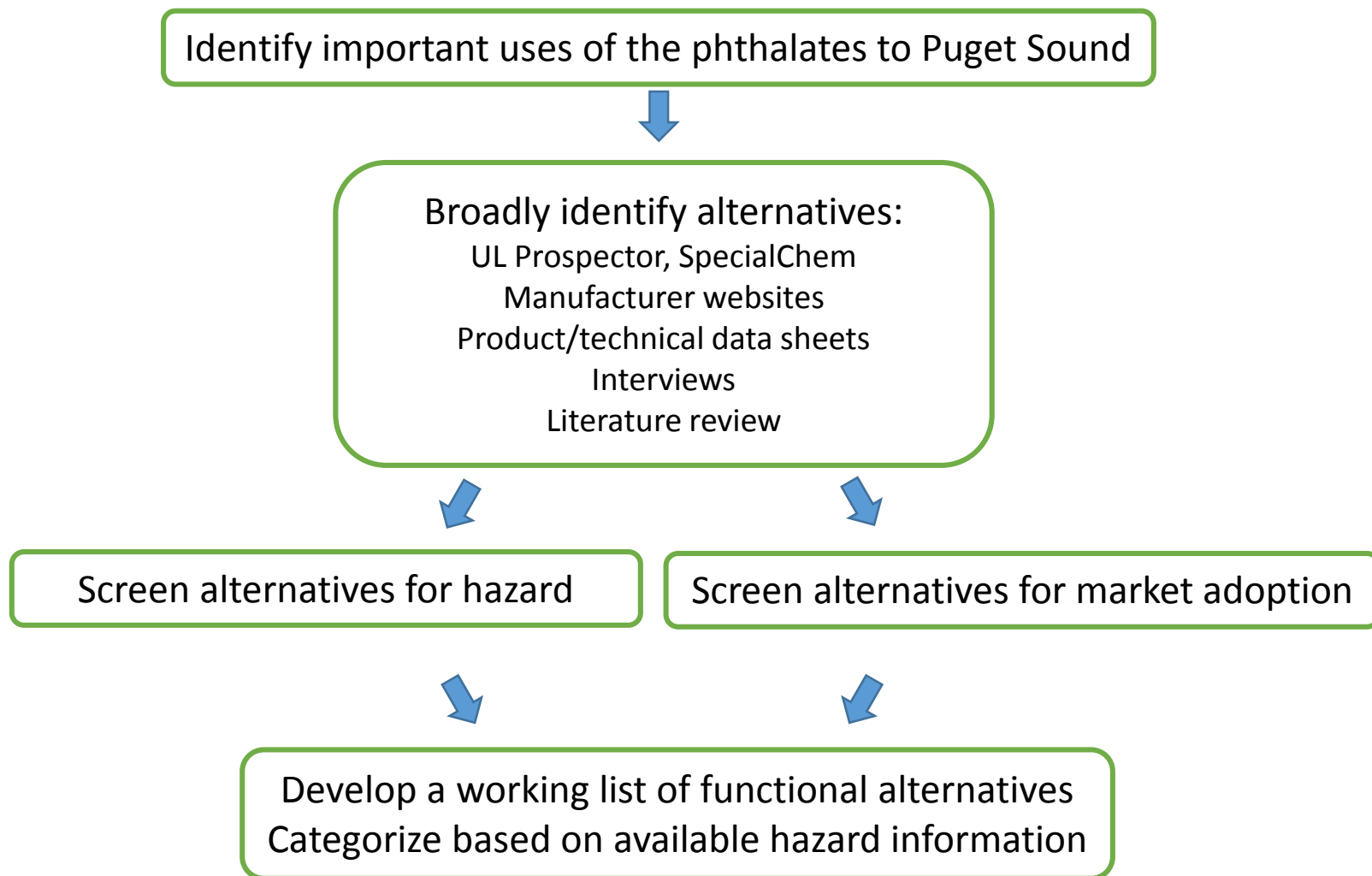
CAS #	Chemical Name	Score	Carcinogenicity	Mutagenicity	Reproductive	Developmental	Endocrine	Acute	Systemic	Systemic Repeat	Neurotoxicity	Neurotoxicity, Repeat	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic	Chronic Aquatic	Persistence	Bioaccumulation	Reactivity	Flammability
84-66-2	DEP (Diethyl phthalate)	GS LT P1	H-L				H-M	M	M				H		H	M	H		vH-H			
131-11-3	DMP (Dimethyl phthalate)	GS LT P1	H-L				H-M	H	M							H	H-M		vH-H			
117-81-7	DEHP (Bis (2-ethylhexyl) phthalate)	GS LT 1	H		H	H	H		H	M		vH-L				M	vH					
84-74-2	DBP (Di-n-butyl phthalate)	GS LT 1	M		H	H	H	L	M	H		vH-M	H			H	vH					
85-68-7	BBP (Butylbenzyl phthalate)	GS LT 1	M		H-M	H	H	L	M	M					M	M	vH	M		vH		

