Plastic Monomers, Additives, and Processing Aids

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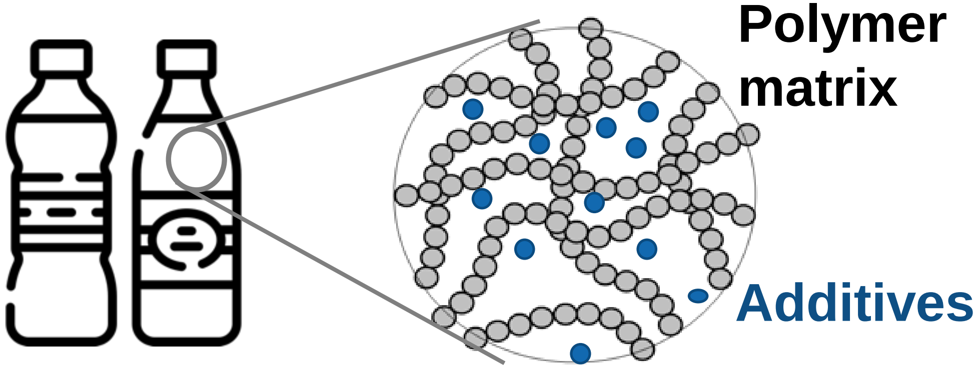
What are Plastics?

- Greek: *plastikos* = capable of being shaped or molded
- **Plastics vs. polymers**

→ Plastics are composed of **organic polymers** (macromolecules that are composed of many repeated sub-units – monomers) and **additives**

→ All plastics are polymers and are often named after the polymer matrix, but not all polymers are plastics.



Different Grouping Methods of Plastics

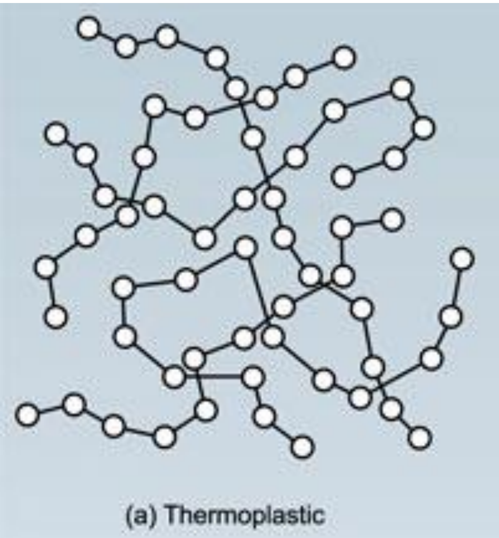
According to their **cost and performance**:

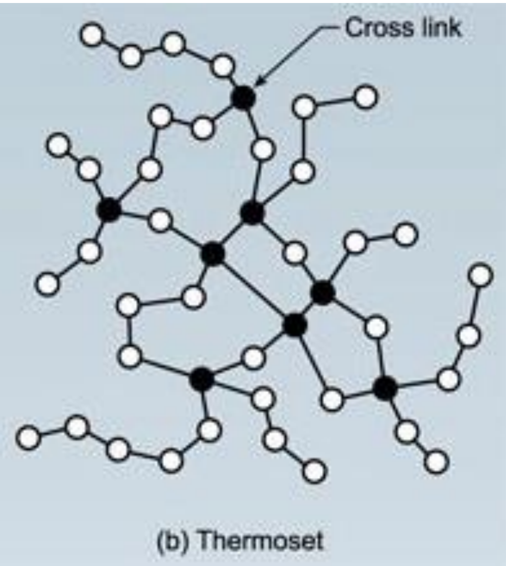
1. **Commodity plastics** (or standard/bulk plastics): produced in great amounts at low cost.
   e.g. PVC, HDPE, LDPE, LLDPE, VLDPE, PP, PS, EPS, PET

2. **Engineering plastics** (or technical plastics): plastics with improved mechanical properties and dimensional stability compared to commodity plastics.
   e.g. PP, PET, PBT, PA, PC, POM, PMMA, SAN, ABS, HIPS, PPO-PS, POM-PUR, PC-ABS, etc.

3. **High-performance plastics** (or specialty plastics): engineering plastics with even more improved mechanical properties.
   e.g. liquid cystal polymers (LCPs), polyetheretherketone (PEEK), fluoropolymers

Different Grouping Methods of Plastics

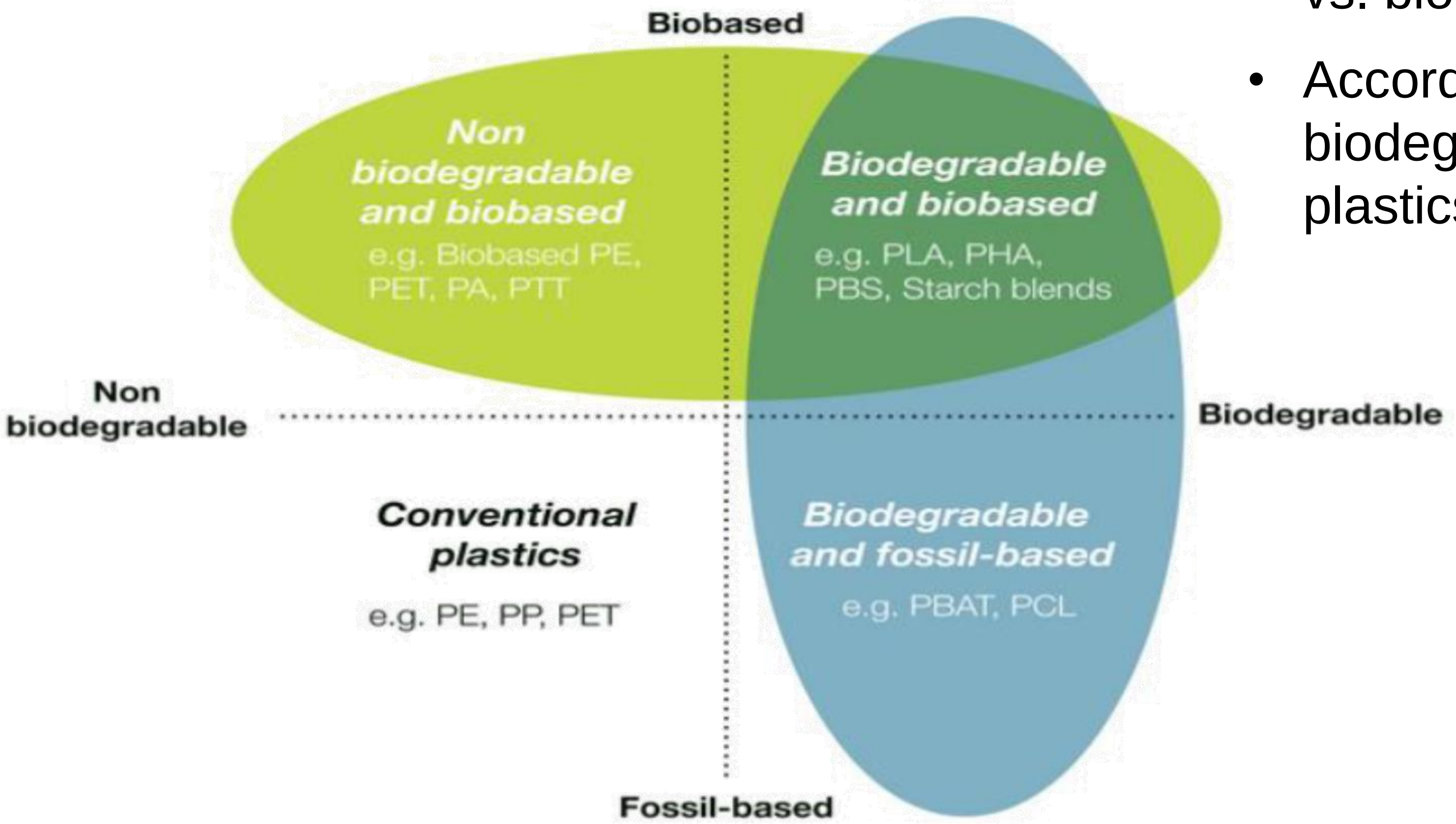




According to their **hardening processes**:

- **Thermoplastics:** harden through simple cooling of a polymer melt (a physical process) and soften while being heated.
  e.g., PE, PP, ABS, PVC, etc.
- **Thermosets:** harden through chemical cross-linking reactions between polymer molecules; when heated, they do not soften but decompose chemically.
  e.g., alkyd, phenolic, amino, epoxy, unsaturated polyesters, polyurethane, and allylic resins

