National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

PBT-assessment of PetCo UVCBs

Petroleum and Coal stream substances

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SVHC Roadmap to 2020

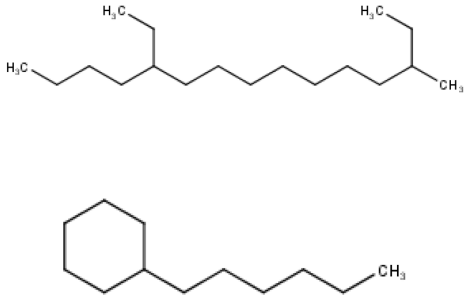
For potential CMR, PBT, ED and sensitiser substances an approach is defined in the roadmap and further elaborated in the implementation plan.

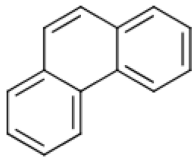
Petroleum substances: Due to difficulties encountered before, the roadmap notes

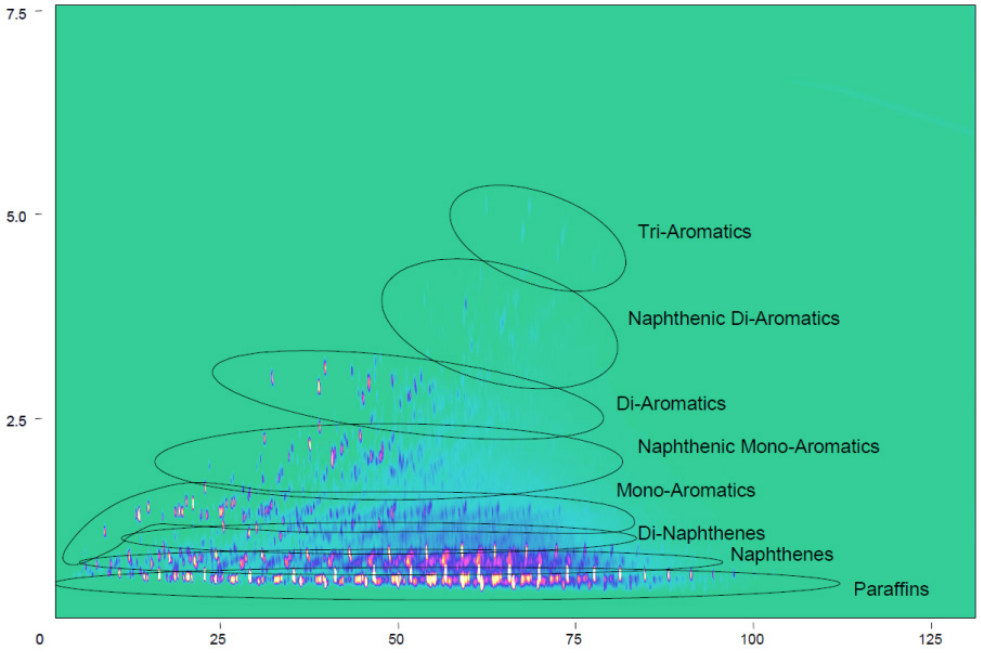
'there is a need to develop an approach to asses the petroleum streams (approach 2013-2015, systematic assessment from 2016)'

PetCo substances

- UVCBs: Substances with an **U**nknown or **V**ariable Composition, **C**omplex Reaction Products and **B**iological materials.
- Crude oil or any specific refinery stream obtained by one or more processes used as starting materials
- Hundreds to thousands of individual constituents
  - Aliphatics
  - Naphthenics
  - Aromatics
- Potential concerns for HH and ENV







- Figures obtained from CONCAWE

Regulatory risk management (RRM) & Petroleum substances – state of play

- Previous prioritisation exercises -> petroleum substances have scored high due to:
  - Intrinsic properties
  - Tonnages and uses pattern

- However, authorities have chosen to postpone selection of petroleum substances for further regulatory risk management (RRM), including identification as SVHCs due to challenges faced

Main Challenges observed for PetCo substances

- Complexity of **substance identification (SID)**
  - substances are registered with **generic SID**, making it difficult to identify the actual constituents that make the substance of concern

- Complexity of **hazard** information and classification according to CLP (C&L):
  - information on the **hazard profile** of the substance aggregated in such a way, that it's difficult to understand which substance in the category has which hazard profile (absence or weak justification of the read across between the members of the categories).
  - The same substance may have several compositions with different hazard profiles

Aims of ECHA's PetCo working group

- Investigate in a systematic way the quality of registration dossiers and prioritize PBT/HH hazerd assessment.

