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Management of Emerging Pollutants in the Marine Environment from the Perspective of a National Monitoring Authority

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Overview

- **Decision processes for selecting emerging pollutants**
- **Realisation of new investigations**
- **Examples**

Challenges for the analysis of organic pollutants in the marine environment

- **Very low concentrations (pg/L, ng/kg)**
- **Sampling**
 - Special techniques
 - Large sampling areas
 - Large dynamic ranges
- **Great variety of compounds**
- **Implementation of new pollutants**
- **Quality Assurance**



Consequences for the Implementation of new pollutants

- Development of new methods or at least improvement of existing procedures
- Procedure development and analysis
 - take more time,
 - are more expensive

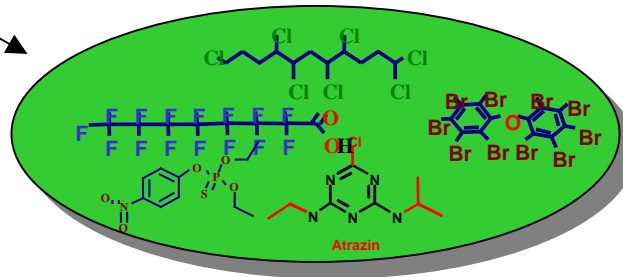
Principles

- Larger sampling amount
- Additional clean-up
- More selective detection

Routes to new Pollutants

Scientific approach

Rational, economic
Approach



Administrative Approach
(priority lists)

Scientific approach

- Structural considerations:
 - analogues, homologues (brominated FR, fluorinated compounds such as PFOS)
- Toxicological results
- Non-target screening
- Toxicity directed analysis

Selection based on industrial Products

Substances with intrinsic biological effects

Pesticides

Pharmaceuticals

„Personal Care“ Products

Insecticides, Herbicides,
Analgesic, Hormons,
Antibiotica, Zytostatica,
Fragrances, Tensides

Large Volume Chemicals

(without intrinsic biological effects)

Tensides,
Plasticizers, Flame
retardents

Priority Pollutant-Lists

- **Classic Pollutants**

- lipophilic **P**ersistent **O**rganic **P**ollutants
- „Dirty Dozen“:
 - Aldrine, Chlordane, **DDT**, Dieldrine, Endrine, Heptachlor, Mirex, Toxaphene
 - **PCB, HCB,**
 - **PCDD, PCDF**
- **HCH**
- **PAH**

- **Novel Contaminants**

- Hazardous Substances
 - OSPAR-List
 - HELCOM-List
 - EU-WFD
- Many different substance classes, often polar

Ways OSPAR and HELCOM deal with hazardous substances

**HSC
(DYNAMEC)**

**Persistency
Bioaccumulation
Toxicity
Large volume product
Ways of exposure
Environm. concentr.
(rivers, air)**

- Lists of Hazardous Substances
- Lists for priority action
- Lead country collects information
- Background papers
 - information lacking ? Mostly environmental concentrations of emerging pollutants are lacking for marine matrices
- One off surveys
- Recommendation for further monitoring

UBA

BSH

Ranking Criteria for implementing emerging Pollutants (for monitoring agencies)

- **Mandatory** (core) **parameter** or voluntary parameter in monitoring program?
- **Request by clients** (politics, administration, public)
- In how many lists is it mentioned?
- Scientific challenge, environmental demand

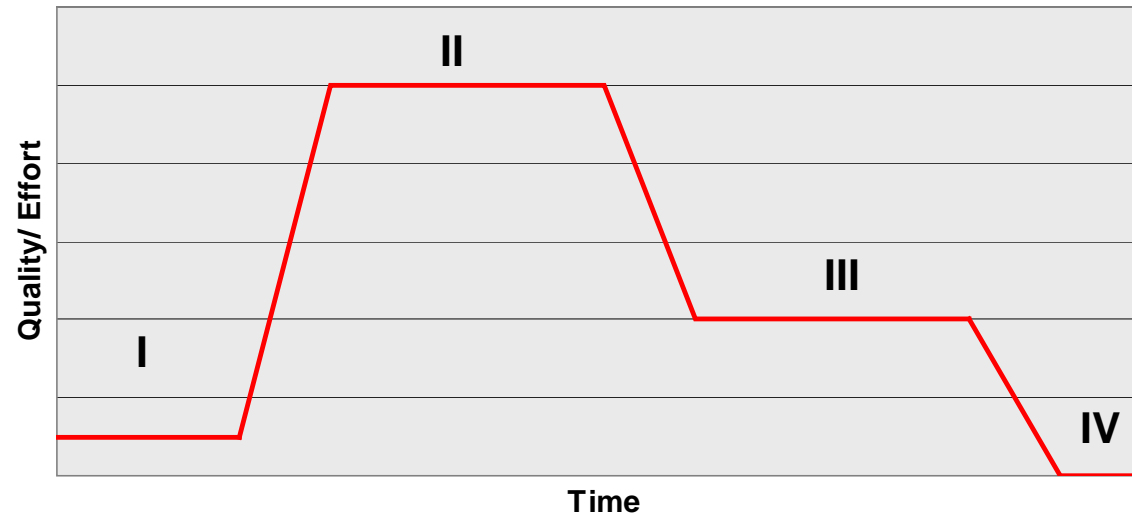
- Amount of work for implementation of new analysis
- Funding available