Different Grouping Methods of Plastics



- According to the **origin of feedstock**: fossil- vs. bio-based plastic
- According to the **biodegradability**: biodegradable vs. non-biodegradable plastics

Plastics – Production overview

Global production (2021): 390 Mt/y

European use by sector [1]

[1] Plastics Europe (2022), Plastics – the facts 2022. https://plasticseurope.org/resources/market-data/

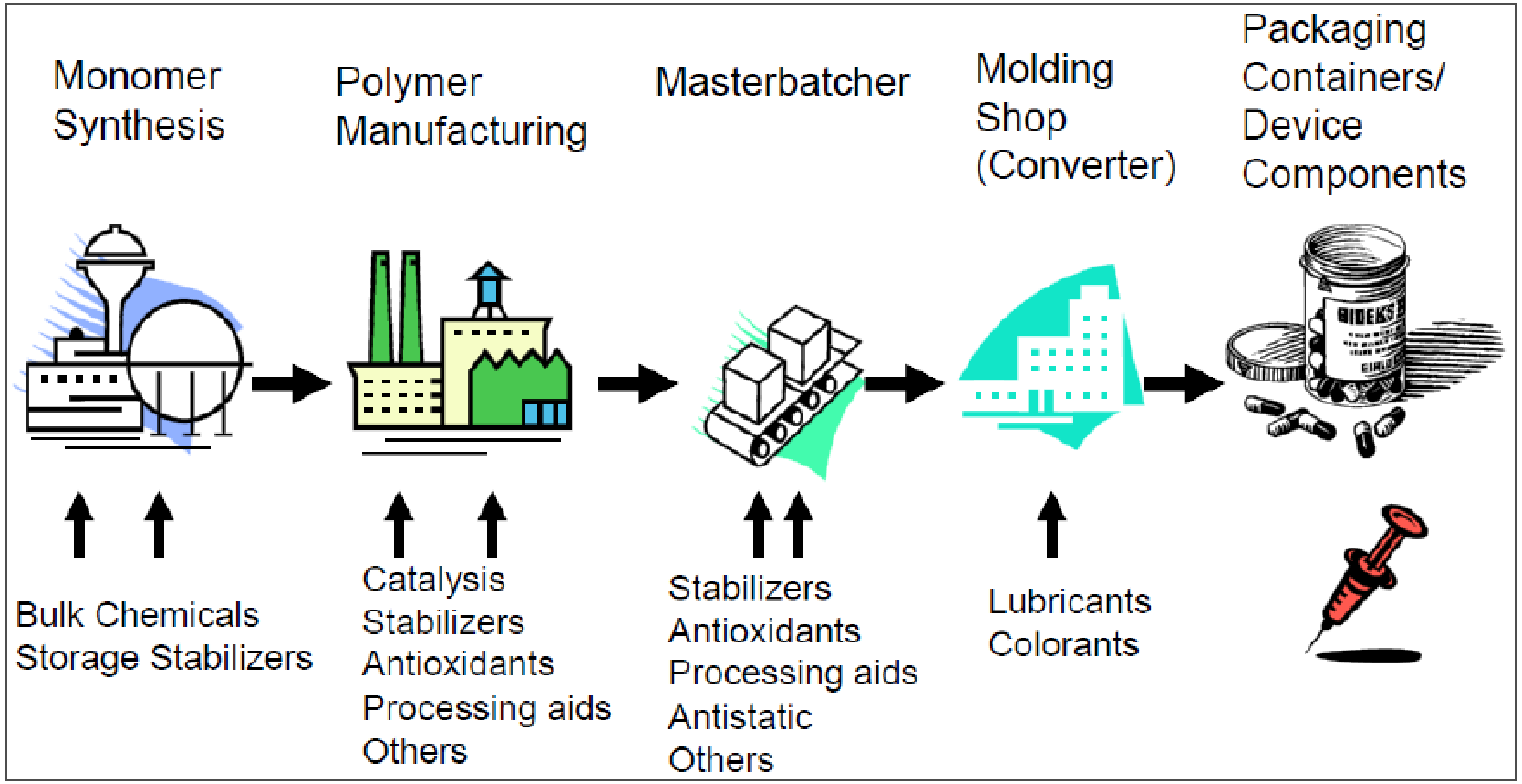
In 2015, **4%** of the global **greenhouse gas emissions** were caused by plastics. [1]

▼

main causes for climate change impact of plastics: **production** and **waste incineration** [2, 3]

[1] Zheng, J., Suh, S., 2019. Strategies to reduce the global carbon footprint of plastics. *Nat. Clim. Chang.*
[2] Cabernard, L. et al., 2022. Growing environmental footprint of plastics driven by coal combustion. *Nat. Sustain.*
[3] Klotz, M. et al., 2022. Limited utilization option for secondary plastics may restrict their circularity. doi.org/10.1016/j.wasman.2022.01.002

A Wide Range of Chemicals are Present in Plastics



Cindy Zweiben, Pfizer, Inc., Characterization of Extractables and Leachable in Parenteral Drug Products

- Unreacted monomers, residual processing aids and additives can be released during the production, use, disposal and recycling of plastics.

Additives and Processing aids

Stabilization

• Antioxidants	*prevents oxidative degradation*
• Light stabilizers	*prevents degradation by sunlight*
• Heat stabilizers	*prevents degradation by heat*

Functionalization

• Biocides	*prevents growth of microbes*
• Colorants	*imparts color*
• Fillers	*increase strength, lower costs*
• Flame retardants	*reduce flammability, smoke generation*
• Impact modifiers	*improve impacts strength*
• Nucleating agents	*promote crystallinity*
• Odor agents	*add fragrance, repress objectionable odors*
• Plasticizers	*increase flexibility, reduce melt viscosity*

Processing aids

• Antistatic agents	*prevents static charge build-up*
• Blowing agents	*decompose during processing to create foamed plastic*
• Catalysts	*enable polymerization reaction*
• Initiators	*start or regulate chain growth during polymerization*
• Lubricants	*reduces friction between polymer and processing surface*
• Solvents	*dissolves monomers, polymers and additives for mixing*
• Viscosity modifiers	*modifies melt flow viscosity*

Global production: ~18 Mt / y

Major types: [2]

- Plasticizers: 7.5 Mt/y
- Fillers
- Flame retardants: 2.1 Mt/y
- Heat stabilizers: 1.2 Mt/y
- Impact modifiers: 1.0 Mt/y
- Lubricants: 0.8 Mt/y
- Antioxidants: 0.5 Mt/y

[1] Ullmann (2018). Plastic Additives. https://doi.org/10.1002/14356007.a20_459.pub2
[2] IHS Markit (2018). Plastics additives - Specialty Chemicals Update Program. https://www.spglobal.com/commodityinsights/en/ci/products/chemical-plastics-additives-scup.html

Concerns about Chemical Release from Plastics

Environmental Science & Technology
Article
Cite This: Environ. Sci. Technol. 2019, 53, 166–175
pubs.acs.org/est

Phthalate Release from Plastic Fragments and Degradation in Seawater

Andrea Paluselli,[†] Vincent Fauvelle,[†] François Galgani,[‡] and Richard Sempéré*[,†]

CRITICAL REVIEWS IN FOOD SCIENCE AND NUTRITION
2020, AHEAD-OF-PRINT, 1-23
https://doi.org/10.1080/10408398.2020.1830747
Taylor & Francis
Taylor & Francis Group

Migration of endocrine-disrupting chemicals into food from plastic packaging materials: an overview of chemical risk assessment, techniques to monitor migration, and international regulations

Hooi-Theng Ong[a], Hayati Samsudin[b], and Herlinda Soto-Valdez[c]

Science of the Total Environment 536 (2015) 568–574
Contents lists available at ScienceDirect
Science of the Total Environment
journal homepage: www.elsevier.com/locate/scitotenv
ELSEVIER

Mass transfer of PBDEs from plastic TV casing to indoor dust via three migration pathways — A test chamber investigation

C. Rauert, S. Harrad *

Science of the Total Environment 720 (2020) 137623
Contents lists available at ScienceDirect
Science of the Total Environment
journal homepage: www.elsevier.com/locate/scitotenv
ELSEVIER

Children's exposure to hazardous brominated flame retardants in plastic toys

Oluwatoyin T. Fatunsin [a], Temilola O. Oluseyi [a], Daniel Drage [b], Mohamed Abou-Elwafa Abdallah [b], Andrew Turner [c], Stuart Harrad [b,*]

Recyling Challenges Associated with PlasticMAP

They may influence recycled plastics in the following ways:

→ **Interfere with recycling or sorting process**

→ **Reduce the (actual) recyclability including aesthetics in mechanical recycling**

- Reduction of mechanical properties: pro-degradant/pro-oxidant metal additives (Aldas et al. 2018, 10.1155/2018/2474176), mixing of additives
- Color-changes through colorants, carbon black, PbS (black) in recycled PVC
- Odor changes

→ **Reduce the safety of secondary materials**

- heavy metals, halogenated flame retardants, phthalates, etc.

chemicals used
in plastics ?

potential hazards ?