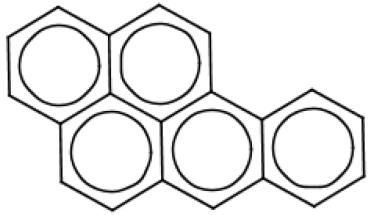
- Provide a starting point for the further work under the SVHC Roadmap
  - Determine baseline situation observed in registration dossiers
  - Focus (first) on petroleum (Pet) substances endorsed by CONCAWE
  - Analysis of uses information and SID done on all categories and registration dossiers
  - Hazard assessment on selected test cases (kerosene and gas oil categories)
  - Agreement on a prioritization scheme for PBT assessment (NL)

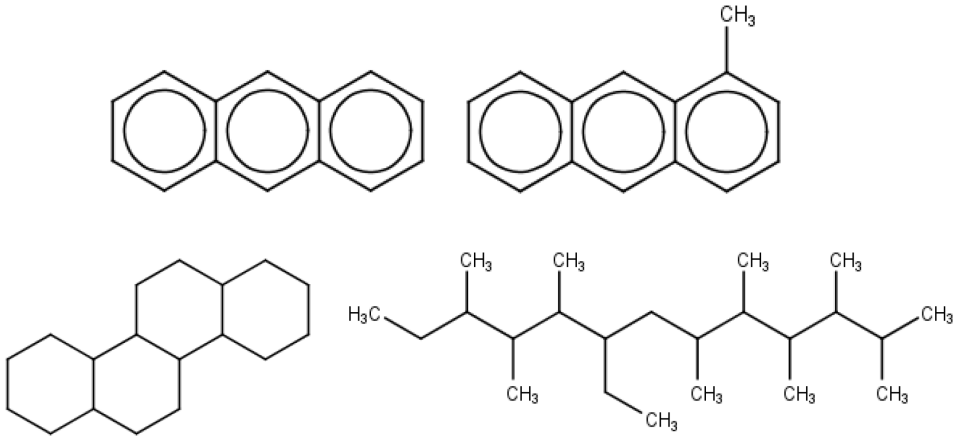
Participants in the PetCo working group

- ECHA
- European Commission
- Member states Competent Authorities
- Industry stakeholders:
  - PetCo registrants consortia:
    - Petroleum stream substances (CONCAWE)
    - Coal stream substances (R4CC)
    - Hydrocarbon solvents (HSPA)
    - Higher Olefins&Poly Alpha Olephins (HOPA)

PetCo PBT/vPvB-concern

- Many hydrocarbon constituents are of (*potential*) PBT-concern
  - Polycyclic aromatic hydrocarbons
    - › Parent PAHs (confirmed PBT/vPvB)
    - › Alkylated PAHs (PBT/vPvB?)
  - Naphthenics (potential PBT/vPvB?)
  - Iso-paraffins (potential PBT/vPvB?)