Realisation of new investigations

- **Problem**
 - No free valences for new method developments
 - No additional resources from our agency
- **Possible solutions**
 - Increase efficiency of all processes (sampling, analysis, data evaluation)
 - Adaptation of quality/effort of existing monitoring
 - Cooperations and research projects (funding)

- Increase of efficiency
- **Adaptation of quality levels**
- Cooperations and research projects

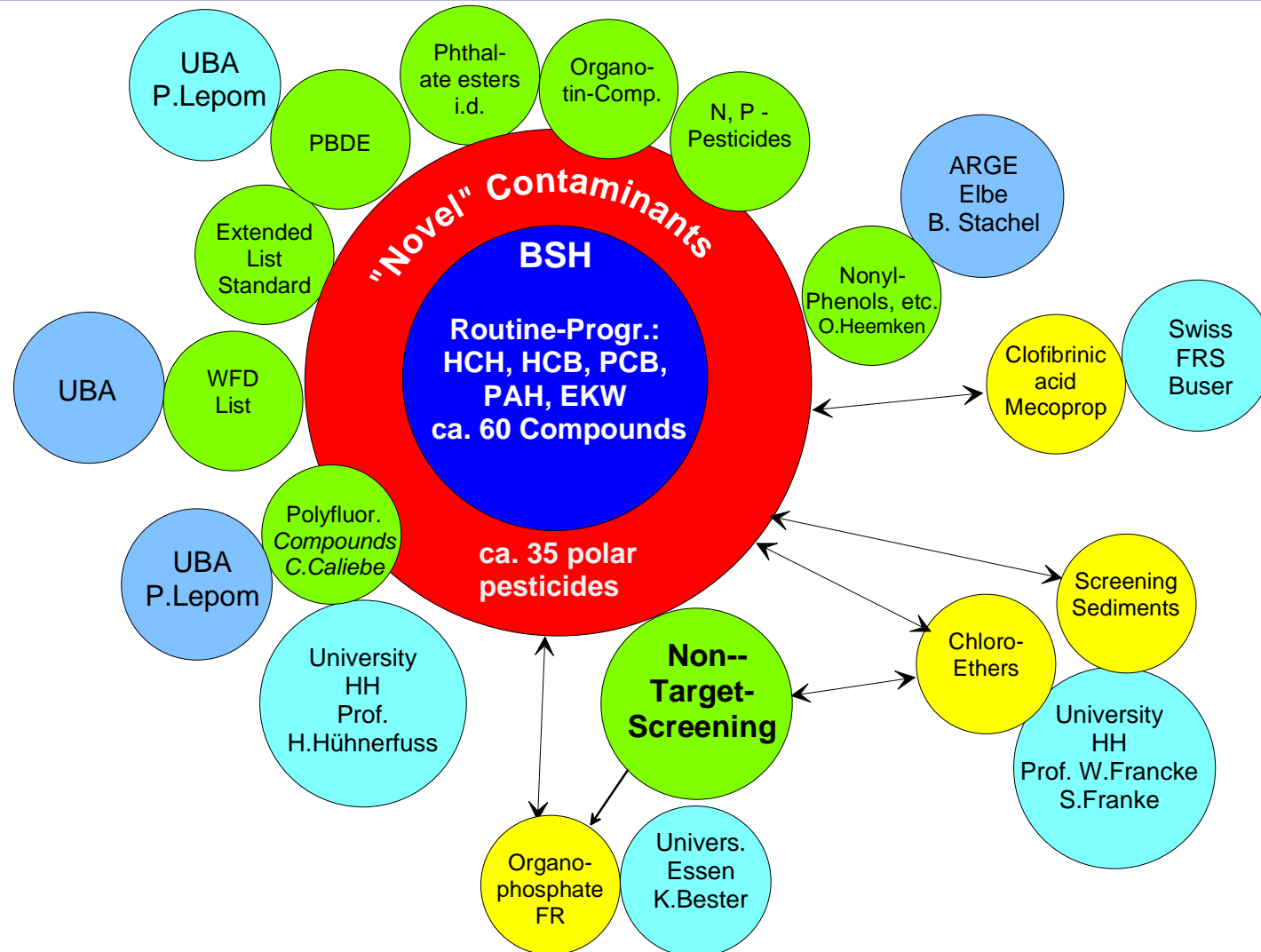
Optimising Quality and Effort - Monitoring Life Cycle



