The role of waste management in the control of hazardous substances: Lessons learned

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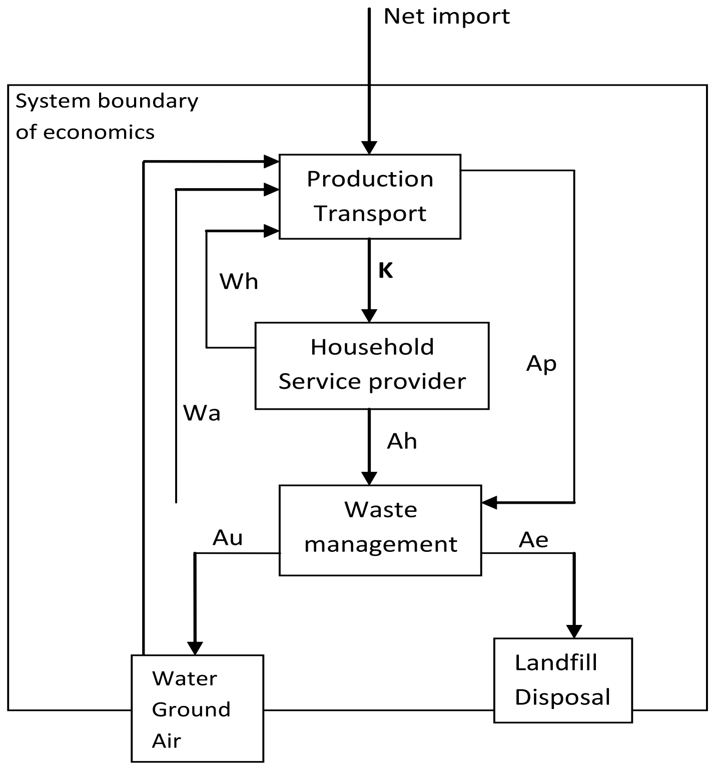
- Scope of the work
- Life cycle of products and substance chain management
- Two examples: PCBs and CFCs
  - Application areas
  - Regulations for products and waste disposal
  - Solved and unsolved problems
- Challenges for waste management
- Conclusions

Propagation of hazardous substances

Scope of the work

- Global propagation is well known from environmental contaminants
- Globalization of contaminated secondary resources will accelerate the propagation of hazardous substances
- Which solutions may be offered by waste management?

Waste management
in the life cycle of products



$$Ae(t) + Au(t) = Ap(t) + Ah[K(t), d, 1/Wh(t)] - Wa(t)$$

Ae (t)	Amount of waste	Wh, Wa	Recycling streams
K (t)	Stream of product	Au (t)	Waste going in the environment
d	Duration of use	Ae (t)	Waste for final disposal zone

Experienced strategy in case of dangerous compounds widely used

- Ban the substance in question
- Close point sources

Chemicals policy

- Clean up the technosphere as far as possible
- Stop the carry-over of contaminants in secondary resources

Waste management

- Avoid transport from the environment back to man or endangered biota

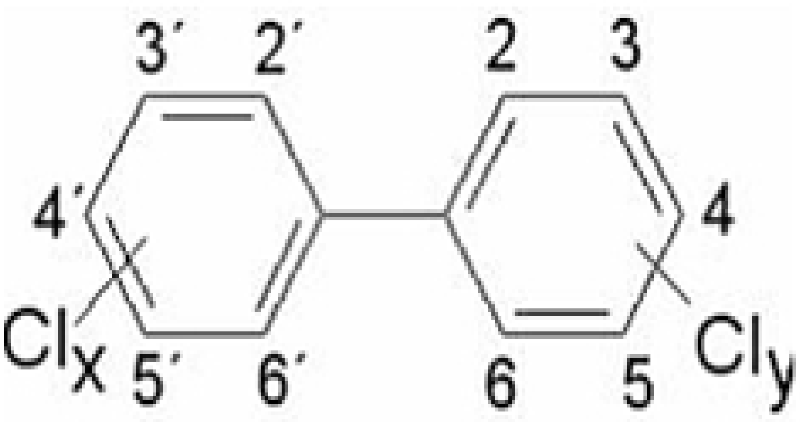
Environmental policy, consumer protection

Waste management acting as a vacuum cleaner for hazardous products?

Imagine the „Recall“ of a dangerous substance – in which problems are we running in?

