

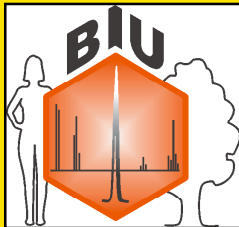


**DGF Workshop:  
„Weichmacher und andere Kontaminanten in pflanzlichen Ölen und Fetten“**

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**„Neue Kriterien für die Untersuchung und Beurteilung von PAKs in  
Speiseölen in der EU (EFSA-Liste)“**

**Albrecht Seidel**



Member of NOE ECNIS

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D-22927 Grosshansdorf**

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**Deutsche Gesellschaft für Fettwissenschaften e.V., Hagen 29. Mai, 2006**



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# PAH-Exposition

**Arbeitsplatz**

**Umgebungsluft**

**Raucherstatus**

**Nahrung**

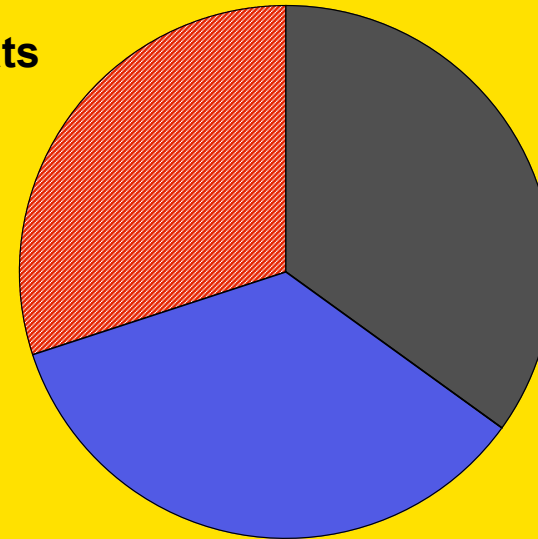


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## PAH in human diet

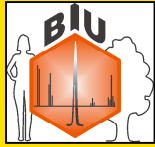
Country	Dietary intake of PAH ( $\mu\text{g}/\text{day}$ )
<b>United Kingdom</b> (Dennis et al. 1983)	<b>5</b>
<b>Netherlands</b> (de Vos et al. 1995)	<b>5-17</b>
<b>Italy</b> (Lodovici et al. 1995)	<b>3</b>
<b>New Zealand</b> (Thompson et al. 1996)	<b>3</b>

Oils and fats



Cereals

Vegetables, grilled meat, fruits,  
smoked fish, milk and milk products



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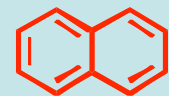
## Die PAK-Prioritätslisten der U.S.-EPA und der EFSA

- ★ **Die U.S.-EPA-Liste (16 PAK) berücksichtigt vorrangig das Umweltvorkommen (z.B. aus Fahrzeugabgasen, Industrieemissionen). Die Auswahl von PAK reicht von leicht- bis zu schwerflüchtigen Verbindungen gewichtet nach Vorkommen und carcinogener Wirkung.**
- ★ **Die neuere EFSA-Liste der EU zielt auf PAK in Lebensmitteln nur unter der Berücksichtigung ihrer carcinogenen bzw. genotoxischen Wirkung.**

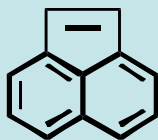


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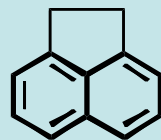
## Priority Polycyclic Aromatic Hydrocarbons (PAH) according to US-EPA