- Phase I: Screening
- Phase II: Monitoring + investigation of processes, correlations, distributions etc.
- Phase III: Reduced monitoring, support by modelling, interpolation, indicator compounds
- Phase IV: End of monitoring as problems are solved

Projects and Cooperations to investigate "novel" Compounds

- Economic aspects
- Increase of efficiency
 - Adaptation of quality levels
 - **Cooperations**
 - **Research projects**



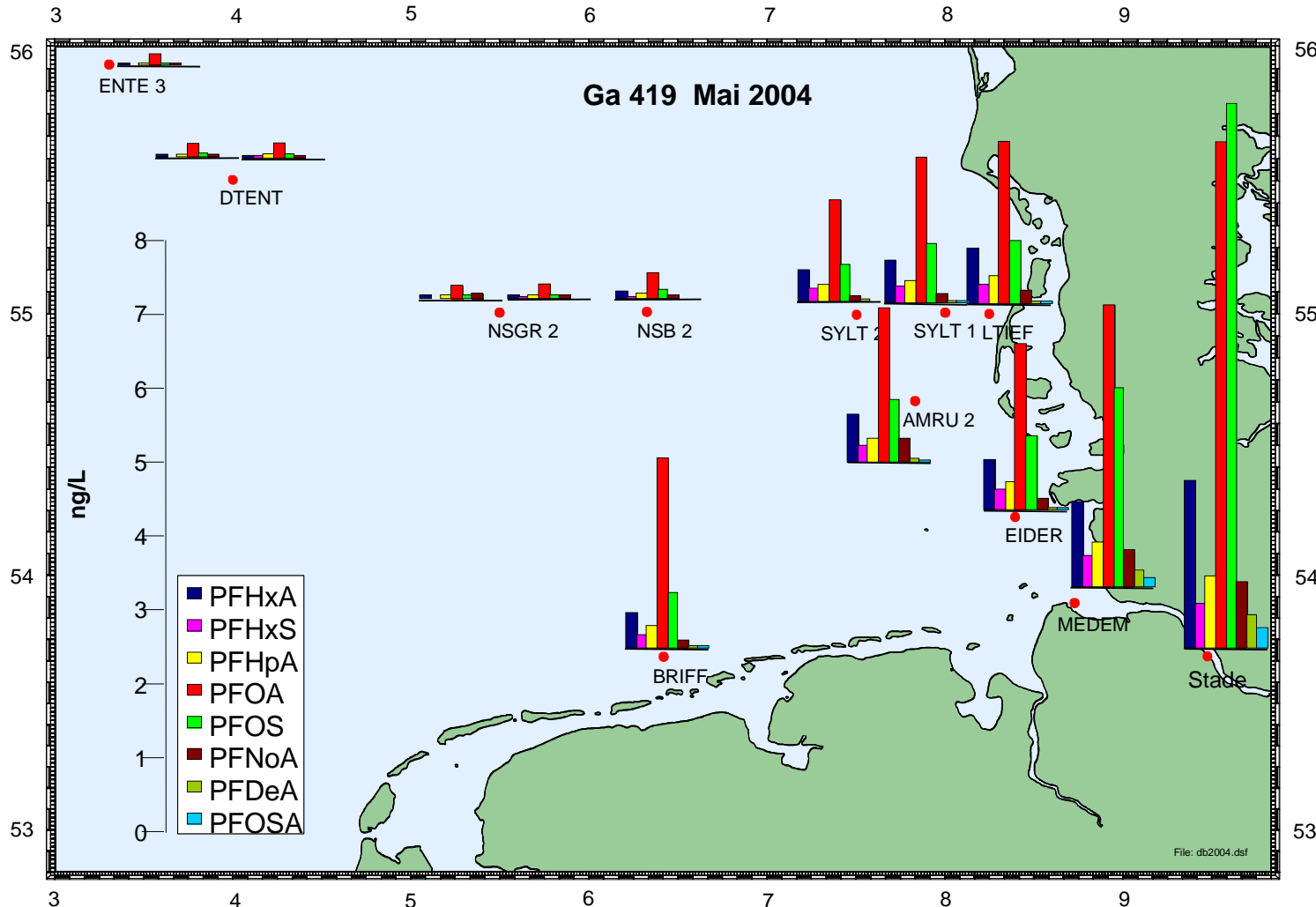
WFD-Priority Pollutants

Substance	Method	LOQ [ng/L]	Remarks
Brom. Diphenylether	GC-NCI-MS (UBA-Project)		Sed. / Biota
C10-30-Chloroalkanes	GC-MS-MS (UBA-Project)		Sed. / Biota
Anthracene	LLE GC-MS	0.003	
Hexachlorbenzene	LLE GC-MS-MS	0.001	
Hexachlorbutadiene	LLE GC-MS	0.01	
Hexachlorcyclohexane	LLE GC-MS	0.01	
Naphthalene	LLE GC-MS	0.05	
PAH (6 to 16 comp.)	LLE GC-MS	0.003	
Pentachlorobenzene	LLE GC-MS	0.005	