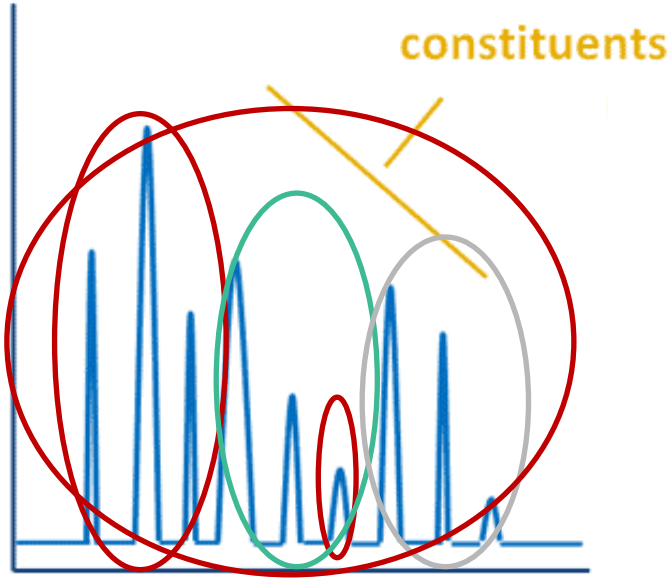


PBT/vPvB-hydrocarbons
Anthracene (3-ring)
Phenanthrene (3-ring)
Fluoranthene (4-ring)
Pyrene (4-ring)
Chrysene (4-ring)
Benz[a]anthracene (4-ring)
Benzo[a]pyrene (5-ring)
Benzo[k]fluoranthene (5-ring)
Benzo[ghi]perylene (6-ring)

PBT-assessment of UVCBs

- Single constituent assessment (constituent-by-constituent)
  - P (half-life), B (BCF) and T criteria

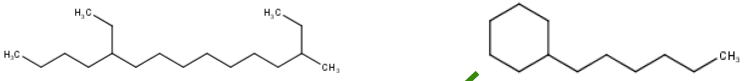
- UVCBs
  - Not feasible to identify, assess or isolate all constituents
  - Alternative methods:
    - Known-constituents approach
    - Whole-substance approach
    - Fraction profiling approach (e.g. Hydrocarbon Block Method)



Hydrocarbon Block Method

- Substance is divided into blocks of structurally similar constituents
- Developed in 1996, but not yet applied to reach consensus on PBT-properties of a hydrocarbon block.

>30,000 constituents

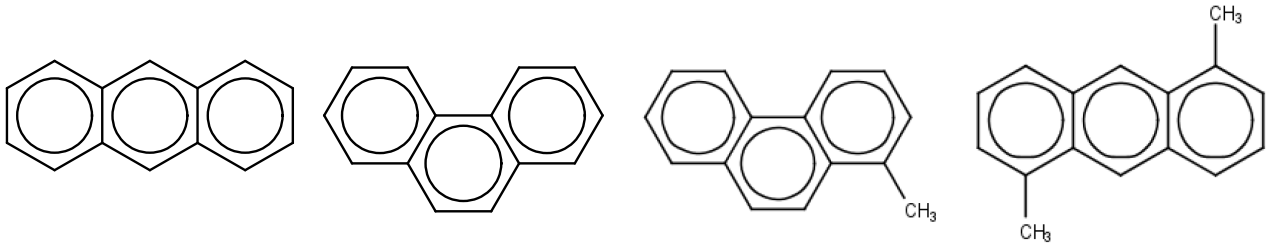


#C	Par	iP	MNap	DiNap	PolyNap	MAr	DiAr	PolyAr	NapMAr	NapDiAr	NapPolyAr	nOlefin	iOlefin	SAl	SAr
…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…

PetCo case-study

Three-ring PAHs

- Anthracene and Phenanthrene derivatives
  - Parents = PBT/vPvB
  - Alkylated forms = …?



#C	Par	iP	MNap	DiNap	PolyNap	MAr	DiAr	TriAr	PolyAr	NapMAr	NapDiAr	NapPolyAr
…	…	…	…	…	…	…	…	…	…	…	…	…
11	…	…	…	…	…	…	…	…	…	…	…	…
12	…	…	…	…	…	…	…	…	…	…	…	…
13	…	…	…	…	…	…	…	…	…	…	…	…
14	…	…	…	…	…	…	…	…	…	…	…	…
15	…	…	…	…	…	…	…	…	…	…	…	…
16	…	…	…	…	…	…	…	…	…	…	…	…
17	…	…	…	…	…	…	…	…	…	…	…	…
18	…	…	…	…	…	…	…	…	…	…	…	…
…	…	…	…	…	…	…	…	…	…	…	…	…