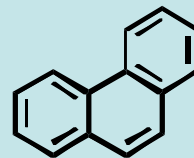
Naphthalene



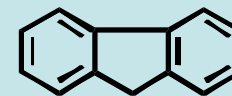
Acenaphthene



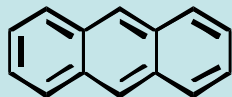
Acenaphthylene



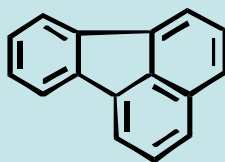
Phenanthrene



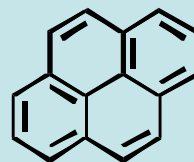
Fluorene



Anthracene



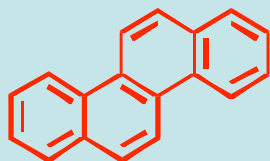
Fluoranthene



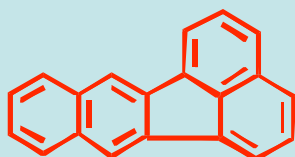
Pyrene



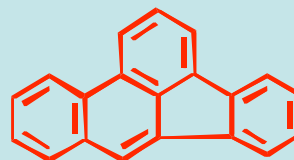
Benz[a]anthracene



Chrysene



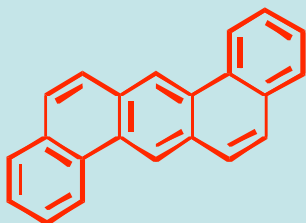
Benzo[k]fluoranthene



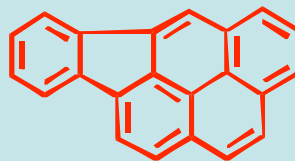
Benzo[b]fluoranthene



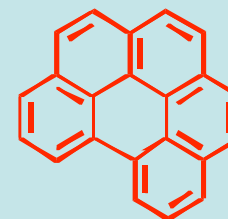
Benzo[a]pyrene



Dibenz[a,h]anthracene



Indeno[1,2,3-cd]pyrene

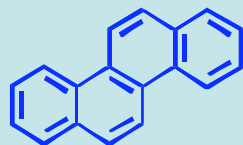


Benzo[ghi]perylene

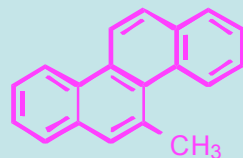


# Priority PAH according to EFSA and JECFA (FAO/WHO) to be included in monitoring programs - EU Recommendation 256/2005

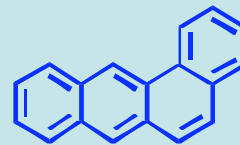
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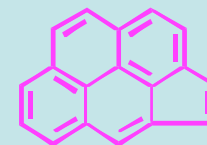
Chrysene



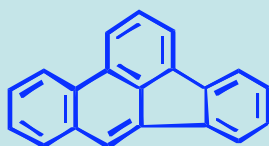
5-Methylchrysen



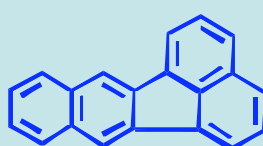
Benz[a]anthracene



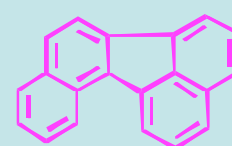
Cyclopenta[cd]pyrene



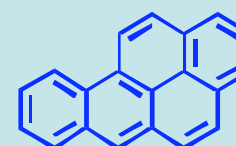
Benzo[b]fluoranthene



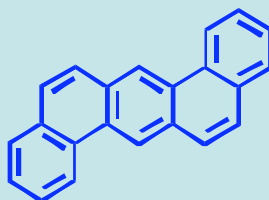
Benzo[k]fluoranthene



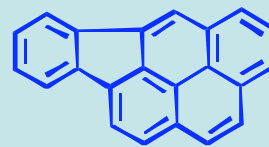
Benzo[j]fluoranthene



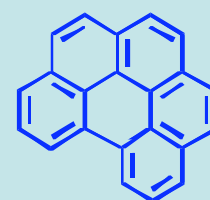
Benzo[a]pyrene



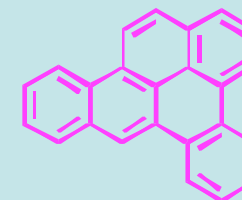
Dibenz[a,h]anthracene



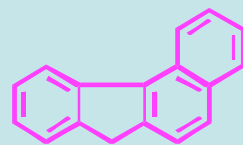
Indeno[1,2,3-cd]pyrene



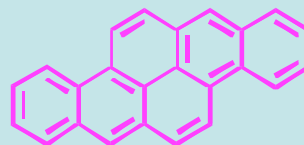
Benzo[ghi]perylene



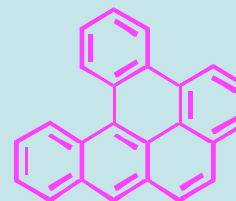
Dibenzo[a,e]pyrene



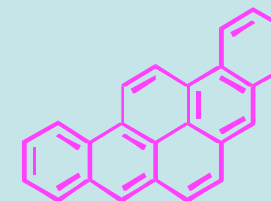
Benzo[c]fluorene



Dibenzo[a,h]pyrene



Dibenzo[a,l]pyrene



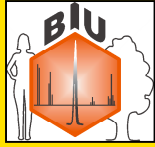
Dibenzo[a,i]pyrene



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## PAH in foodstuffs - EU Regulation 208/2005 (Apply 1st April 2005)