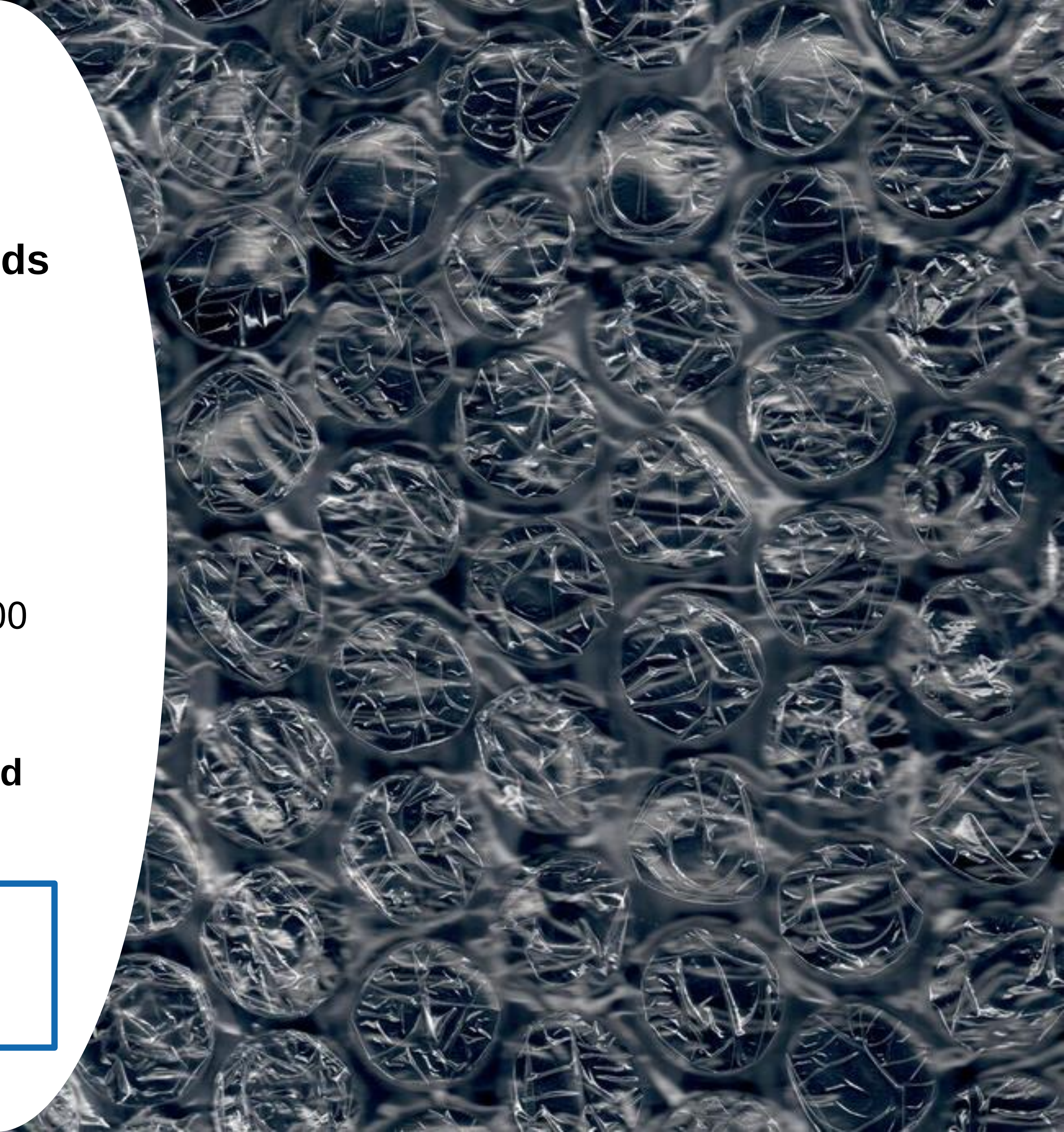
Plastic Monomers, Addtives and Processing Aids Database

Monomers, additives and processing aids are highly diverse

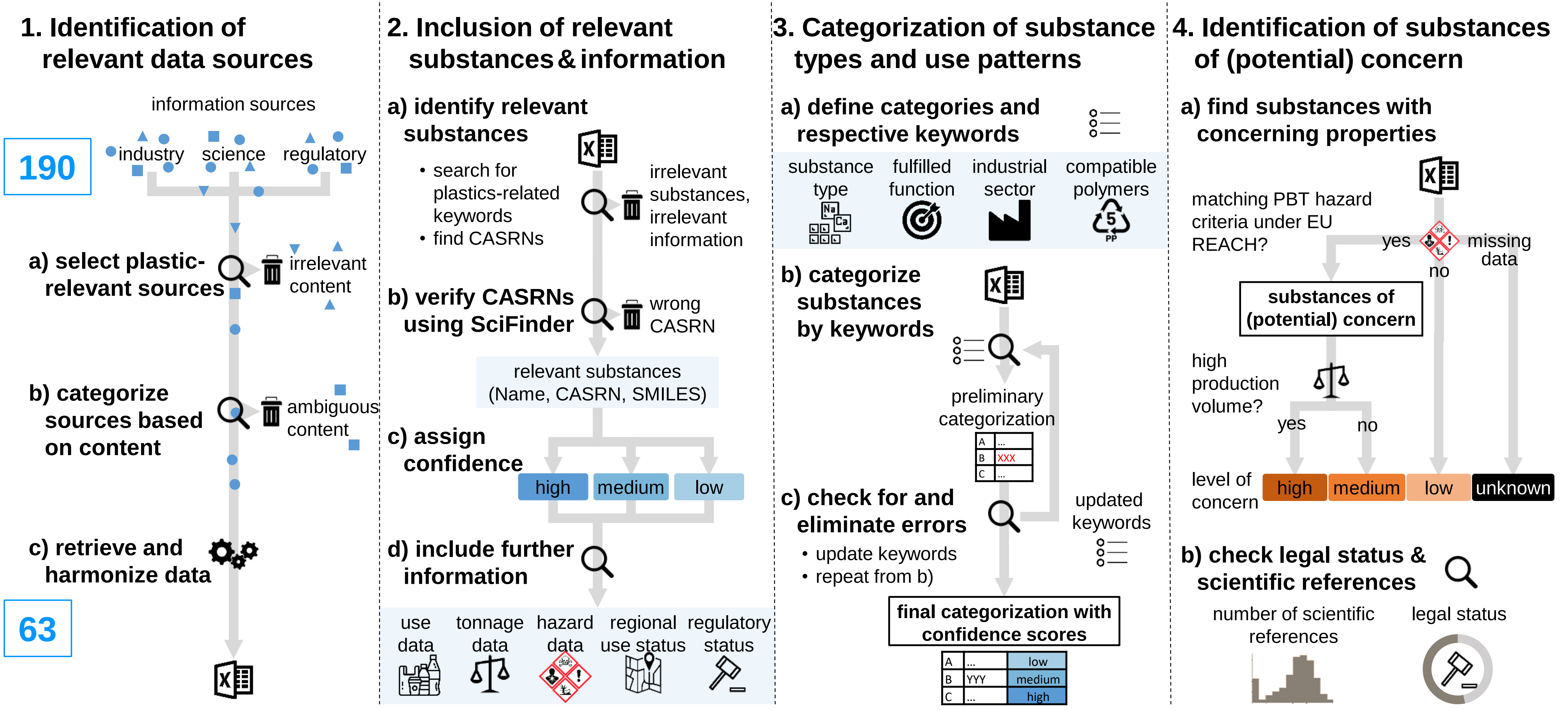
- ECHA + industry: over 400 plastic additives registered under REACH at above 100 tonnes/year
- Groh et al. (2018): over 3’000 additives in plastic packaging
- SpecialChem additives database: over 30’000 commercially available formulations

Only few substances are regularly discussed in scientific literature

➔ Need for an overview of their chemical identities and priority setting



Methods



Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

Methods – *Inclusion of relevant substances and information*

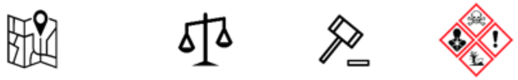
a) Identify relevant substances
   – Search for plastic-related keywords
   – Search for CASRNs