BM 1	Avoid - chemical of high concern
BM 2	Use, search for safer substitutes
BM 3	Use, opportunity for improvement
BM 4	Safer Chemical
BM U	Unknown

GS LT 1	Likely BM 1
GS LT P1	Some uncertainty, potential BM 1
GS LT UNK	Insufficient information from lists

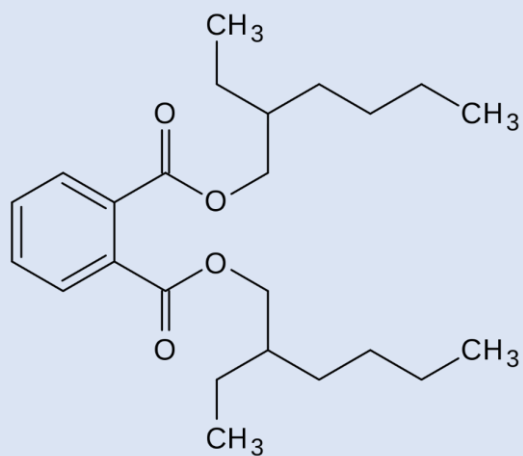
vL	very Low
L	Low
M	Moderate
H	High
vH	very High
DG	Data gap
	Not listed on relevant lists

Our approach to identify inherently less hazardous, functional alternatives to the five phthalates



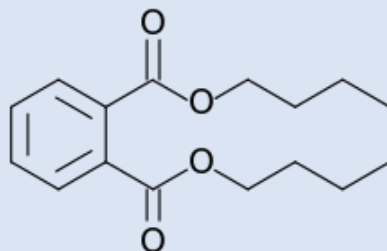
Alternatives for Plasticizers and Fast Fusers