		Maximum levels ( $\mu\text{g}/\text{kg}$ fresh weight)
7.1	<b>Benzo[a]pyrene (lead compound)</b>	
7.1.1	<b>Oils and fats (excluding cocoa butter)</b>	<b>2.0</b>
7.1.2	<b>Smoked meat and smoked meat products</b>	<b>5.0</b>
7.1.3	<b>Smoked fish and smoked fish products</b>	<b>5.0</b>
7.1.4	<b>Meat of fish, other than smoked fish</b>	<b>2.0</b>
7.1.5	<b>Crustaceans, cephalopods, other than smoked</b>	<b>5.0</b>
7.1.6	<b>Bivalve molluscs</b>	<b>10.0</b>
7.1.7	<b>Baby foods for infants and young children - processed cereal based food</b>	<b>1.0</b>
7.1.8	<b>Infant milk and follow-on milk</b>	<b>1.0</b>
7.1.9	<b>Dietary food for special medical purposes intended specifically for infants</b>	<b>1.0</b>

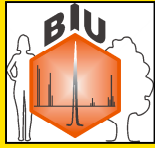


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## Verordnungen und Empfehlungen in EU-Ländern

PAH	Fleischverordnung (Deutschland, Österreich, Niederlande, Polen)	DGF in Deutschland
<b>„leichte PAH“ (3-4 Ringe)</b> Phenanthrene Anthracene Fluoranthen Pyren <b>Benz[a]anthracen</b> Chrysen		} <b>Summe: 25 ppb</b>
<b>„schwere PAH“ (5 Ringe und mehr)</b> <b>Benzo[b]fluoranthene</b> <b>Benzo[k]fluoranthene</b> <b>Benzo[a]pyren</b> <b>Benzo[ghi]perylene</b> <b>Indeno[1,2,3-cd]pyrene</b> <b>Dibenz[a,h]anthracene</b>	<b>1 ppb</b>	





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## IARC carcinogen classification for PAH and mixtures containing PAH

Gruppe 1*	Gruppe 2A*	Gruppe 2B*
Coal-tar pitches	Diesel engine exhaust	Gasoline engine exhaust
Coal-tar	Creosotes	Carbon black
Coal gasification		
Coke production	<b>Benzo[a]pyrene</b>	<b>Benzo[b]fluoranthene</b>
Aluminum production	<b>Benz[a]anthracene</b>	<b>Benzo[j]fluoranthene</b>
Mineral oils	<b>Dibenz[a,h]anthracene</b>	<b>Benzo[k]fluoranthene</b>
Shale-oils		<b>Dibenzo[a,e]pyrene</b>
Soots		<b>Dibenzo[a,h]pyrene</b>
Tobacco smoke		<b>Dibenzo[a,i]pyrene</b>
Smokeless tobacco products		<b>Dibenzo[a,l]pyrene</b>
		<b>5-Methylchrysene</b>
		<b>Indeno[1,2,3-cd]pyrene</b>

IARC Supplement 7, 1987, and IARC Volumes 46, 1989 and 65, 1996.



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## Neue IARC-Klassifizierung carcinogener PAK (2005)

Gruppe 1*	Gruppe 2A*	Gruppe 2B*
Benzo[a]pyren	Cyclopenta[cd]pyren Dibenz[a,h]anthracen Dibenzo[a,l]pyren	Benzo[a]anthracen Benzo[b]fluoranthren Benzo[j]fluoranthren Benzo[k]fluoranthren Chrysene Dibenzo[a,h]pyren Dibenzo[a,l]pyren Indeno[1,2,3-cd]pyren 5-Methylchrysen  Benz[j]aceanthrylen Benzo[c]phenanthren

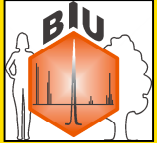
•Policy watch: Streif et al. (2005) Carcinogenicity of polycyclic aromatic hydrocarbons. *The Lancet* 6, 931-932.