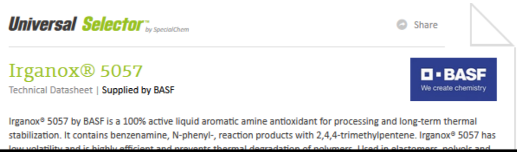
b) Verify CASRNs using SciFinder

c) Assign confidence to sources and substances

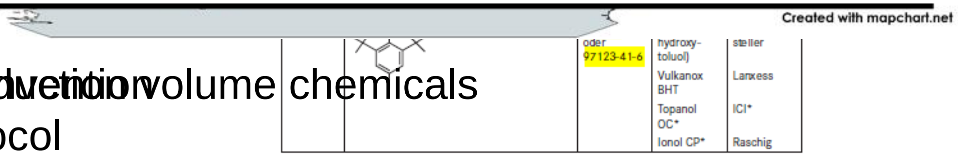
d) Include further information

regional use status	tonnage data	legal status	hazard data



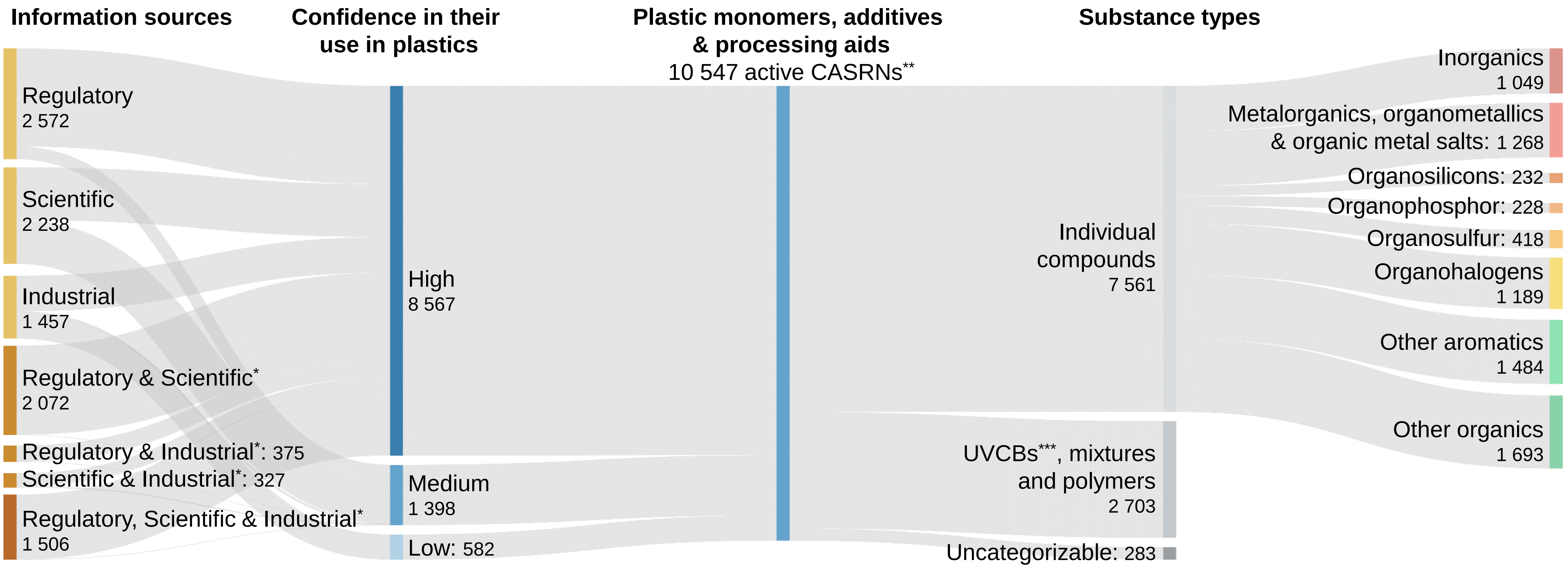


Type	Included Sources
Regulator-Harmonized	- EU C&L inventory – harmonized - EU REACH Authorization List - EU REACH PBT Assessment List - EU REACH EDC Assessment List - EU REACH SVHC List - Japanese GHS Classification Results - Australian Hazardous Chemicals Information System - OECD eChemPortal - IARC Classified Agents List
Company-reported	- EU REACH registration dossiers - EU C&L inventory – not harmonized



Global:
- OECD High production volume chemicals
- Stockholm Convention
- Montreal Protocol
- Rotterdam Convention

Results – Overview of the Substances

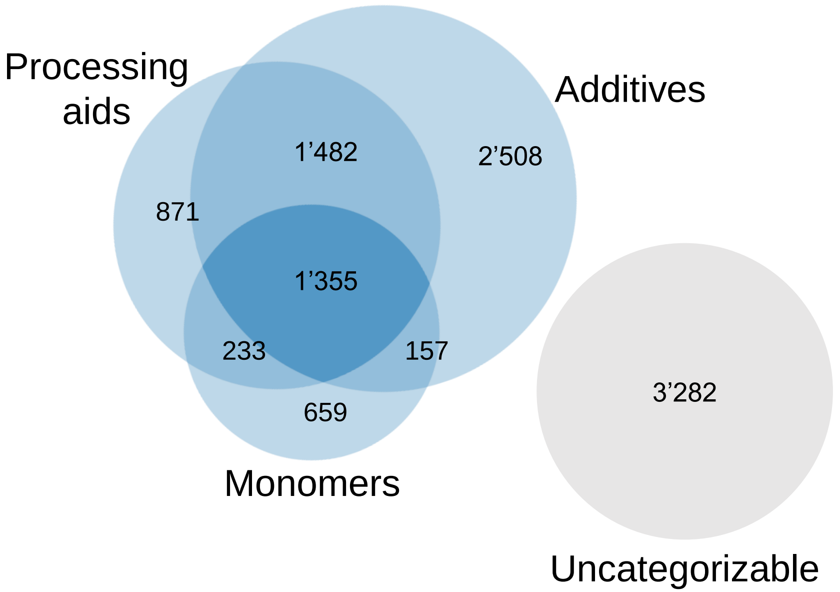


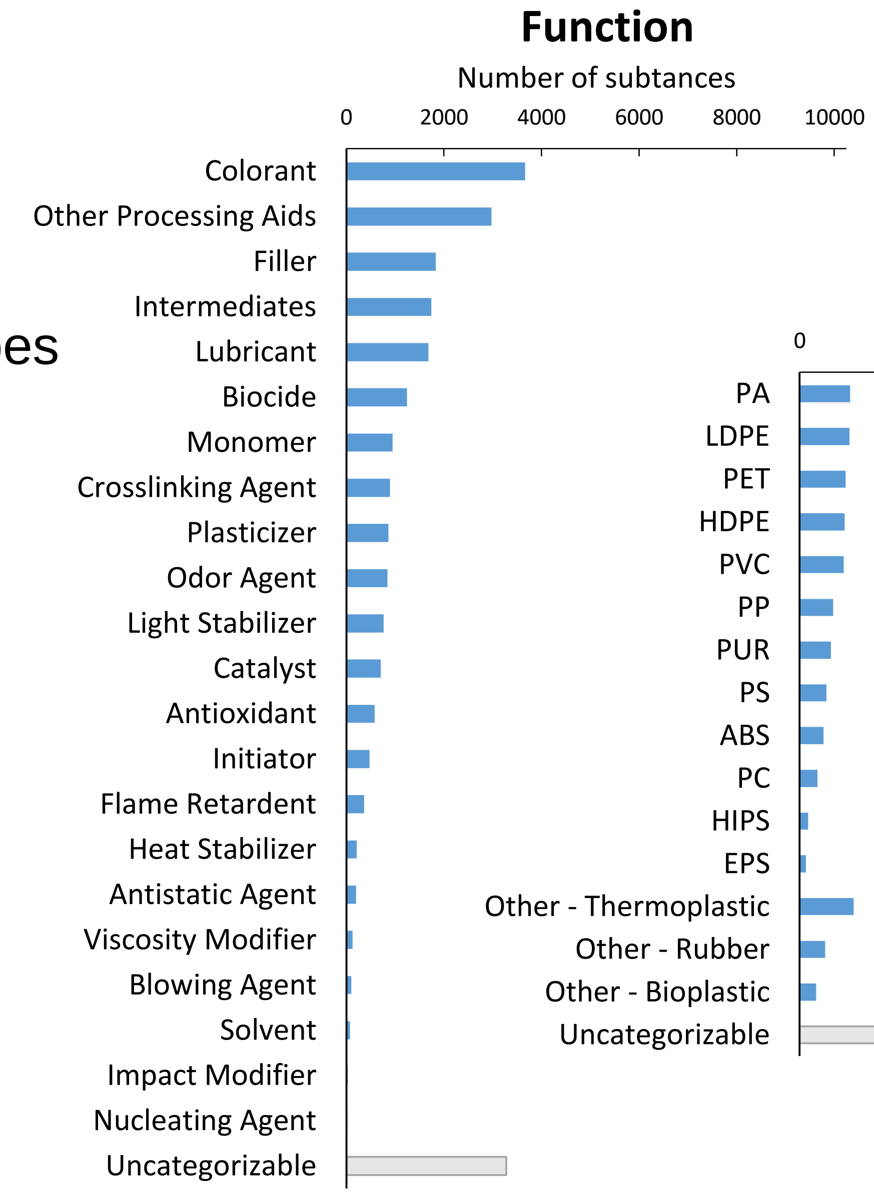
* Substances are found in sources of all mentioned types
** These active CASRNs are associated with 24 901 deleted CASRNs and 22 alternate CASRNs
*** Substances of unknown or variable composition, complex reaction products and biological materials