Persistence

- Relative trend within experimental data

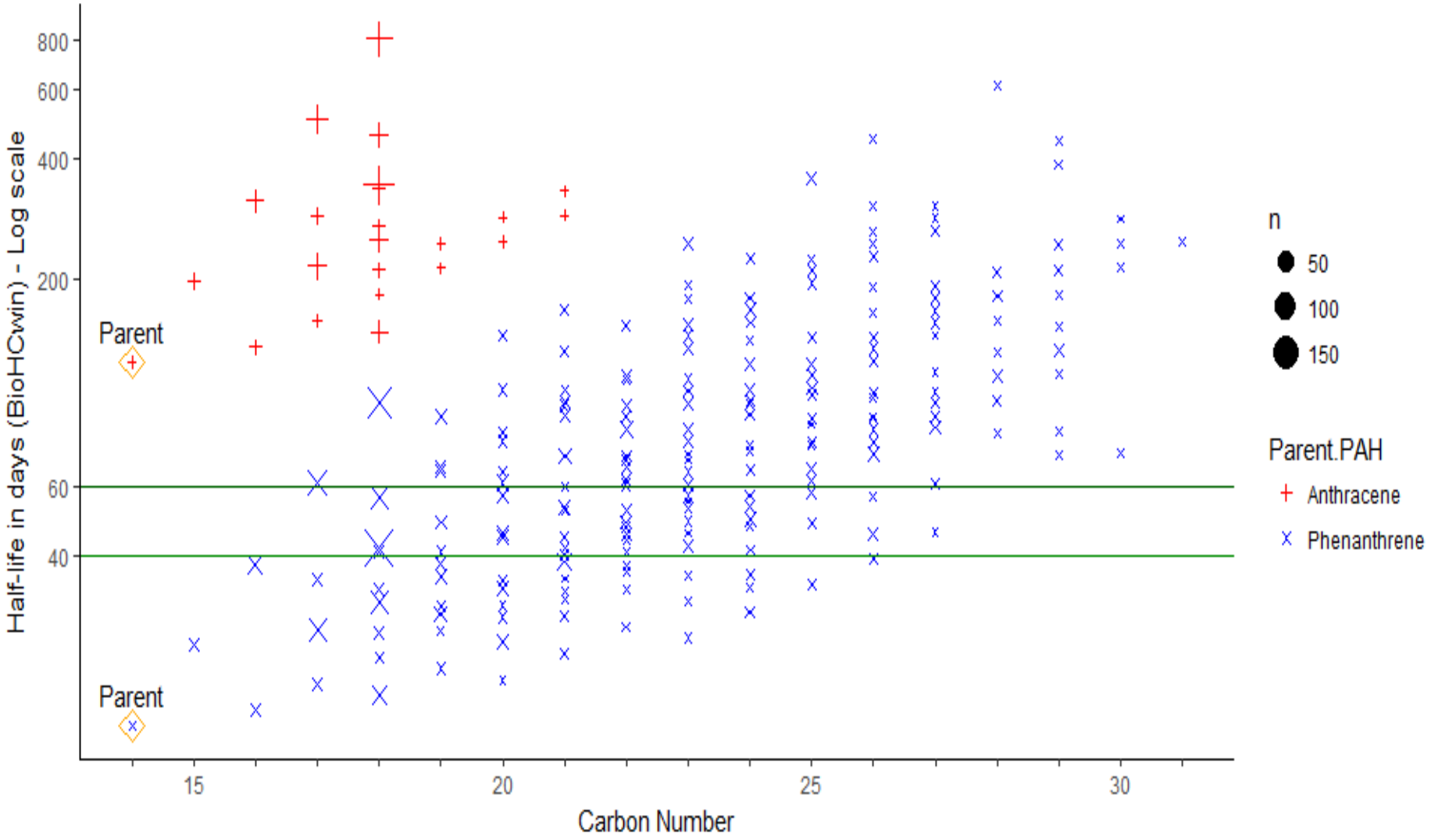
Legend
Shortest degradation time
Longest degradation time