Plasticizers and fast fusers



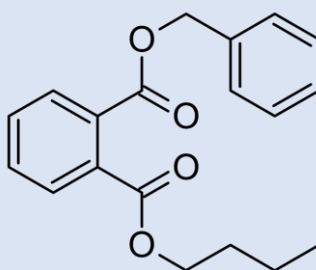
DEHP

Bis(2-ethylhexyl) phthalate



DBP

Dibutyl phthalate



BBP

Butylbenzyl phthalate

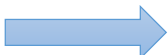



Full list of potential alternative plasticizers/fast fusers



- Dipropylene glycol dibenzoate (CAS# 27138-31-4)
- Triacetin (CAS# 102-76-1)
- Acetylated monoglycerides derived from fully hydrogenated castor oil (CAS# 736150-63-3, COMGHA)
- Bis (2-ethylhexyl) terephthalate (CAS# 6422-86-2, DEHT)
- Diisononyl cyclohexanedicarboxylate (CAS# 166412-78-8 and 474919-59-0, DINCH)
- Dibutylterephthalate (CAS# 1962-75-0, DBT)
- Tris (2-ethylhexyl) trimellitate (CAS# 3319-31-1, TOTM)
- 2-ethylhexyl adipate (CAS# 103-23-1, DEHA)
- Acetyl tributyl citrate (CAS# 77-90-7, ATBC)
- Diisononyl adipate (CAS# 33703-08-1, DINA)
- Epoxidized soybean oil (CAS# 8013-07-8, ESBO)
- Pentaerythritol tetravalerate (CAS# 15834-04-5)
- Alkylsulfonic phenyl ester (CAS# 91082-17-6, ASE)
- Methyl esters of epoxidized soybean oil fatty acids (CAS# 68082-35-9)
- Diethylene glycol dibenzoate (CAS# 120-55-8)
- Di (2-propylheptyl) phthalate (CAS# 53306-54-0, DPHP)
- Dioctyl Phthalate (CAS# 117-84-0, DNOP)
- diundecyl phthalate (CAS# 3648-20-2, DUP)
- Di-2-ethylhexyl azelate (CAS# 103-24-2, DOZ)
- Di-butyl adipate (CAS# 105-99-7, DBA)
- Di-butyl sebacate (CAS# 109-43-3, DBS)
- Triethylene glycol dibenzoate (CAS# 120-56-9)
- Isosorbide Diesters (CAS# 1215036-04-6)
- Butylated hydroxytoluene (CAS# 128-37-0, BHT)
- Dioctyl sebacate (CAS# 122-62-3, DOS)
- Acetyltri-n-hexyl citrate (CAS# 24817-92-3, ATHC)
- Di-isodecyl sebacate (CAS# 28473-19-0, DIDS)
- Di(2-ethylhexyl) phosphate (CAS# 298-07-7, DEHPA)
- Isodecyl benzoate (CAS# 131298-44-7)
- Isononyl Benzoate (CAS# 670241-72-2)
- Propylene glycol dibenzoate (CAS# 19224-26-1)
- Di(butoxyethoxyethoxyethyl) glutarate (CAS# 65520-42-5)
- Epoxidized soybean fatty acid (CAS# 68082-34-8)
- 2,2,4-trimethyl-1,3 pentanediol diisobutyrate (CAS# 6846-50-0, TPIB, TXIB)
- 1,2,4-Benzenetricarboxylic acid, tri-C7-9-branched and linear alkyl esters (CAS# 68515-60-6)
- Epoxidized propylene glycol dioleate (CAS# 68609-92-7)
- Tributyl Trimellitate (CAS# 1726-23-4)
- Acetyl triethyl citrate (CAS# 77-89-4)
- Tributyl Citrate (CAS# 77-94-1)
- Tri(2-ethylhexyl) phosphate (CAS# 78-42-2, TEHPA)
- Epoxidized linseed oil (CAS# 8016-11-3)
- n-Butyryltri-n-hexyl Citrate (CAS# 82469-79-2)
- o-toluene sulfonamide (CAS# 88-19-7, OTSA)
- Trioctyl trimellitate (CAS# 89-04-3)
- 1,2,4-Benzenetricarboxylic acid, mixed decyl and hexyl and octyl esters (CAS# 68130-50-7)
- Hexanedioic acid, polymer with 2,2-dimethyl-1,3-propanediol and 1,2-propanediol, isononyl ester (CAS# 208945-13-5)
- Adipic acid and polyhydric alcohols (CAS# 208945-12-4)
- Naphthenic Hydrocarbon (CAS# 64742-53-6)
- Diisononyl phthalate (CAS# 68515-48-0, DINP-1; CAS# 28553-12-0, DINP-2 and DINP-3)
- Diisodecyl phthalate (CAS# 26761-40-0, DIDP)
- Diisobutyl Phthalate (CAS# 84-69-5, DIBP)
- Diisoheptyl phthalate (CAS# 71888-89-6, DIHP)
- Diisodecyl phthalate (CAS# 68515-49-1, DIDP)
- Tricresyl Phosphate or Tritolyl Phosphate (CAS# 1330-78-5, TCP)

Screening criteria for plasticizers/fast fusers as alternatives to phthalates

Hazard criteria

- Inclusion 
 - Included on the US EPA Safer Chemical's Ingredients List
 - Listed on CleanGredients
- Exclusion 
 - No GS Benchmark 1 or LT-1
 - No CMR(DE)s, no PBT combos

Market adoption /performance

- Inclusion 
 - Used to replace DEHP, BBP, DBP
 - Broad market adoption
 - Limited but promising market adoption
 - Commonly used in Europe
- Exclusion 
 - Limited or poor functionality
 - No reasonably price competitive