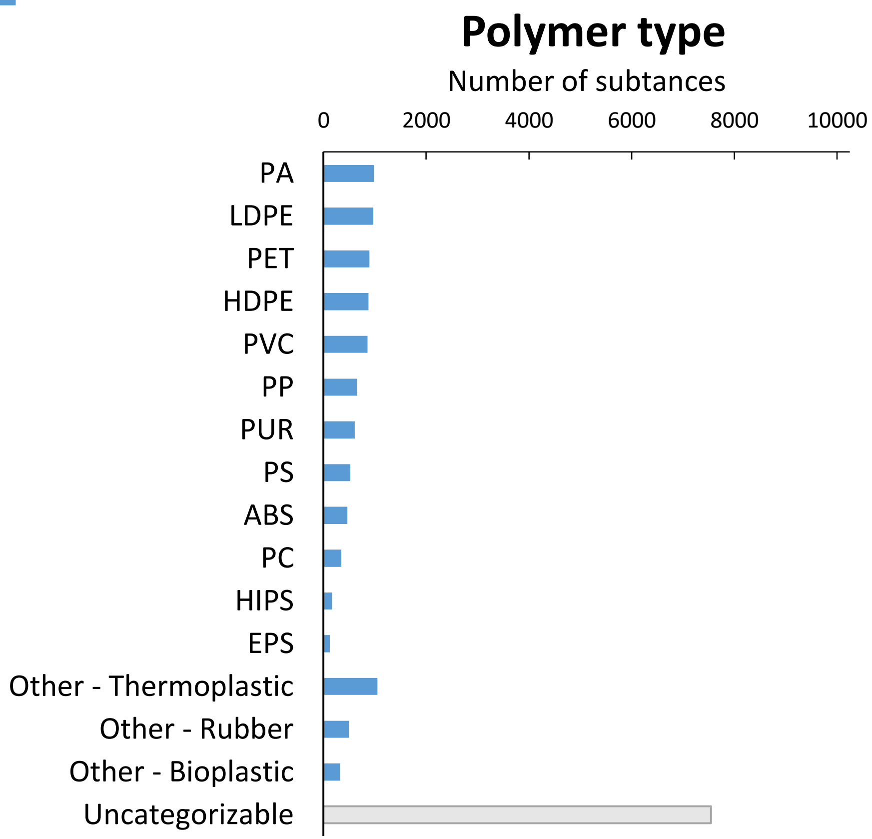
Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

Results – Use Patterns

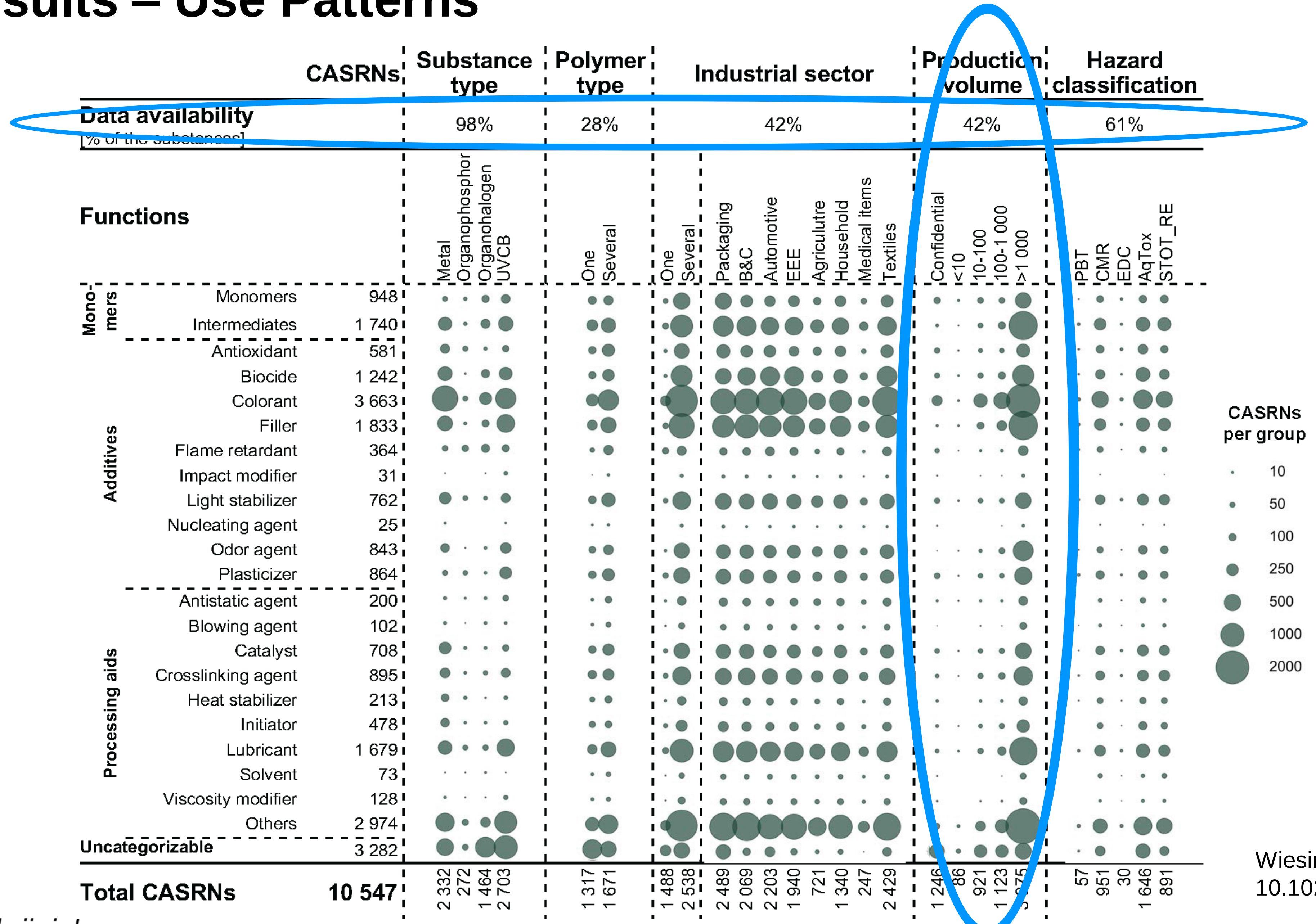
Many substances
- fulfill several functions
- are compatible with several polymer types
- are used in several industrial sectors