- Time lag between the placing of the product on the market and the restrictions for use
- Time lag between the start of production and the disposal of the last products in use.
- Dilution of the hazardous substance as one (potentially low concentrated) component in products
- High dissipation of products with the substance in question in the technosphere.
- Costs for proper disposal of products contaminated by a hazardous component (as an incentive for mixing it up with normal waste)

Example #1: PCBs



- **Good isolating properties**
- **Hardly inflammable**
- **Very stable against heat and light**
- **209 congeners**
- **1.5 Mio Mg sold as technical mixtures (oils, waxes) between ~1930 and ~1990**
- **Use: One third in „open“ and two third in „closed“ applications**
- **By-product of uncomplete combustion of chlorine containing products**

Important physicochemical properties of PCBs in relation to chlorine substitution

	101	118	138	153	180
	2 4 5 2'5'	2 4 5 3'4'	2 3 4 2'4'5'	2 4 5 2'4'5'	2 3 4 5 2'4'5'

Density	1.182-1.566 kg/l →
Melting point	26°C - 306°C →
Ignition point	170° - 380°C →
Solubility in water	← 0.0027 – 0.42 ng/l
Log Kow	4.5 – 8.26 →
Vapor pressure	← 10^{-4} - 10^{-12} atm (25°C)
Henry constant	← 0.018 – 0.8 atm.l/mol
Toxicity	Structure related toxicity · 0.0001 TEQ · Toxicity not depending on chlorine content

PCBs: Areas of application and disposal

	Type of PCB used	Type of application	Intended vs. *usual* way of disposal	Separation from other items
Isolating agent in transformers	Cl >=54%	„closed“	Special waste	Easy
Hydraulic fluid for mining equipment	Tri- and tetra-CBs	„closed“	Special waste	Difficult in under-ground mines
Isolating agent in small capacitors	Cl<=42%	„closed“	WEEE (special collection) vs. *household waste*	Possible in sorting plants
Additive to joint sealer	All technical mixtures	„open“	Hazardous waste vs. *mixed construction waste*	Only in BAT dismantling process

PCBs: Problems to be solved

- **Cleaning and disposal (or refilling) of large transformers**
- **Collection and disposal of large capacitors used for industrial applications.**
- **Collection and disposal of hydraulic oils contaminated with PCBs**
- **Disposal of small capacitors filled with PCB from electric equipment, normally used in discharge lamps and electric household appliances**
- **Collection and destruction of contaminated building rubble**
- **Collection and disposal of other goods (e.g. PVC parts containing PCB) from households and commerce**
- **Reclamation of contaminated sites like former production plants, ruins from large building fires (e.g. department stores, administrative buildings with own electricity supply)**
- **Prevention of “de novo” PCB synthesis.**

Regulations for PCBs

- **Ban of PCBs for all applications within a given time frame**
  - **Items with maximum volume 1000 ml until 2000 / 2010**
- **Labeling of all large items containing PCB > 5000 ml or an overall concentration of > 50 mg/kg**
- **Limit values for ambient air (workers‘s protection)**
- **Limit values for fodder and food**
- **Limit values for (used) mineral oil**
- **Waste containing PCBs > 50 mg/kg classified as hazardous**
- **Regulation of disposal methods**
- **Restriction of transboundary shipment**
- **World wide ban (POP convention)**

Successful attempts for the „recall“

- PCBs in large industrially used items (transformers, large capacitors, heat exchanger…)
  - Exception: Mining equipment
- PCBs from destruction or reconstruction of old buildings
  - Only in the case of a contamination identified by systematic research (e.g. from ambient air measurements)
- PCBs from contaminated grounds
  - If the contaminated areas are digged out
- PCBs from small capacitors
  - Only if electronic waste is separately collected
  - And only if the collected items are handled properly