Alternatives that pass screening are sorted into categories based on hazard data

Category A

- Publicly available chemical hazard assessment that achieves GS BM 2 or better
- Eliminates carcinogens, mutagens, repro/dev toxicants, endocrine disrupters, and chemicals with combined persistence and bioaccumulation and/or aquatic toxicity
- Relatively lower hazard than the five phthalates of interest
- Viable with respect to performance

Category B

- Chemical hazard assessment reviewed by third party, and listed on positive list, but no publicly available assessment:
 - Listed on US EPA SCIL with a full or half green circle or yellow triangle
 - Listed on CleanGredients
- Viable with respect to performance

Category C

- Lacks comprehensive chemical hazard assessment report, or publicly available report includes key data gaps (GS BM U)
- Not listed on regulatory or hazard lists of concern
- Viable with respect to performance

BM 1	Avoid - chemical of high concern
BM 2	Use, search for safer substitutes
BM 3	Use, opportunity for improvement
BM 4	Safer Chemical
BM U	Unknown

Working List

Common name	Abbreviation	CHA Score	Carcinogenicity	Mutagenicity	Reproductive	Developmental	Endocrine	Acute	Systemic	Systemic Repeat	Neurotoxicity	Neurotoxicity, Repeat	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic	Chronic Aquatic	Persistence	Bioaccumulation	Reactivity	Flammability	US EPA SCIL	NGC List
Bis (2-ethylhexyl) phthalate	DEHP, DOP	GS LT 1	H		H	H	H					vH-L		M		M	vH	H	pC	pC			-	CoC
Di-n-butyl phthalate	DBP	GS LT 1	M		H	H	H	L				vH-M	H	M		H	vH	H	pC	pC			-	CoC
Butylbenzyl phthalate	BBP	GS LT 1	M		H-M	H	H	L						M	M		vH	H	pC	vH			-	CoC
Bis (2-ethylhexyl) terephthalate	DEHT, DOTP	GS BM 3dg	L	L	L	L	DG	L	L	L	L	DG	L	L	L	L	L	L	vL	L	L	L	-	A
Diisononyl cyclohexanedicarboxylate	DINCH, D9CH	GS BM 2	L	L	L	L	M	L	L	L	L	L	L	L	M	L	L	L	M	L	L	L	-	A
Triacetin	-	GS LT UNK						M																B
Dipropylene glycol dibenzoate	-	GS LTP1														pC								B
Acetylated monoglycerides derived from fully hydrogenated castor oil	COMGHA	GS LT NoGS																						B
Dibutylterephthalate	DBT	GS LT NoGS												M			pC						-	C
Tris (2-ethylhexyl) trimellitate	TOTM, TEHTM	GS BM U	DG	L	M	L	DG	L	M	L	L	DG	L	DG	L	L	L	L	M	vL	L	L	-	C
2-ethylhexyl adipate	DEHA	GS LTP1	M	pC	M		H-M								M	pC	pC		pC	pC			-	C
Acetyl tributyl citrate	ATBC	GS LTP1															pC						-	C
Diisononyl adipate	DINA	GS LT UNK																					-	C
Epoxidized soybean oil	ESBO	GS LT UNK													M								-	C
Pentaerythritol tetravalerate	-	GS LT UNK															pC						-	C
Alkylsulfonic phenyl ester	ASE	GS LT UNK																					-	C
Methyl esters of epoxidized soybean oil fatty acids	-	GS LT UNK																		vH			-	C
Diethylene glycol dibenzoate	DEGD	GS LTP1						L															-	C
Di (2-propylheptyl) phthalate	DPHP	Expired GS BM	DG	L	L	L	M	L	DG	L	DG	DG	L	DG	L	L	L	L	L	vL	L	L	-	C

Working List: Alternatives for Plasticizers/Fast Fusers

A

Diisononyl cyclohexanedicarboxylate
(DINCH, D9NCH)

Bis (2-ethylhexyl) terephthalate (DEHT,
DOTP)

B

Triacetin (GTA)

Acetylated monoglycerides derived from
fully hydrogenated castor oil (COMGHA)