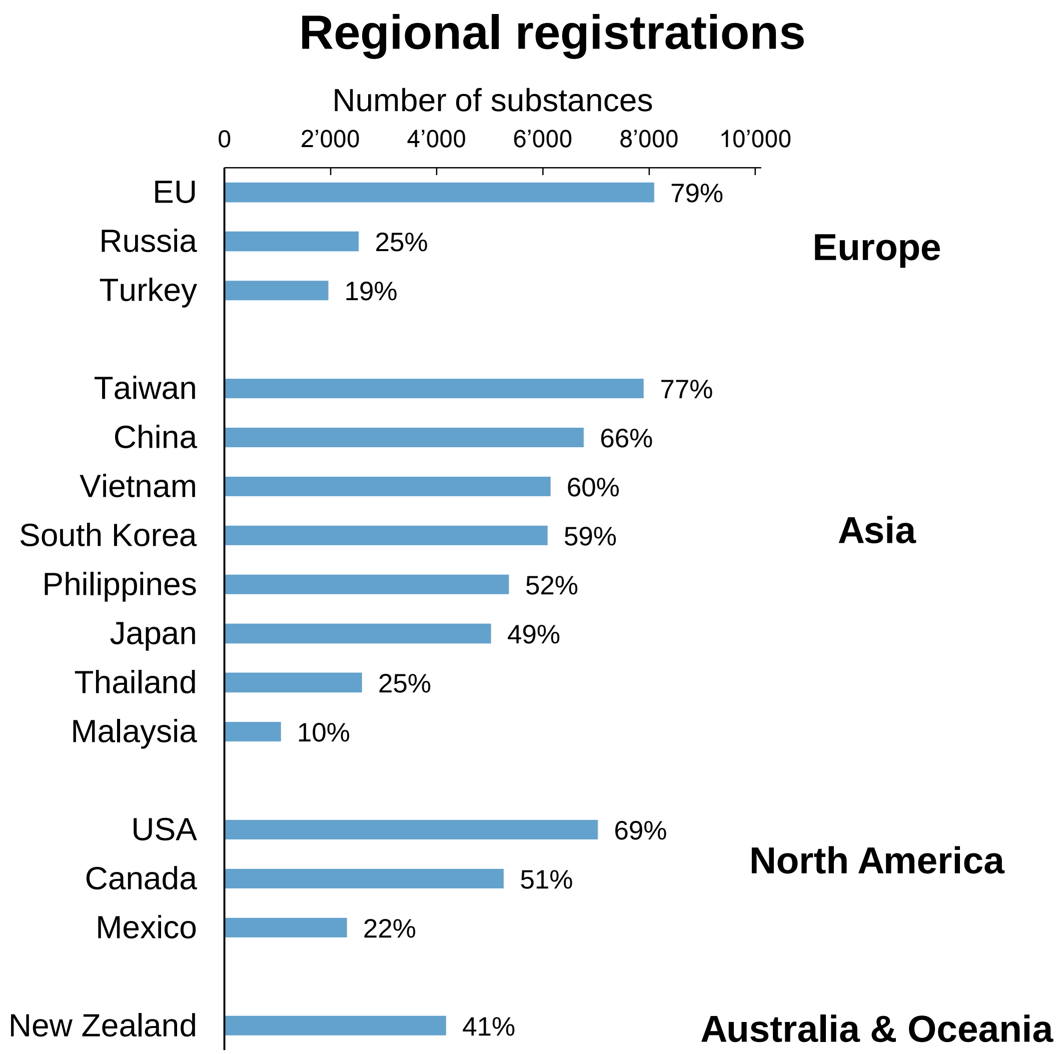
Results – Use Patterns



Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

Results – Regional relevance

– 10–80% of substances registered in inventories from different parts of the world
– the commercial status, extent of use and concentrations in plastic articles remain unknown



Results – Substances of Potential Concern

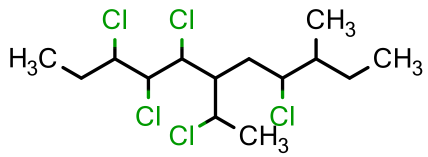
- more than 2’400 substances = 25% of the identified substances
- about 900 substances of potential concern are also approved for use in food-contact plastics

HAZARD TYPE		TOTAL	HPVC	NOT REGULATED[1]	NOT RESEARCHED[2]
PBT	Persistent, bioaccumulative & toxic	22	7	7	2
vPvB	Very persistent & very bioaccumulative	35	19	3	8
CMR	Carcinogenic, mutagenic, reproductive toxic	951	501	350	91
ED	Endocrine disrupting	30	17	3	3
AqTox	Chronic aquatic toxicity	1’646	754	897	188
STOT_RE	Specific target organ toxicity	891	562	331	57
TOTAL		**2’486**	**1’254**	**1’327**	**266**

[1] regulated by international regulatory lists or in the EU, USA, Japan or Republic of Korea
[2] no scientific references according to SciFinder

Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

Results – Examples of Unregulated Substances of Potential Concern

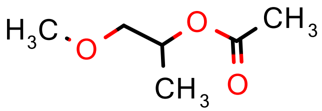


Chloroalkanes, C14-17

Lubricant, flame retardant, plasticizers…

CASRN: 85535-85-9

POP candidates

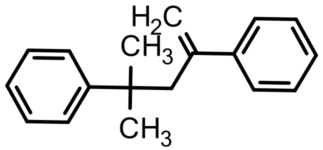


1-Propanol, 2-methoxy-, 1-acetate

Solvent, used in colorants, …

CASRN: 70657-70-4

Repr. 1B

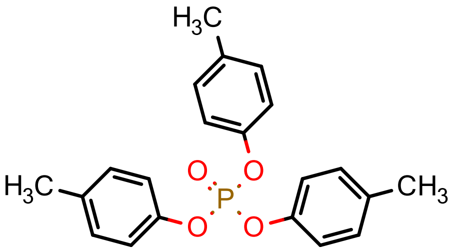


Benzene, 1,1'-(1,1-dimethyl-3-methylene-1,3-propanediyl)bis-

Polymerization control agent

CASRN: 6362-80-7

Skin Sens. 1, STOT RE 2
Aquatic Acute 1, Aquatic Chronic 1

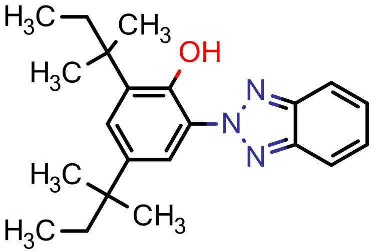


Phosphoric acid, tris(methylphenyl) ester

Flame retardant,..

CASRN: 1330-78-5

Skin Sens. 1, Repr. 2
STOT RE 2, Aquatic Acute 1
Aquatic Chronic 1

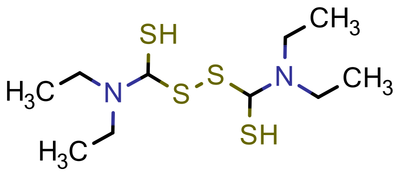


2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol (Tinuvin 328)

Antioxidant

CASRN: 25973-55-1

STOT RE 2



Thioperoxydicarbonic diamide ([(H2N)C(S)]2S2), N,N,N',N'-tetraethyl-

Crosslinking Agent

CASRN: 97-77-8

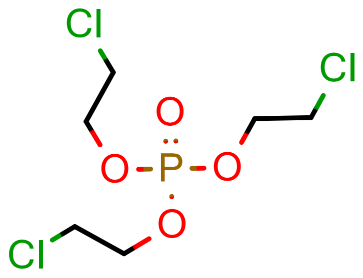
Skin Sens. 1, STOT RE 2
Aquatic Acute 1, Aquatic Acute 2

Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

Results – Examples of Inconsistently Regulated Substances

- **901** substances of potential concern are approved for use in food-contact plastics

  → **265** substances of potential concern are restricted/banned in other use areas

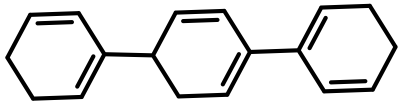


Ethanol, 2-chloro-, 1,1',1''-phosphate

Flame retardant, other processing aid…

CASRN: 115-96-8

SVHC (Repro)

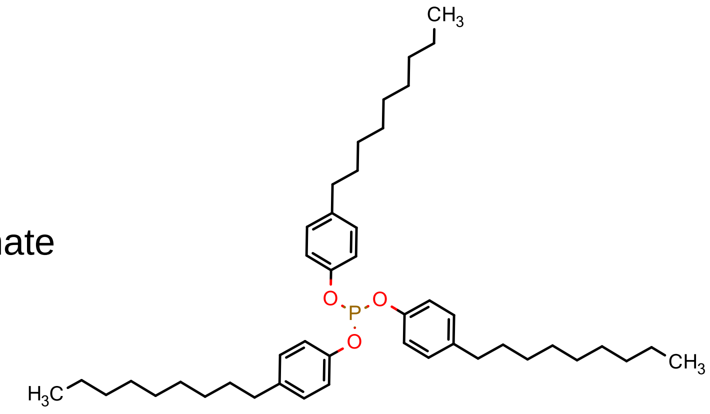


Terphenyl, hydrogenated

Colorant, other processing aid,…

CASRN: 61788-32-7

SVHC (vPvB)

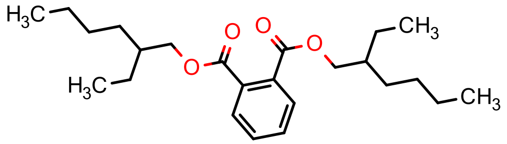


Ethane, 1,1,1-trichloro-

Antioxidant, stabilizer, lubricant,…

CASRN: 26523-78-4

SVHC (EDC)



1,2-Benzenedicarboxylic acid, 1,2-bis(2-ethylhexyl) ester

Colorant, plasticizer, …

CASRN: 117-81-7

SVHC (Repro, EDC)

Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

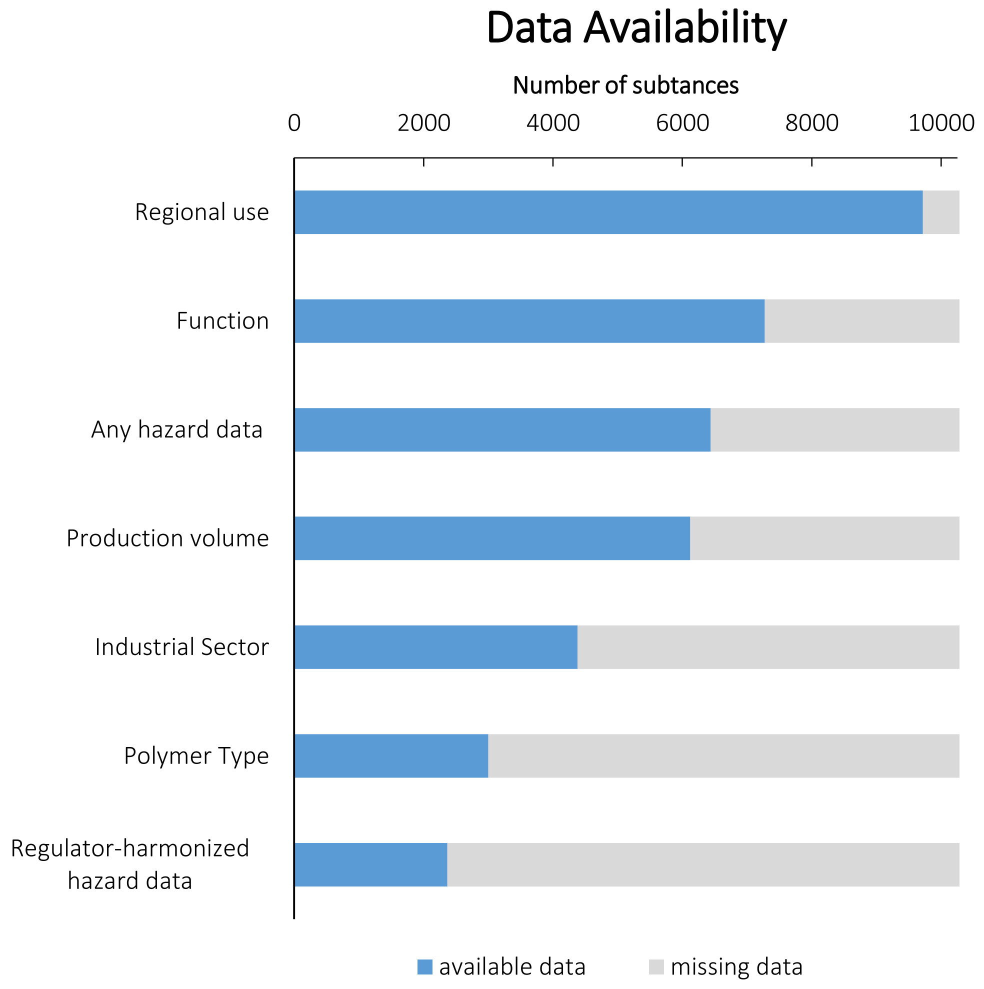
Discussion – Data Availability & Uncertainties

Critical data and knowledge gaps:

- Regulator-harmonized hazard data
- Use details and concentration ranges

Our numbers may still well be underestimates, due to focuses on:

- digitized sources (vs. print sources)
- sources where assigned CASRNs are provided (vs. sources where no assigned CASRNs provided)
- intentionally added substances (vs. NIAS)
- existing GHS hazard data (vs. literature values)



Wiesinger et al. 2021. ES&T, 10.1021/acs.est.1c00976

Discussion – Possible Ways Forward

- **Establishing a centralized knowledge base**

  → e.g. through public-private partnerships and corporate social responsibility; harmonizing information exchange standards

- **Ensuring transition to a safe and sustainable circular plastic economy**

  → e.g. developing standardized approaches to assessing the sustainable circularity of plastics and chemicals therein; avoiding hazardous substances, reducing product complexity and embedding sustainable circularity in the design phase; fostering innovative and enabling business models and practices

- **Expanding and harmonizing regulatory efforts**

  → e.g. group- or class-based approaches; one substance, one assessment; complementary market-based policy instruments to internalize externalities

Wiesinger et al. 2021. ES&T, https://pubs.acs.org/doi/10.1021/acs.est.1c00976
Wang et al. 2021. https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.1c00243

Take-Home Messages

- **A messy situation regarding intentionally added chemicals in plastics**
  - Thousands of diverse substances (potentially) used
  - 25% having concerning properties, and only a part researched and regulated (including conflicting regulations in different domains)
  - A general lack of transparency on their actual occurrence in products and hazards

- **Concerted efforts from all actors are urgently need to ensure transition to a safe and sustainable circular economy, starting from the design phase!**

Outlook

Following policy actions are urgently needed

- Design for recycling – also on the chemical level
- Supply chain transparency
- Expand focus of research, regulation and monitoring

Research needs and opportunities

- Target list for non-targeted analysis
- Support alternatives assessment
- New research foci
- Need for analytical standards
- Need for standardized terminology regarding chemicals

Publication of paper and database soon

"Clean Cycle" Strategy

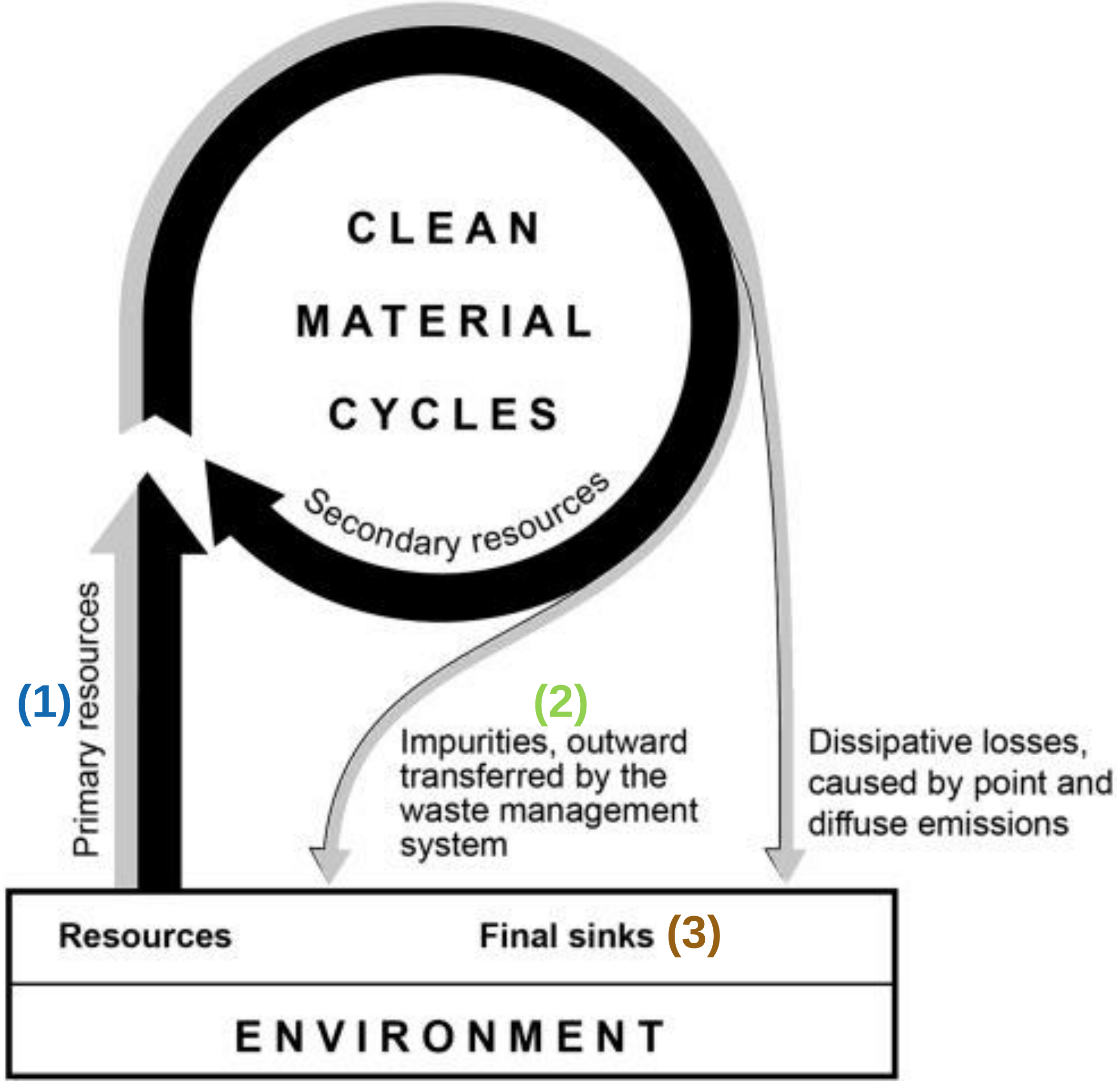
Key components of the strategy

(1) Phase-out of hazardous chemicals in primary materials

(2) Separation of contaminated used materials

(3) Safe treatment/disposal of contaminated materials

→ "Clean Cycle" Project @ETHZ



Clean Cycle Project @ETHZ

Plastic Additives and Human Exposure

→ identify and prioritize hazardous chemicals used in plastics

→ quantify current levels of target hazardous chemicals in target plastic flows

Plastic Material Flows and Environmental Assessment

→ Map and model current plastic flows in Switzerland

→ Model future scenarios of plastic flows in Switzerland

→ model the current and future levels of **human exposure to selected hazardous chemicals** via plastics and the associated **risks to human health**