Safe disposal methods for PCBs

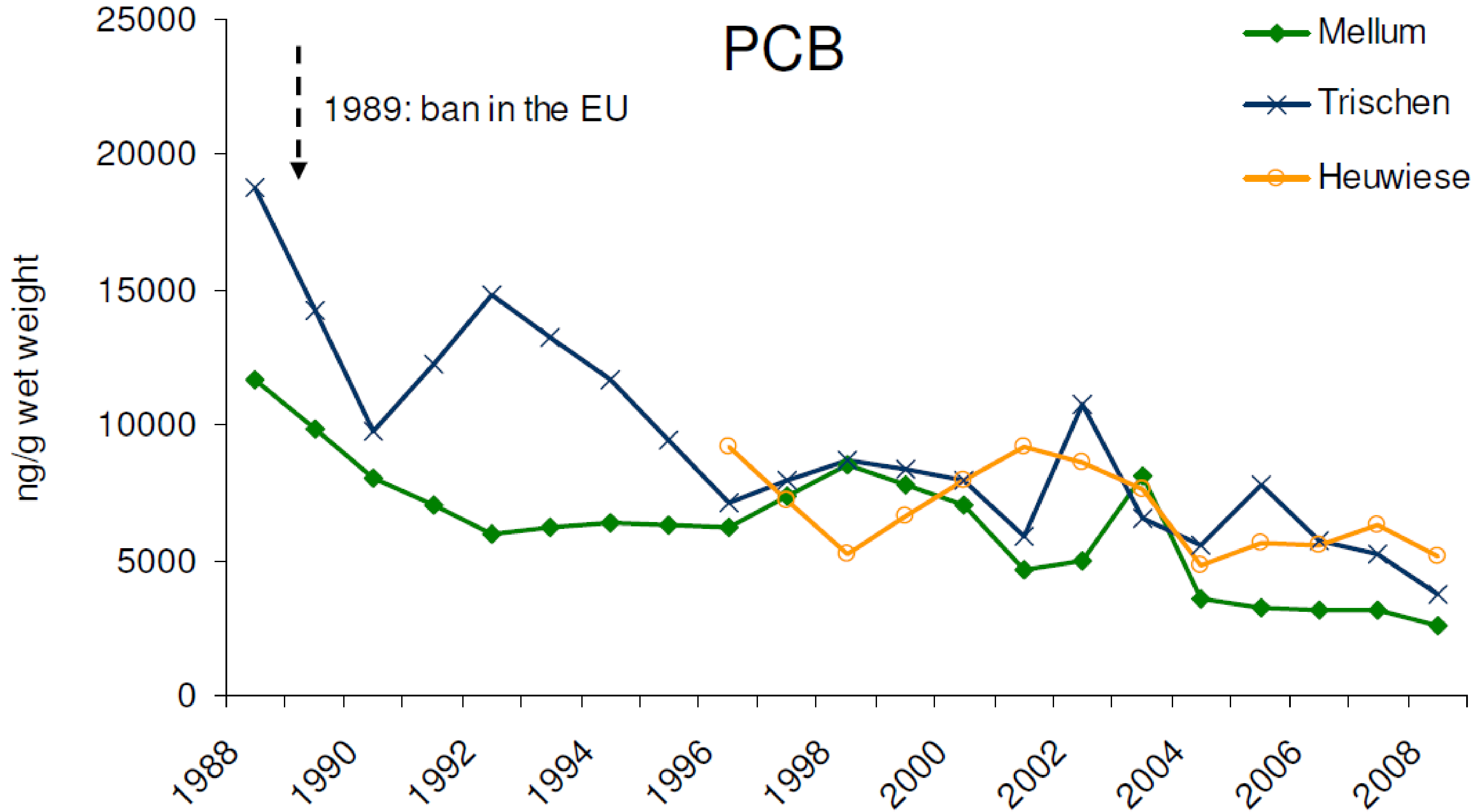
- **Safe sinks**
- **Incineration ~1200° C (rotary kiln for high contaminated waste)**
- **Incineration ~ 1000° C (MWI for low contaminated waste)**
- **Plasma torch…**
- **Chemical destruction by Na, K… (useful for high concentrated waste)**
- **Disposal of contaminated products (non-flammable) in salt mines**

- **Unsafe storage**
- **Landfill**
- **New partioning equilibria**
- **MBT**
- **Potential new source**
- **Incineration << 1000° C, e.g. use of contaminated marine diesel**

PCB contaminated items: properly disposal or uncontrolled emissions?

- **Yearly emissions from residual appliances (assessed by UBA):**
  - **1,700 kg in 1990**
  - **221 kg in 2009**
- **PCBs from small capacitors collected, sorted and destructed (cf. Bundesregierung):**
  - **3.5 Mg of PCB containing capacitors in 2008**
- **Waste contaminated with PCB disposed: More than 11,000 Mg waste in 2008 (cf. Statistisches Bundesamt)**
- **PCBs from transformers and large capacitors:**
  - **85,500 Mg disposed in salt mines (1990-1996)**
- **New problems:**
  - **Contaminations in sorting facilities**
  - **Contaminations in transformer recycling facilities (14,000 Mg transformers recalled from salt mines)** [http://starweb.hessen.de/cache/DRS/18/6/02666.pdf]
- **No actual PCB balance on a national or international level available**