Trichlorobenzenes	LLE GC-MS	0.005	
Di(2ethylhexyl)phthalate	LLE GC-MS <i>special</i>	5.0	
Organotin Compounds	LLE/Derivat. GC-AED	0.5	
Nonylphenols	LLE/Derivat. GC-MS	2	
Octylphenols	LLE/Derivat. GC-MS	0.5	
Atrazine	SPE HPLC-MS-MS	0.3	
Diuron	SPE HPLC-MS-MS	0.1	
Isoproturon	SPE HPLC-MS-MS	0.1	
Simazine	SPE HPLC-MS-MS	0.4	
Alachlor	SPE HPLC-MS-MS	0.1	
Pentachlorophenol	SPE HPLC-MS neg.	0.2	
Chlorfenvinphos	SPE GC-NCI-MS	0.02	
Chlorpyrifos	SPE GC-NCI-MS	0.01	
Endosulfan	SPE GC-NCI-MS	0.03	
Trifluralin	SPE GC-NCI-MS	0.005	

Performance of Methods

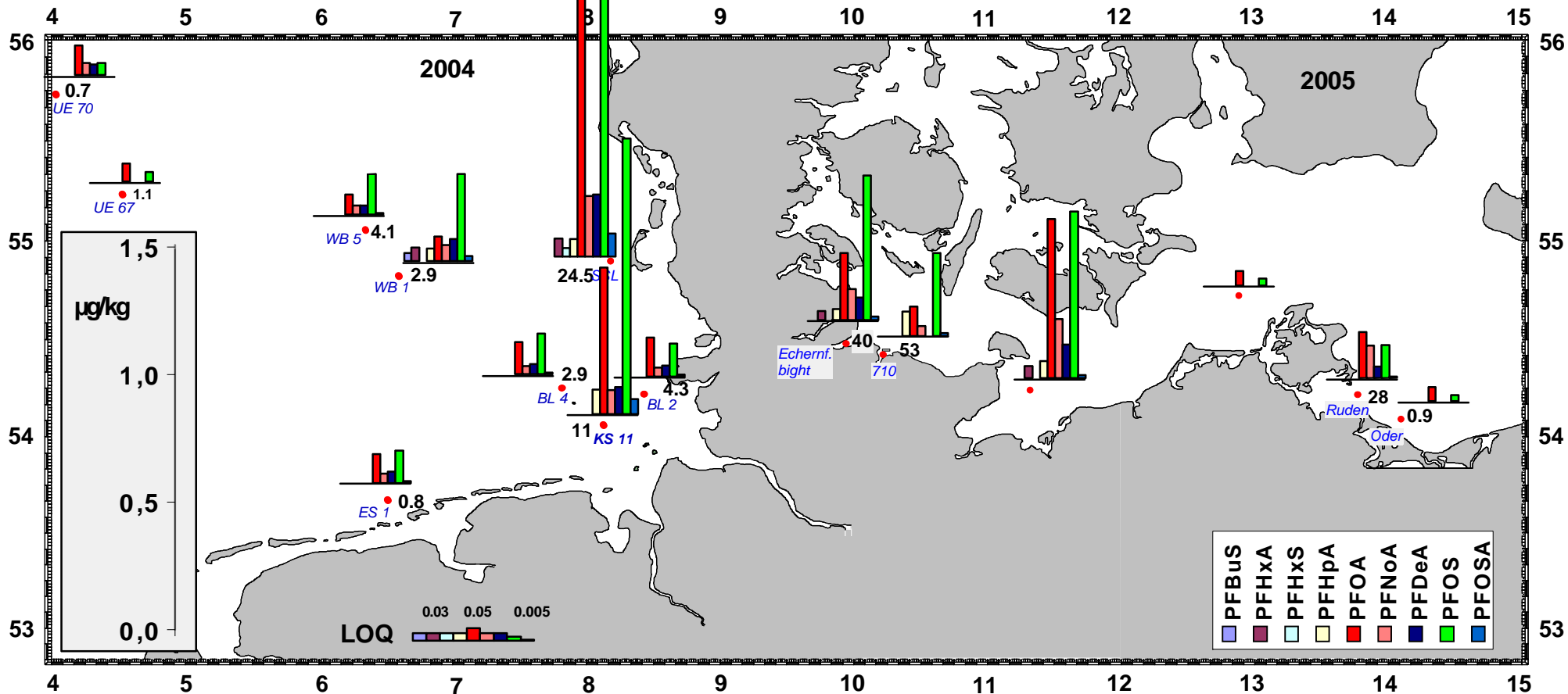
- Down to 50 pg/L: reasonable amount of effort
- Sensitivity and selectivity of GC-MS (EI-SIM) ok
- Below 10 pg/L: problems are getting bigger
 - Matrix background
 - Blanks
- Selectivity of GC-MS (EI -SIM) often insufficient:
 - additional pre-cleaning
 - NCI-MS
 - MS-MS
 - HR-MS
- Blank reduction: generally real hard work