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## Generelle Wirkungsweise carcinogener PAK

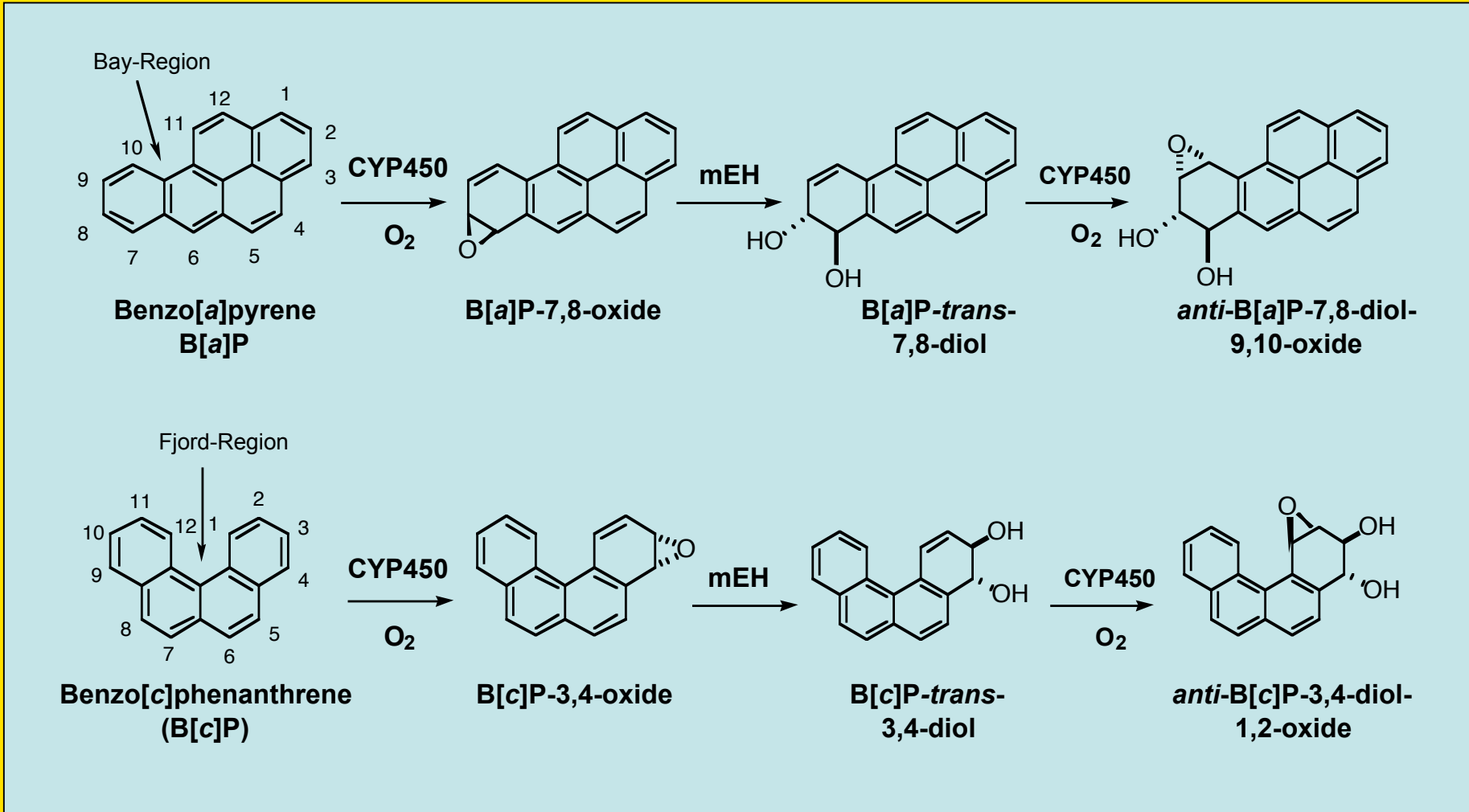
- ★ **Oxidativer Metabolismus zu reaktiven elektrophil-reaktiven Intermediaten, welche kovalent an die DNA, RNA und Proteine binden.**
- ★ **Bildung von DNA Addukten.**
- ★ **Tumorinitiation aufgrund der Genotoxizität und Mutationsbildung in spezifischen Oncogenen**
- ★ **Tumorpromotion aufgrund der Wechselwirkung mit dem „Aryl hydrocarbon (Ah)“-Rezeptor und Hochregulierung von Genen, welche in Bezug stehen zu Biotransformation, Zellwachstum und Zelldifferenzierung.**



# Structure-Activity-Relationships I

(Bay- and Fjord-Region Dihydrodiolepoxides)