References	Substance	Parent	C1	C2	C3	C4
Prince et al. 2008	Phenanthrene					
CONCAWE 2012	Phenanthrene					
	Anthracene					
Prince et al. 2013	Phenanthrene					
McFarlin et al. 2014	Phenanthrene					
Brakstad et al. 2015	Phenanthrene					
Venosa et al. 2007	Phenanthrene 5					
	Phenanthrene 20					
Garret et al. 2003	Phenanthrene					
Brakstad et al. 2014	Phenanthrene					
Kristensen et al. 2015	Phenanthrene					
Prince et al. 2017	Phenanthrene					
Wang et al. 2016	Phenanthrene					
Campo et al. 2013	Phenanthrene					

Persistence – QSAR data

QSARs are contradicting each other.

- BioWin3: overestimation of effect of alkylation
- BioHCWin: phenanthrene starting point is off


Half-life in days (BioHCwin) - Log scale
800
600
400
200
60
40
Parent
Parent
15
20
25
30
Carbon Number
n
50
100
150
Parent.PAH
Anthracene
Phenanthrene

Persistence

- Experimental data seems to indicate overall *slower* degradation of alkylated PAHs.

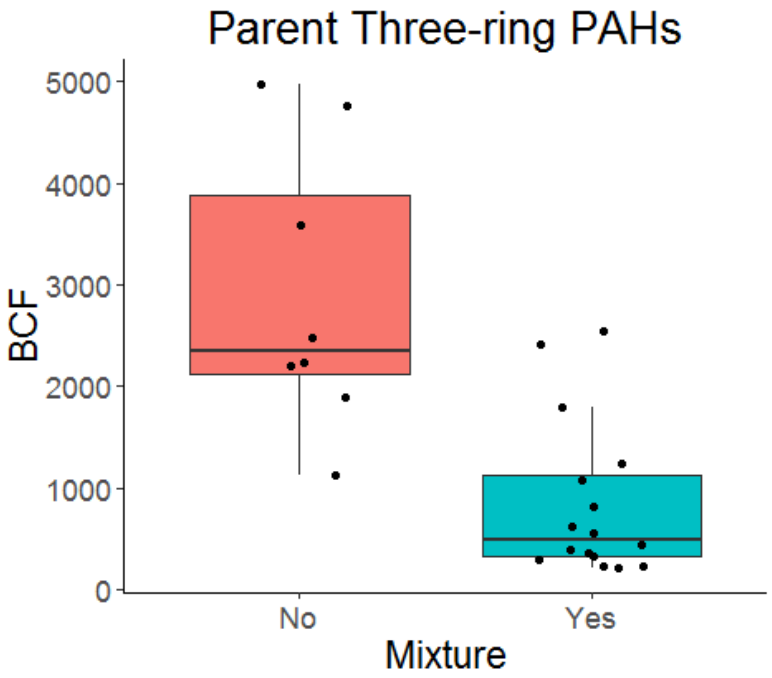
  - Alkylation seems a (steric) hindrance to oxidation, and/or
  - Alkylation leads to lower bioavailability

Hydrocarbon block	Conclusion
C14	P/vP (SVHC)
C15	P/vP
C16	P/vP
C17	P/vP
C18	P/vP

Bioaccumulation

Thresholds	BCF
B-criteria	2000
vB-criteria	5000

- Few experimental (fish) data available
- High variation between studies
  - Phenanthrene BCFs range from 339 to 6118
  - Mixture exposure
    - Induction of MFO system
- Alkylated PAHs only tested in mixtures
  - Trend observation