Development of ambient PCB concentrations: Herring gull eggs from the North Sea and the Baltic



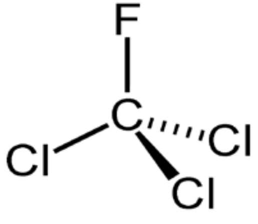
Fliedner et al.: Levels and trends of industrial chemicals (PCBs, PFCs, PBDEs) in archived herring gull eggs from German coastal regions

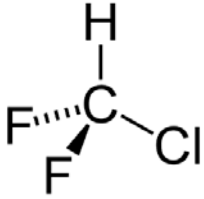
Environmental Sciences Europe 2012, **24**:7 doi:10.1186/2190-4715-24-7

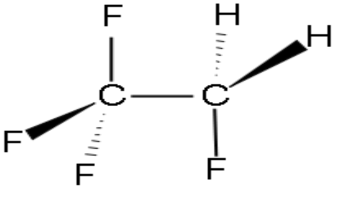
Development of ambient PCB concentrations: Blood of German students

Sample origin		1997			2010	
	PCB 138	PCB 153	PCB 180	PCB 138	PCB 153	PCB 180
Münster	0.91	0.55	0.43	0.19	0.21	0.14
Greifswald	0.68	0.52	0.31	0.15	0.16	0.11
Halle	0.74	0.44	0.30	0.15	0.17	0.11
Ulm	0.62	0.45	0.34	0.15	0.17	0.12

Example # 2: CFC‘s, HCFCs







- **Non-flammable**
- **High Joule Thomson coefficients**
- **Gases or low boiling liquids at normal temperature**
- **Use: Refrigerants, solvents, foaming agents, propellant gases,…**
- **Not toxic for humans**
- **Very persistent in ambient air**
- **Fugitive**

Comparison of ODPs and GWPs of some typical CFCs and HCFCs

	Formula	Global emissions in 2008 [Gg yr^{-1}]	ODP	GWP
F-11	CCl_3F	52-91	1.0	4,000
F-12	CCl_2F_2	41-99	1.0	8,500
F-22	$CHClF_2$	385-481 (sum of all HCFCs)	0,05	1,700
F-23	CHF_3	12	0	14,200
F-134a	CF_3 -CH_2F	149$\pm$27	0	1,370

CFCs / HCFCs and substitutes: Types of application

Area of use	Type of chemical used	Application
Cooling agent (freezers, refrigera-tors…)	F-11 → HCFCs → Pentane	Closed
Propellant gases for aerosols	F-11, F-12 → F-134a and other fluorinated hydrocarbons → Pro-pane/Butane → pressurized air	Open
Foam blowing agent for polyurethane and polystyrene	F-11, F-12 → F-22 → F-134a, F-152a	Open
Air condition for automobiles	F-22 → F-134a → 2,3,3,3-Tetrafluoropropene → CO_2	partially open

CFCs / HCFCs: Montreal Protocol and beyond

- Ban of CFC (with respect to their ODP) in a time frame economically tolerable also for developing countries
  - With the exception of the amount needed for the production of other chemicals
  - with the exception of special applications (security, medicine)
  - Reduction of production and consumption to decreasing fractions of the production and use in foregoing years
  - No international regulations for banks
  - „… facilitate early phase-out of the production and consumption…“
- Ban of HCFCs (substitutes for CFCs) in a similar way
- Ban of some fluorinated hydrocarbons (with respcet to their GWP)

Further European / German regulations

- **Avoid emissions from leakages of closed systems**
  - By technical guidelines for their smooth and safe operation
  - By ensuring maintenance to be performed by skilled personal
- **Avoid emissions from devices after use**
  - By collection of the devices not longer in use
  - By separation of CFCs, HCFCs,…
  - By proper disposal of CFCs, HCFCs,… (incineration)

Phasing out CFCs – what‘s going wrong?

- **Obtaining CDM certificates by fraud**
  - **Unnecessary production of F-22 obtaining the by-product F-23 (3% related to F-22, GWP=11,700) to be destroyed**
- **Losses of Freon from partially closed systems**
  - **Automobile climate systems not completely sealed**
- **Theft of copper tubes from used refrigerators**
  - **Before or during collection**

Emissions of Freon gases [Mg/yr.]