Dipropylene glycol dibenzoate

Epoxidized soybean oil (ESBO)

Acetyl tributyl citrate (ATBC)

Diisononyl adipate (DINA)

2-ethylhexyl adipate (DEHA, DOA)

Pentaerythritol tetravalerate

Dibutylterephthalate (DBT)

Methyl esters of epoxidized soybean oil fatty
acids

Alkylsulfonic phenyl ester (ASE)


Di(2-propylheptyl) phthalate (DPHP)

Tris (2-ethylhexyl) trimellitate (TOTM, TEHTM)

Diethylene glycol dibenzoate (DEGD)

C

Interpreting a hazard table

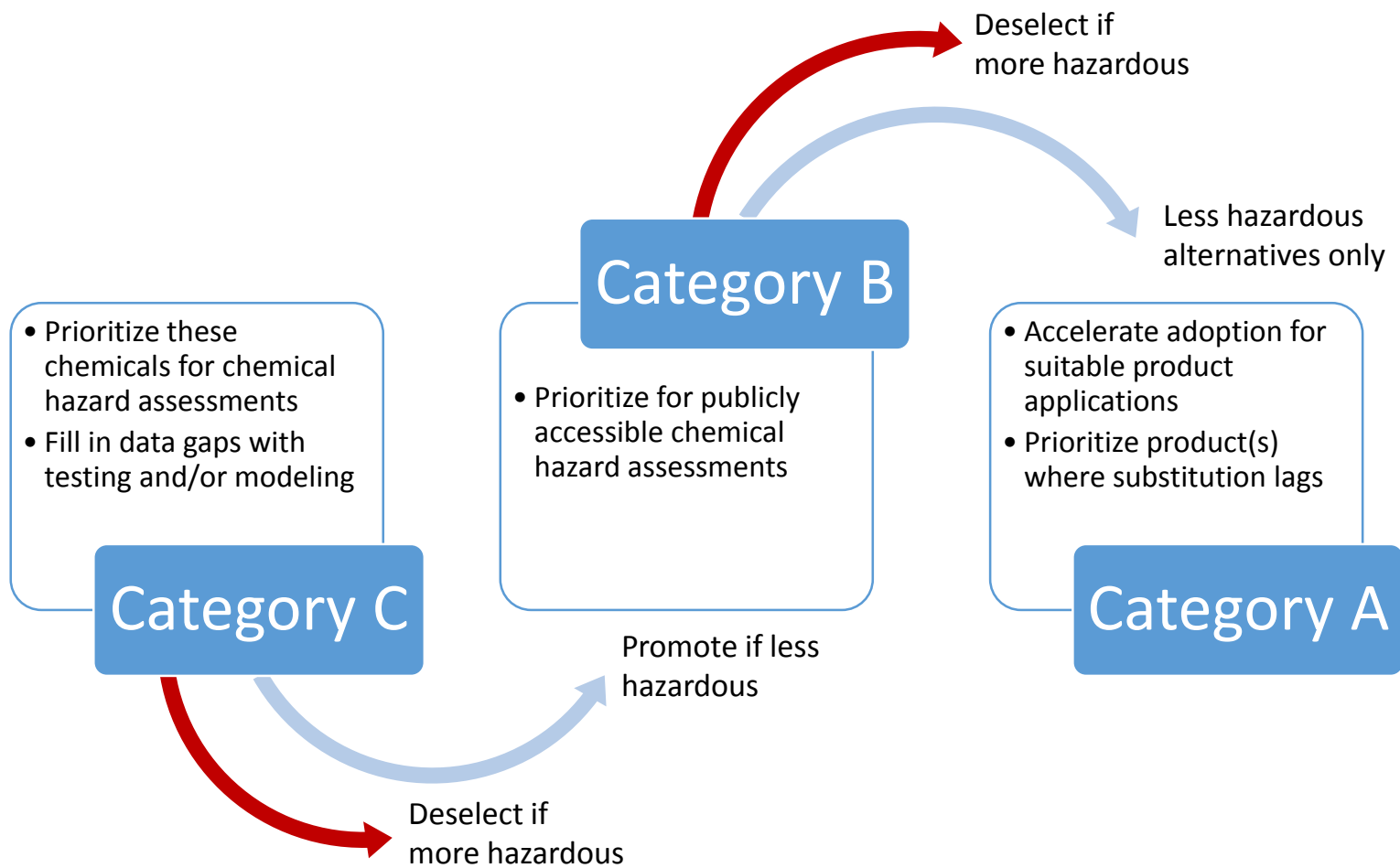
Abbreviation	CHA Score	Carcinogenicity	Mutagenicity	Reproductive	Developmental	Endocrine	US EPA SCIL	NGC List
DEHP, DOP	GS LT 1	H		H	H	H	-	CoC
DEHT, DOTP	GS BM 3dg	L	L	L	L	DG	-	A
DINCH, D9CH	GS BM 2	L	L	L	L	M	-	A
Triacetin	GS LT UNK							B
DBT	GS LT NoGS						-	C
TOTM, TEHTM	GS BM U	DG	L	M	L	DG	-	C