Polyfluorinated Compounds in water of the German Bight (May 2004)



- Elbe ist significant source
- PFOA and PFOS are main compounds
- Concentrations similar to PAH and Herbicides
- Pattern of the compounds change
- PFCs can be detected in the open sea

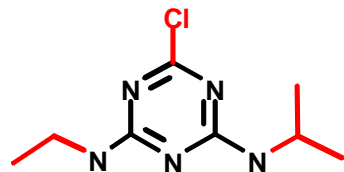
Polyfluorinated Compounds in marine Sediments (2004/ 2005)



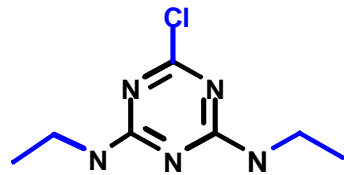
Triazine Herbicides



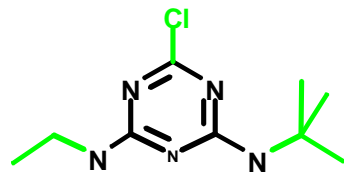
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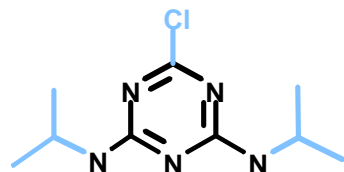
Atrazin