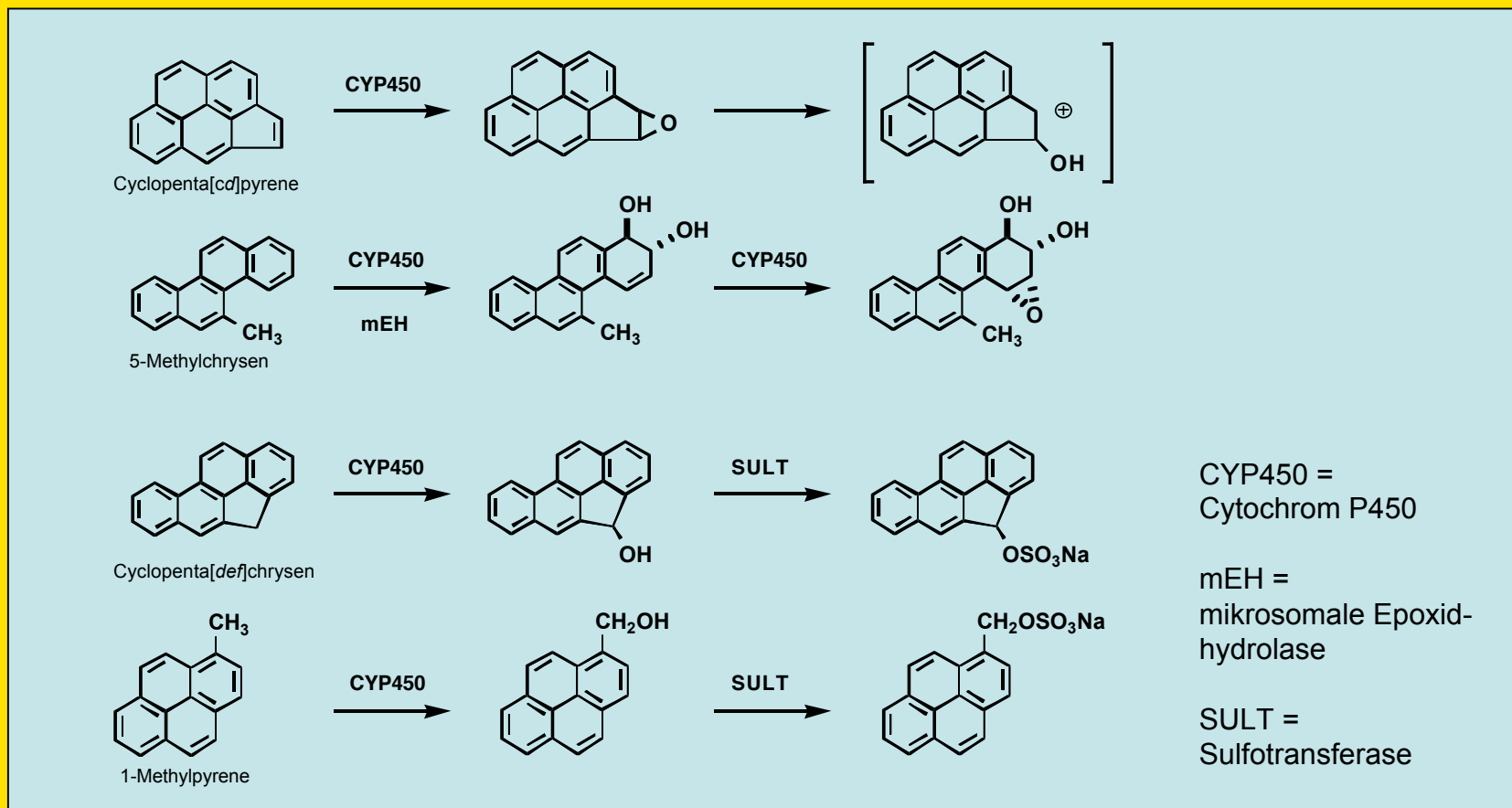
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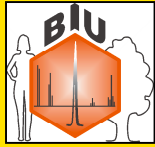




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## Structure-Activity-Relationships II (electrophilic benzylic carbo-cations)



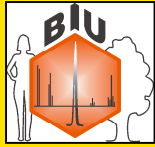


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## Toxic Equivalence Factors (TEF) for PAH