→ model **environmental impacts** of the current and potential future plastic recycling systems

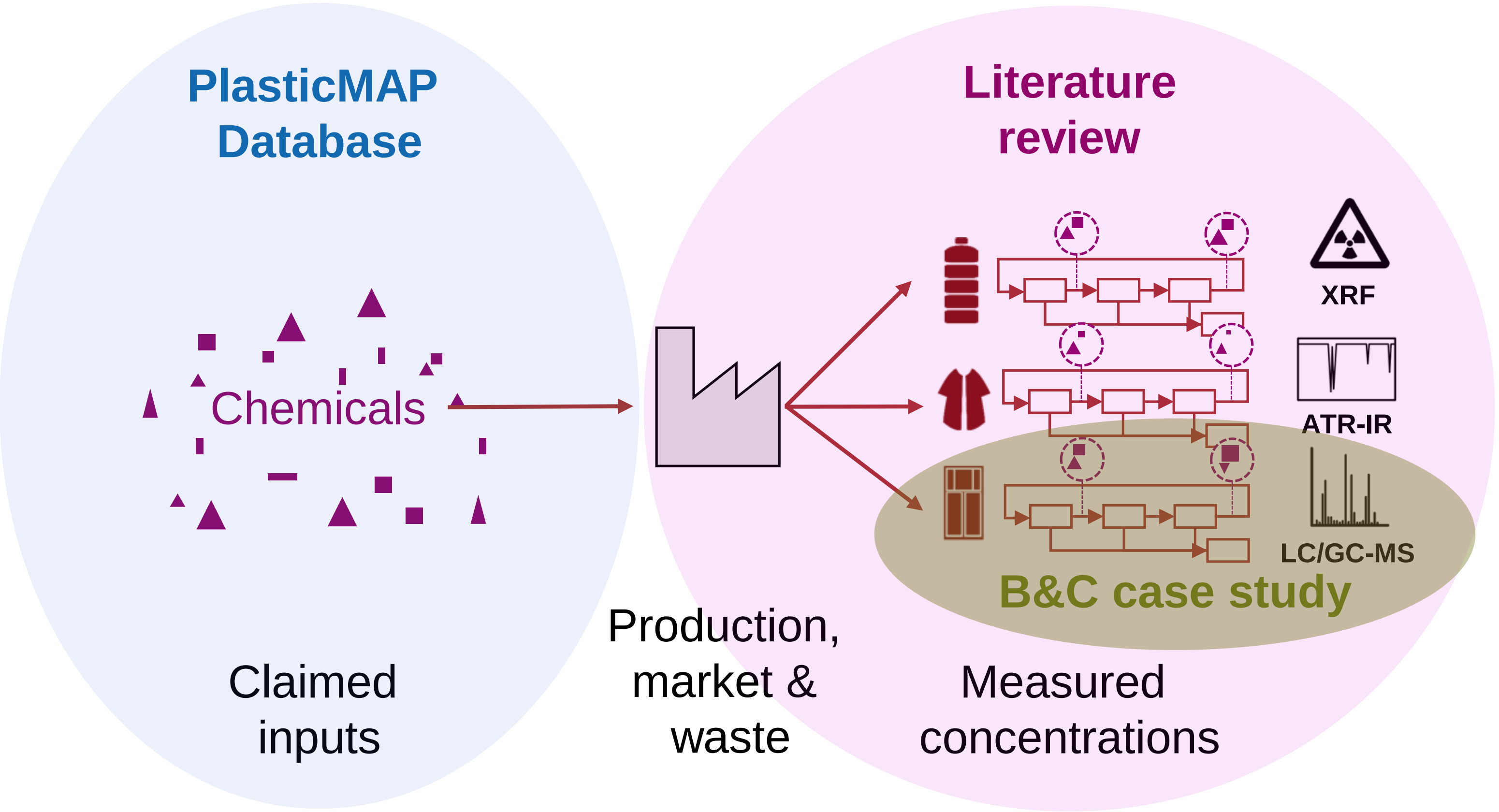
→ develop strategies to **maximize the resource efficiency** of plastics **with minimized risks to human health**

→ inform policy- and decision-makers

Current research – Measurements of chemicals in plastics

Goal: Fill the data gaps from PlasticMAP regarding con-centrations and actual uses

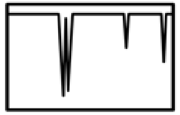
- Which chemicals are **actually** present in plastics samples?
- Which **concentrations** are relevant for different **products**?
- Where are **hot/blind-spots** in plastic screening literature?



Current research – B&C case study

150 Building & Construction samples, PVC

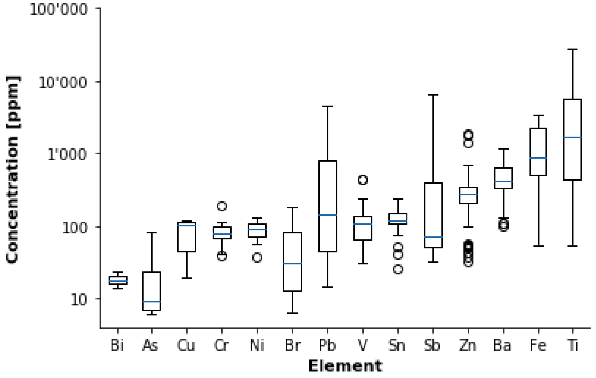
ATR-IR



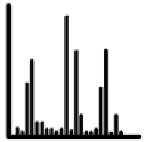
polymer type, phthalate screening

XRF

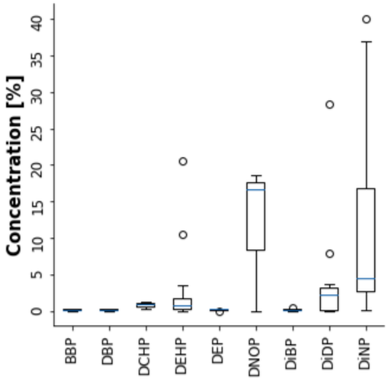
elemental composition



GC-MS



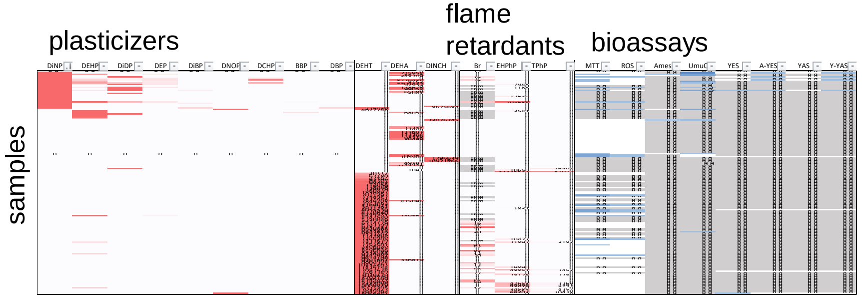
phthalate concentration
DF: 26%



presence of other substances

Bioassays

biological activity



Acknowledgement

Thank you very much for your attention!
Thanks to RECETOX and Ondřej and Peter for the invitation!

Further, I thank for the support from:

- the Clean Cycle project team: Magdalena Klotz, Dr. Zhanyun Wang, Dr. Melanie Haupt, Prof. Stefanie Hellweg
- the Swiss Federal Office for the Environment (FOEN), the Swiss Federal Office of Public Health (FOPH) and Canton of Zurich‘s Office of Waste, Water, Energy and Air (AWEL).