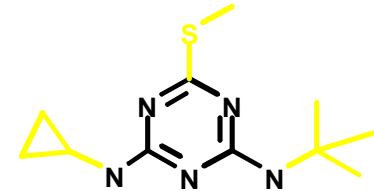
Simazin



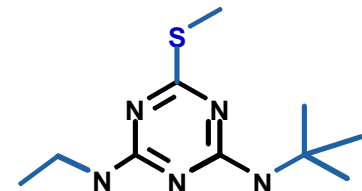
Terbutylazin



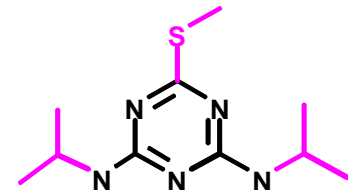
Propazin



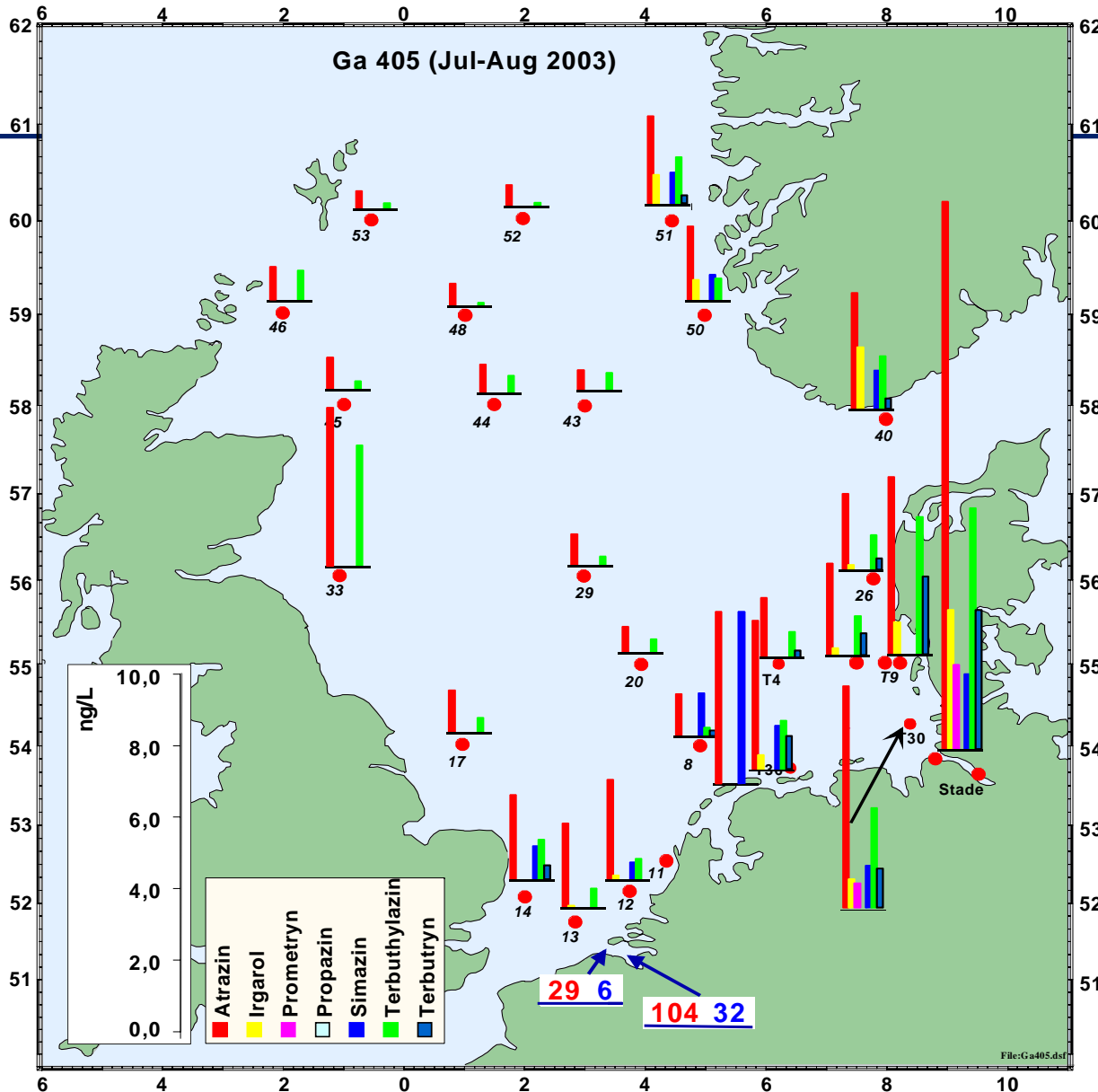
Irgarol



Terbutryn

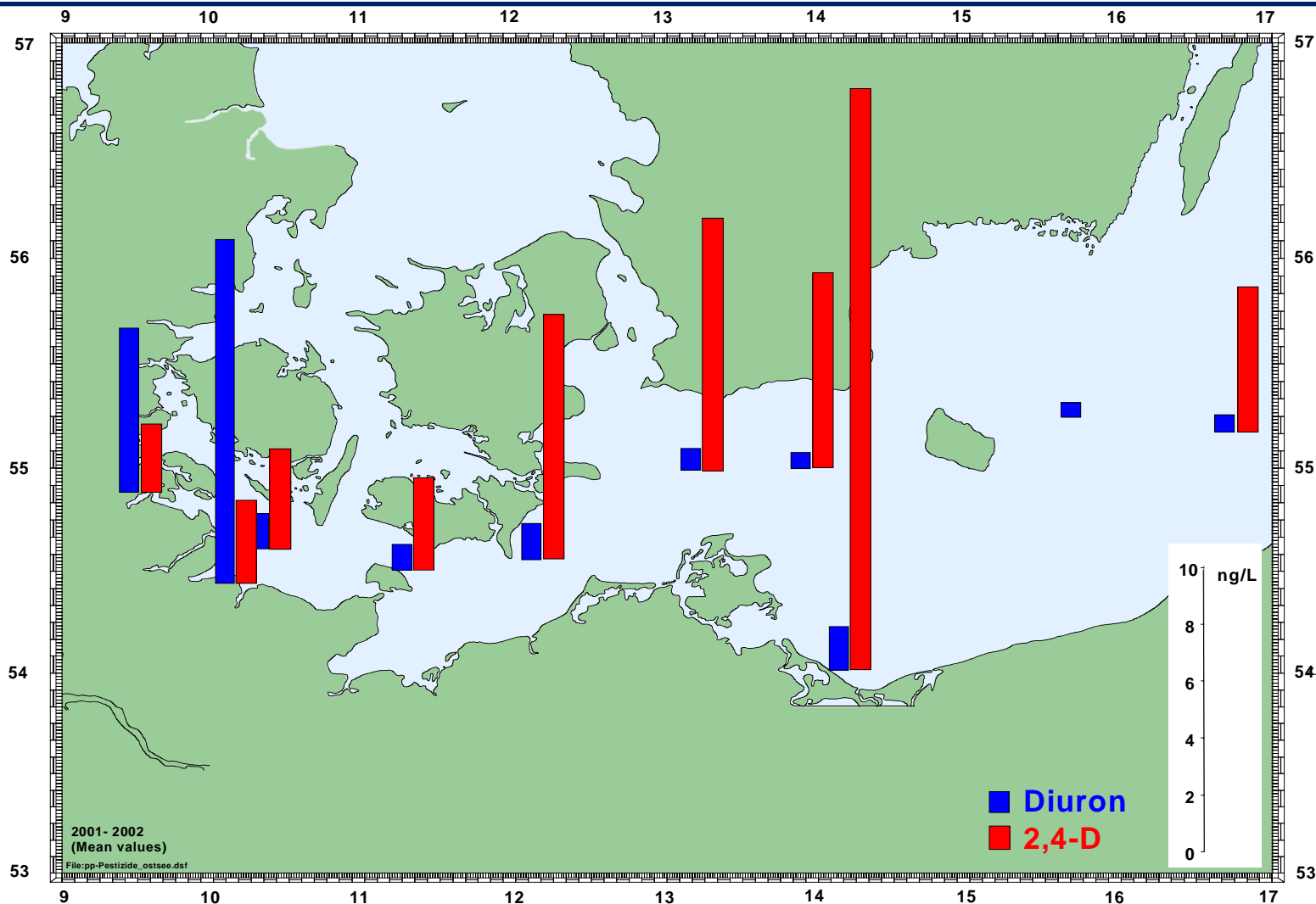


Prometryn

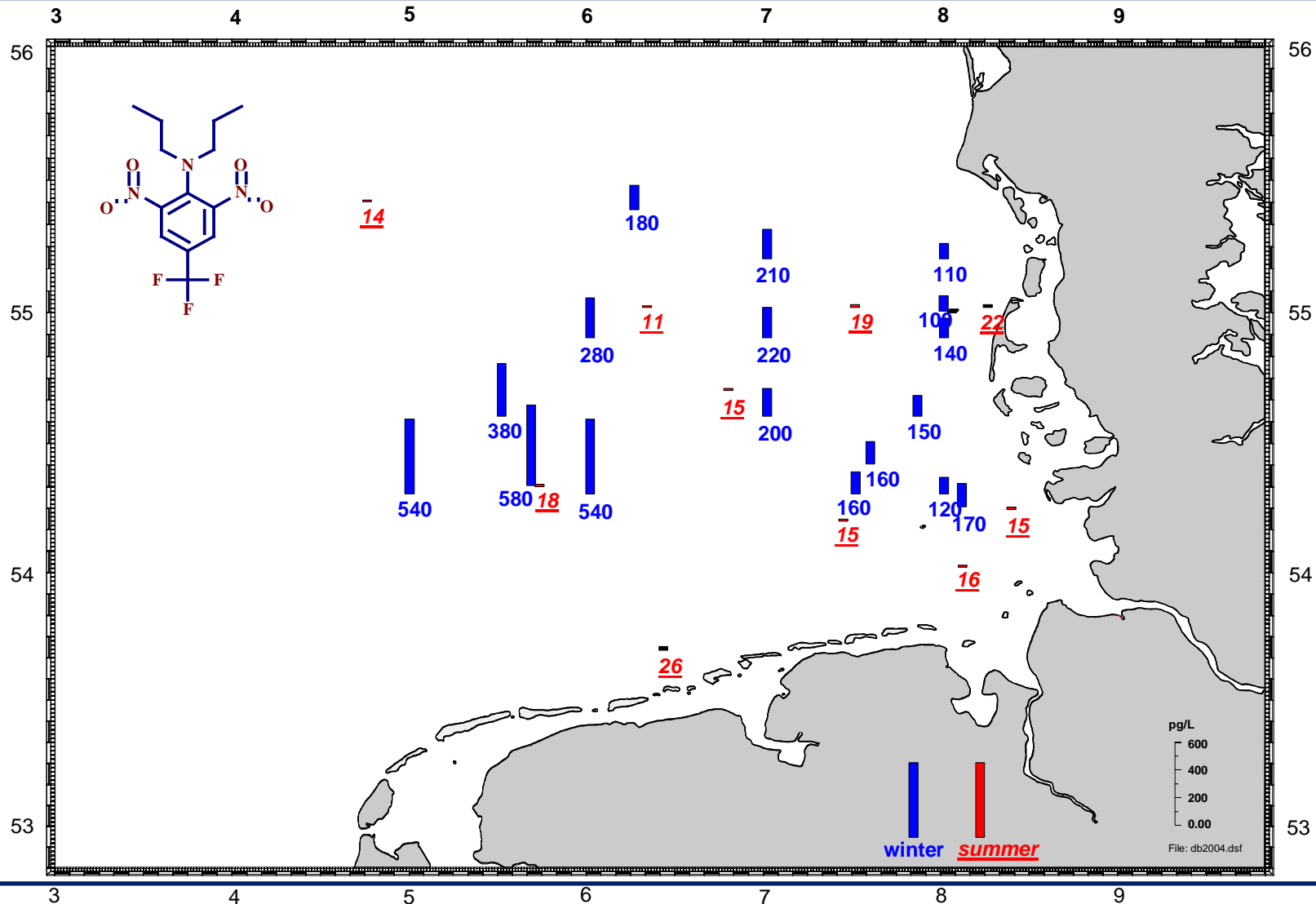


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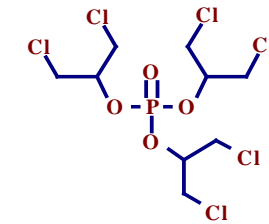
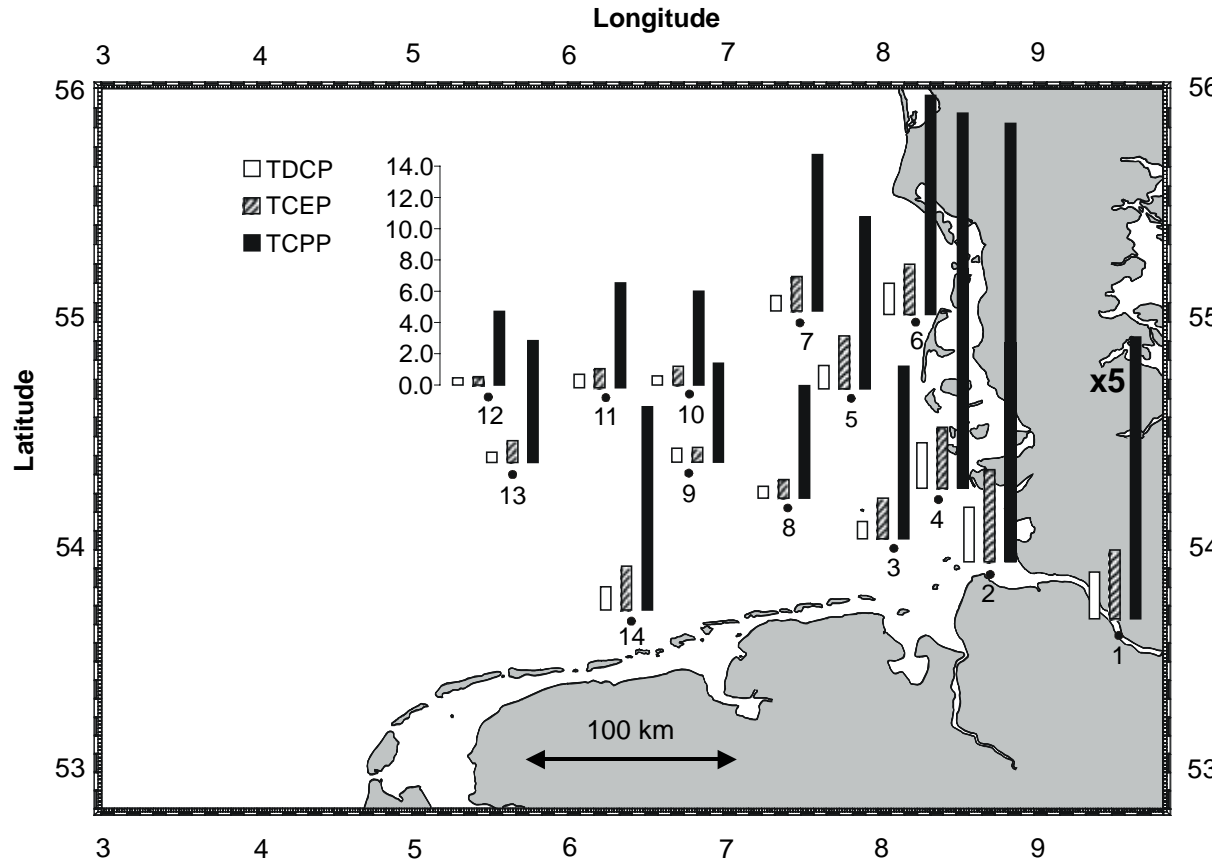
Diuron and 2,4-D in the Baltic Sea (Mean values 2000 -2002)



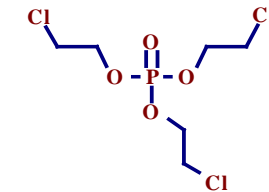
Trifluralin in the German Bight [pg/L] 2004 - 2005



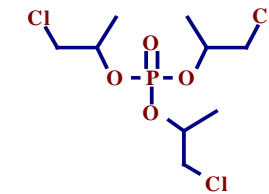
Chlorinated Organophosphate Esters



TDCP



TCEP



TCPP

New contaminants for Future Surveys

Polybrominated flame retardents

Chlorinated and brominated phenols

Endocrine disrupting compounds

TBT in sediments

Nonylphenols (re-evaluation)

Phthalate esters (re-evaluation)

Pharmaceuticals

Komplexing agents (EDTA, NTA)

New pesticides (Glyphosat)

Others

Summary

- OSPAR, HELCOM and EU have set up valuable tools for identification and ranking of emerging pollutants
- Investigations on emerging pollutants is a very demanding analytical and logistic challenge - especially in the Marine Environment
- It is a permanent challenge, as the list of analysing compounds has to be updated constantly
- Rapid information exchange is necessary
- Cooperation with other institutions is of vital importance

Thank you for your attention



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