PAH - EPA	TEF	PAH - EPA/EFSA	TEF	PAH - EFSA	TEF
<b>Naphthaline</b>	<b>0,001</b>	<b>Benz[a]anthracene</b>	<b>0,1</b>	<b>Benzo[c]fluorene</b>	<b>-</b>
<b>Acenaphthylene</b>	<b>0,001</b>	<b>Benzo[a]pyren</b>	<b>1</b>	<b>5-Methylchrysene</b>	<b>-</b>
<b>Acenaphthene</b>	<b>0,001</b>	<b>Benzo[b]fluoranthene</b>	<b>0,1</b>	<b>Dibenzo[a,l]pyrene</b>	<b>10</b>
<b>Fluorene</b>	<b>0,001</b>	<b>Benzo[k]fluoranthene</b>	<b>0,1</b>	<b>Dibenzo[a,h]pyrene</b>	<b>10</b>
<b>Phenanthrene</b>	<b>0,001</b>	<b>Benzo[ghi]perylene</b>	<b>0,01</b>	<b>Dibenzo[a,l]pyrene</b>	<b>10</b>
<b>Pyrene</b>	<b>0,001</b>	<b>Chrysene</b>	<b>0,01</b>	<b>Dibenzo[a,e]pyrene</b>	<b>1</b>
<b>Fluoranthene</b>	<b>0,001</b>	<b>Indeno[1,2,3-cd]pyrene</b>	<b>0,1</b>	<b>Benzo[j]fluoranthene</b>	<b>0,1</b>
<b>Anthracene</b>	<b>0,01</b>	<b>Dibenz[a,h]anthracene</b>	<b>1</b>	<b>Cyclopenta[cd]pyrene</b>	<b>0,1</b>

<sup>a</sup> Collins, J.F. et al. (1998) *Regul Toxicol Pharmacol*, **28**, 45-54; <sup>b</sup> Jacob, J. and Greim, H. (Ed's) Polycyclische aromatische Kohlenwasserstoffe (PAH) Forschungsberichte (DFG), Wiley-VCH, Weinheim (2004).



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## Trennprobleme bei der GC-MS (SIM)

**Chrysen / Triphenylen** - abhängig von der GC-Kapillare

**Benzo[b]fluoranthen**

**Benzo[j]fluoranthen**

**Benzo[k]fluoranthen**

- abhängig von der GC-Kapillare

**5-Methylchrysen**

(BA, B[c]P und CHR = 24 Isomere mit gleichem MG)

**Benzo[c]fluoren**

- abhängig von der GC-Kapillare, B[a]F, B[b]F, B[c]F

**Dibenzo[a,/]pyren**

(LOQ = 0.1 ppb; MG 302 fragliche Spezifität)



# Zusammenfassung und Schlussfolgerungen

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- ★ Die aktuell empfohlene PAH-Monitoringliste der EFSA für Öle und Fette besteht aus 16 PAH (15 EFSA + 1 JECFA), deren Auswahl ausschließlich auf der carcinogenen Wirkung der einzelnen Verbindungen beruht .
- ★ Kakao-Butter soll am 1. April 2007 bewertet werden.
- ★ Die Belastung verschiedener Nahrungsmittel mit den 16 PAH (und andere) wird derzeit mittels einer Datenbank bei der EU erfasst und bewertet.
- ★ Insbesondere die Relevanz des 5-Methylchrysens als Leitverbindung für alkylierte PAH gilt es anhand des Vorkommens zu überprüfen.

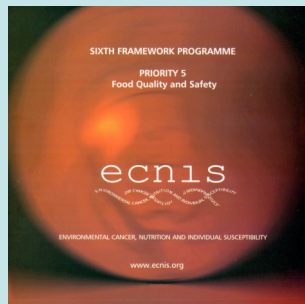




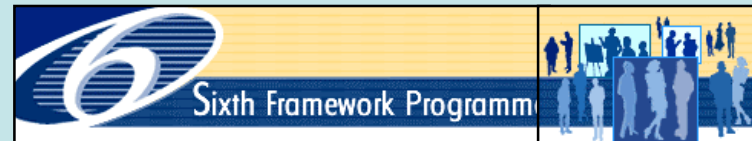
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## Acknowledgement

Financial support from the Network of Excellence ECNIS ([www.ecnis.org](http://www.ecnis.org)) is gratefully acknowledged.



**Network of excellence (NoE)  
Environmental Cancer, Nutrition and Individual  
Susceptibility**



**Priority 5, Food Quality and Safety**