Bioaccumulation

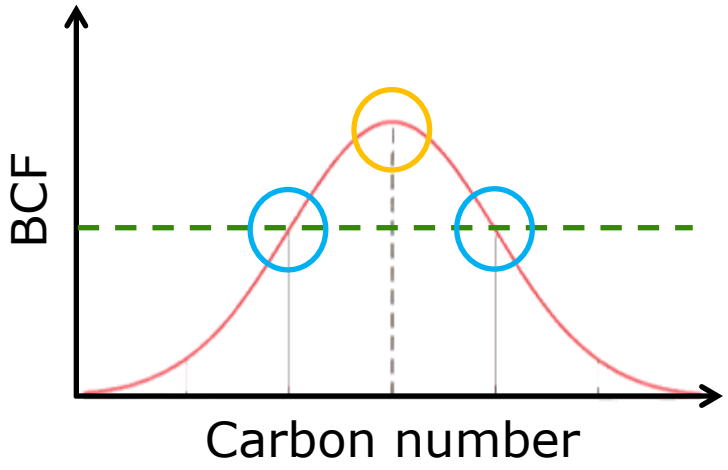
- Inconsistent trends within studies
  - Few data (4 trends, 16 constituents)

Legend
Lowest BCF
Highest BCF

References	Substance	Parent	C1	C2	C3	C4
Lo et al. 2016	Anthracene	237-554	653			1446
Lo et al. 2016	Phenanthrene	1237	1286			257-1137
Jonsson et al. 2004	Phenanthrene	393-1081	176-420	207-633		
Carlson et al. 1979	Phenanthrene	2538	1497			

Bioaccumulation

- QSAR data
  - Useful in weight-of-evidence approach



Hydrocarbon block	Experimental
C14	B/vB
C15	?
C16	?
C17	?
C18	?

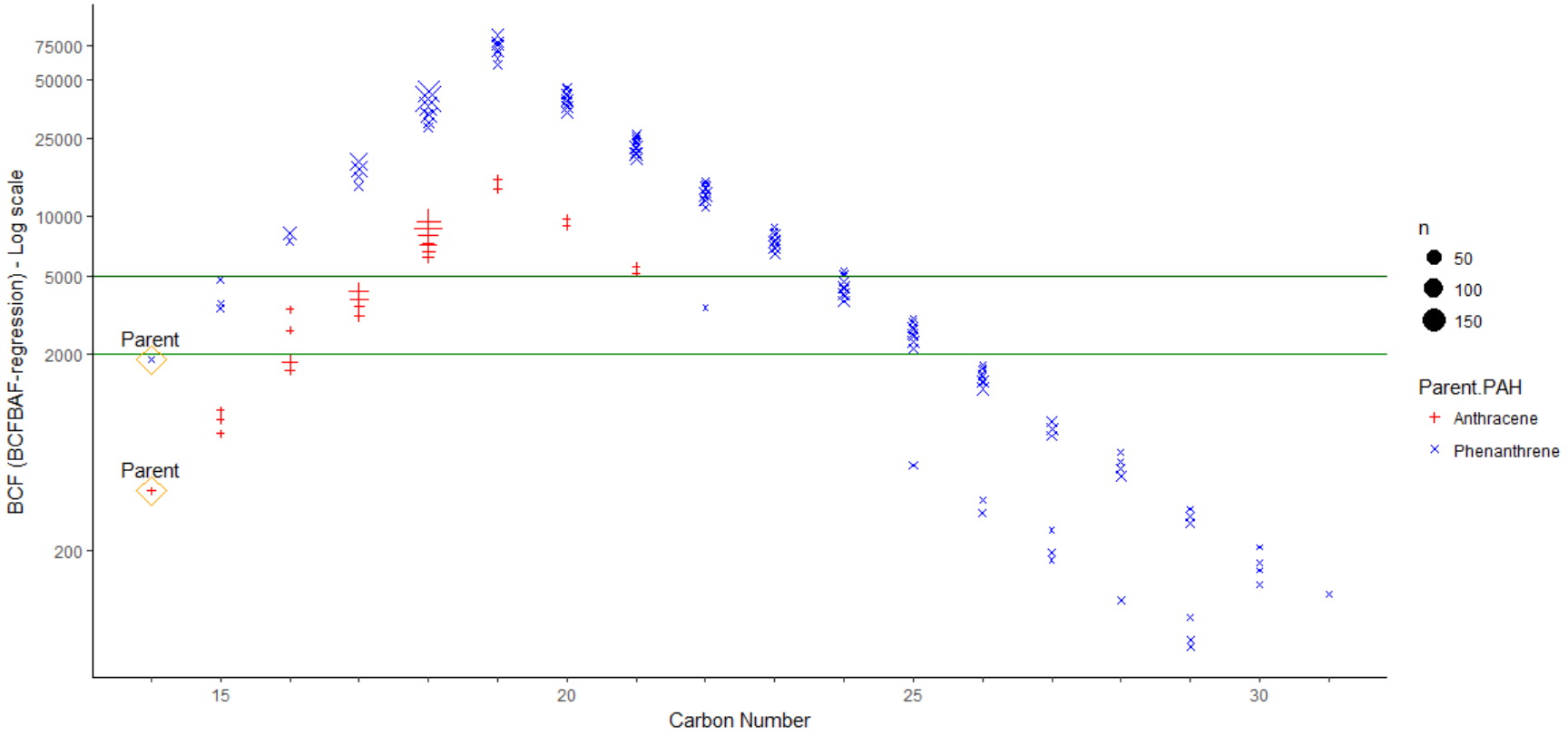
QSAR models differ in **whether** B-threshold is met:

- De
  est

QSAR
thres
- De

Carbon number	Number of constituents
14	2
15	8
16	48
17	176
18	650
…	…
31	…

QSAR data


BCF (BCFBAF-regression) - Log scale
75000
50000
25000
10000
5000
2000
200
Parent
Parent
15
20
25
30
Carbon Number
n
50
100
150
Parent.PAH
Anthracene
Phenanthrene

Data challenges

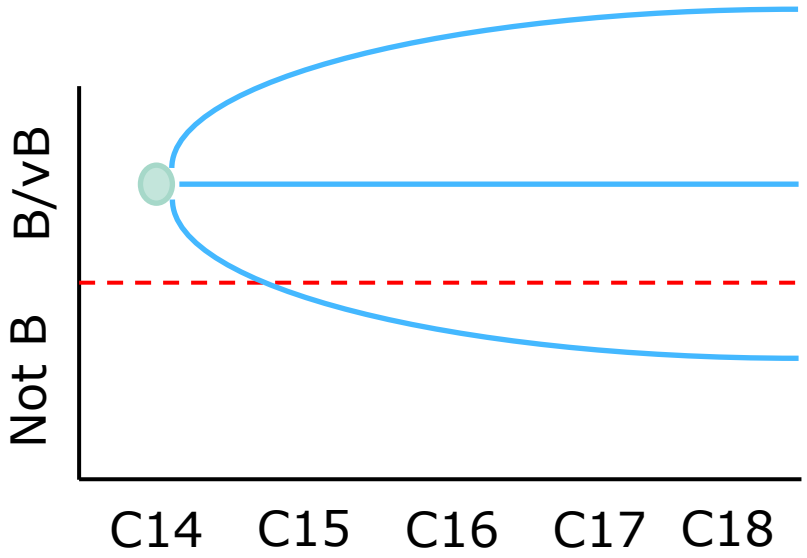
- How to reach conclusion when experimental and estimated data are not consistent and conclusive?
  - Worst-case assumptions
  - Request additional experimental data
    - Test strategy

Hydrocarbon block	Experimental	QSARs
C14	B/vB (SVHC)	?
C15	?	?
C16	?	?
C17	?	?
C18	?	?

Test strategy

- Select representative constituents
- Select test organism

Selection criteria?
Number of constituents
QSAR estimates
Availability
Presence
Extrapolation possibilities



Political and process challenges/considerations

Data request

- Selecting registrants
- Proportionality

Consequences of PBT identification (by blocks)

- Acceptance of uncertainty
- Focus on substances that matter
  - Fuels are exempted from authorization
- Social and economical consequences
- Enforceability

Conclusions

Hydrocarbon block	Conclusion	
C14	P/vP	B/vB
C15	P/vP	?
C16	P/vP	?
C17	P/vP	?
C18	P/vP	?

To consider:

- REACH came into force in 2007
- Substances with highest volume
- Three-ring PAHs is best studied category
- If not accept methodology: constituent-by-constituent