BM 1	Avoid - chemical of high concern
BM 2	Use, search for safer substitutes
BM 3	Use, opportunity for improvement
BM 4	Safer Chemical
BM U	Unknown
BM Ndg	Data gaps prevent better score

GS LT 1	Likely BM 1
GS LT P1	Some uncertainty, potential BM 1
GS LT UNK	Insufficient information from lists

vL	very Low
L	Low
M	Moderate
H	High
vH	very High
DG	Data gap
	Not listed on relevant lists

Categorizing the working list



Substitution is hard



Left, madame.furie, https://www.flickr.com/photos/madame_furie/2505664126

Right, Pattie, <https://www.flickr.com/photos/piratealice/4009205963z>

Recommended future work

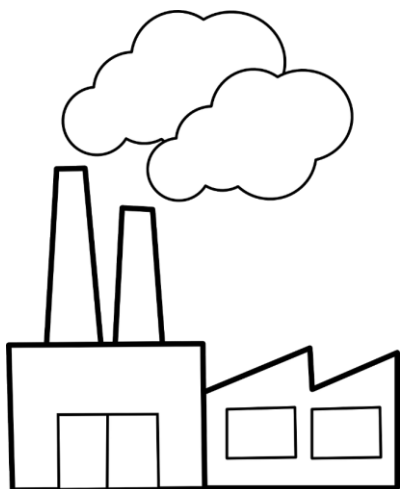
- Accelerate adoption of Category A alternatives
- Public hazard assessments for Category B alternatives
- Hazard assessment of Category C alternatives and fill in data gaps
- Prioritize key applications
 - High exposure products to sensitive populations and environments like Puget Sound
 - Applications that are not addressed by the alternatives cited here



- DEHP protects red blood cell viability
- Alternatives like DINCH and DEHT required additives
- Additives should be screened for hazard to ensure these are truly safer alternatives

Additional strategy for eliminating DEHP

- Switch to an alternative material that doesn't require plasticizers
 - PVC polymer may be inert, but PVC polymer production is concerning
 - Other plastics, wood, metal, and ceramics may be alternatives for some applications

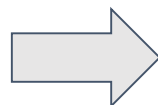
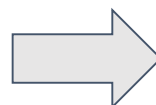


Material Wise: Taking the next step



Challenge

- Comprehensive chemical hazard assessments are expensive, duplicative and protected on private systems
- Chemical profiles are not peer reviewed or independently validated; different assessors come up with different results
- Identifying which chemicals to avoid does not help with identifying safer, functional alternatives




Solution

- Shared repository of CHAs; can be commissioned as a consortium, and purchased at reduced cost
- Expert verification of assessments; harmonization of results; and a program to allow for technical challenges
- Hazard assessments of safer alternatives organized and grouped in functional portfolios (i.e. plasticizers, durable water repellents, etc.)

MaterialWise: Alternatives to ortho-phthalate plasticizers initial priorities for pilot

CAS RN	Chemical Name	Abbreviation	Category
131-11-3	Dimethyl phthalate	DMP	CoC
77-90-7	Acetyl tributyl citrate	ATBC	C
6422-86-2	Bis(2-ethylhexyl) terephthalate	DEHT, DOTP	A
166412-78-8, 47919-59-0	Diisononyl cyclohexane-1,2-dicarboxylate	DINCH	A
736150-63-3	Acetylated monoglycerides derived from fully hydrogenated castor oil	COMGHA	B
27138-31-4	Dipropylene glycol dibenzoate		B
8013-07-8	Epoxidized soybean oil	ESBO	C
15834-04-5	Pentaerythritol tetravalerate	Pevalen	C
6846-50-0	Trimethyl pentanyl diisobutyrate	TXIB	-
1962-75-0	Dibutylterephthalate	DBT	C

DMP: Potentially a safer plasticizer?



TCO CERTIFIED
ISSUES
PROCUREMENT
BRANDS & VERIFIERS

dmp
1/1

TCO Certified Accepted Substance List

Substance name	CAS	Type	Benchmark	Date of assessment	Profiler	Comment
2-Ethyl-1-Hexanol	104-76-7	PL	2	Aug, 2018	Toxservices	
Acetyl tri-butyl citrate (ATBC)	77-90-7	PL	3	Aug, 2018	Toxservices	
Aluminum diethylphosphinate	225789-38-8	FR	3	Oct, 2016	Toxservices	1
Aluminum Hydroxide	21645-51-2	FR	2	Feb, 2016	Rosenblum	
Ammonium Polyphosphate	68333-79-9	FR	3	Feb, 2016	Rosenblum	
Bis(2-ethylhexyl) Adipate (DEHA)	103-23-1	PL	2	Aug, 2018	Toxservices	
Bis(2-propylheptyl) phthalate (DPHP)	53306-54-0	PL	2	Apr, 2018	Gradient	
Bisphenol A diphosphate	181028-79-5; 5945-33-5	FR, PL	2	Feb, 2016	Toxservices	2
Di(2-ethylhexyl) Terephthalate (DEHT)	6422-86-2	PL	3	Aug, 2018	Toxservices	
Diisononyl Adipate (DINA)	33703-08-1	PL	2	Aug, 2018	Toxservices	
Diisononyl Cyclohexanedicarboxylate (DINCH)	166412-78-8; 474919-59-0	PL	2	Aug, 2018	Toxservices	2
Dimethyl phthalate (DMP)	131-11-3	PL	2	Aug, 2018	Toxservices	
Epoxidized soya bean oil (ESBO)	7/8/13	PL	3	Aug, 2018	Toxservices	
Magnesium Hydroxide	1309-42-8	FR	3	Feb, 2016	Rosenblum	
Melamine Polyphosphate	15541-60-3; 218768-84-4	FR	2	Feb, 2016	Rosenblum	2
Oxydipropyl Dibenzoate	27138-31-4	PL	2	Jan, 2019	Toxservices	

Resources for finding alternatives

Detailed hazard profiles included

- Category A of our report:
<http://bit.ly/NGCPhth>
- MaterialWise: <https://www.materialwise.org/>
 - Will still publish profiles of hazardous chemicals

Some hazard or sustainability criteria

- Category B of our report:
<http://bit.ly/NGCPhth>
- US EPA Safer Chemicals Ingredients List (SCIL):
<https://www.epa.gov/saferchoice/safer-ingredients>
 - CleanGredients:
<https://cleangredients.org/>
- TCO Certified Accepted Substances List:
<https://tcocertified.com/accepted-substance-list/>
- ChemSec Marketplace:
<https://marketplace.chemsec.org/>

No/minimal hazard criteria for listing

- Category C and supplemental file of our report:
<http://bit.ly/NGCPhth>
 - Full list of all potential alternatives identified in supplement
 - Category C included minimal hazard screening and some performance
- UL Prospector:
<https://www.ulprospector.com/en/na>
- SpecialChem: <https://www.specialchem.com>

Thank you!



**Northwest
Green Chemistry**

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Amelia Nestler, Ph.D. anestler@northwestgreenchemistry.org

Download the phthalate report: <http://bit.ly/NGCPhth>

Learn about Material Wise: <https://www.materialwise.org/>