Point sources	CFCs	HCFCs
Germany	0.83 (+0.11)	18.7 (+5.5)
Europe	85.6 (+0.11)	770 (+44)

Assessment for Germany: Losses from destroyed refrigerators and freezers 140 Mg/yr.

Point sources documented in the PRTR (E-PRTR)

http://prtr.ec.europa.eu/

Experience from waste management for dangerous substances I

The clean up phase is significantly retarded

- by the lifetime of products containing the contaminants in question,
- by the amount of these chemicals emitted during their life cycle,
- by the persistence of the emitted substances in natural environment.

Experience from waste management for dangerous substances II

- **The clean up will be extremely difficult**
  - In case of forgotten applications
  - In case of dissipative uses
  - In case of highly entropic applications
- **In the clean-up phase, closed systems must be carefully controlled**
  - to prevent losses by leakages or improper maintenance
- **The clean up will be considerably disturbed**
  - If there is lack of suitable disposal techniques
  - If the costs for proper disposal are relatively high
  - If the contaminant is mixed up in used products or waste with valuable resources

Conclusions I

- Substances banned for further use will show up in the waste chain even if the products are out of use.
- Globalization of trade without harmonizing the rules for the use of hazardous substances may end up with serious contamination of secondary raw materials.
- Hazardous compounds may be separated successfully from used products or waste,
    - If they are mostly used in industry and not in households,
    - if they can be identified as part of certain products,
    - if their concentration in these products is rather high,
    - if technical problems come up with secondary raw materials,
    - if there is international support for proper waste management.
- Regulations for workers' protection against the substances in question facilitate the identification of contaminated areas and equipment.

Conclusions II

- **Activities of the informal sector may considerably disturb the “cleanup” of the technosphere by collection and recycling of products contaminated with hazardous substances.**
- **Incineration (WtE) is a “safe sink” for hazardous waste and as well for contaminated products, if separation of hazardous materials and resources is not possible.**
- **Material input for long-range application should be very carefully documented (e.g. construction passport for houses) to facilitate safe deconstruction.**
- **Regulations for the waste management of products should be supported by mass flow balances for hazardous chemicals as well as for scarce non-renewable resources.**

Thank you for your attention!

Capacitor filled with PCBs at idr-eg‘s decontamination site for hazardous waste, Düsseldorf

Riskcycle Conference
Dresden, May 8-9, 2012

The Assessment of mixtures of Chemicals

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Toxicity and the assessment of mixtures of chemicals

Joint Opinion of DG SANCO SCs 2011

- Scientific Committee on Health and Environmental Risks
- Scientific Committee on Emerging and Newly Identified Health Risks
- Scientific Committee on Consumer Safety

BACKGROUND

The EU Chemicals legislation, in common with the situation in other parts of the world, is based predominantly on assessments carried out on individual substances. However, in reality humans are exposed to a wide variety of chemicals throughout their lives as indeed are animals and plants. While current assessment methods incorporate safety factors to take account of a range of uncertainties,
the Commission is concerned to ensure that EU chemicals' legislation takes proper account of the latest scientific information on mixture toxicity.

In the light of the above considerations,
SCHER/SCCS/SCENIHR (and experts of relevant agencies: EFSA, EEA, EMA, ECHA) have been asked to advise the Commission on 6 issues related to chemical mixture.

Structure of the Opinion

3.1 Problem formulation

3.2 Scope of the opinion

3.3 General Principles of Mixture Toxicology

3.4 Methodology

3.4.1 Effects assessment

3.4.1.1 Whole-mixture approaches

3.4.1.2 Component based approaches

3.4.2 Specific aspects relating to ecological effects assessments

3.4.3 Exposure assessment

3.4.3.1. Human

3.4.3.2. Environment

3.5 Uncertainty

3.6 Discussion

3.7 Conclusions and Recommendations

3.3 General Principles of Mixture Toxicology

Already more than 50 years ago, three basic types of action for combinations of chemicals were defined (Loewe und Muischnek, 1926; Bliss, 1939; Plackett and Hewlett, 1948, 1952):

- similar action (dose/concentration addition)
- dissimilar action (independent action)
- interactions

Dose/concentration addition (similar action, similar joint action): chemicals in a mixture act by the same mechanism/mode of action, and differ only in their potencies.

Independent action (response addition, effect addition): chemicals act independently from each other, usually through different modes of action that do not influence each other (simple dissimilar action).

Interactions: synergism and antagonism
describes the combined effect of two or more chemicals as stronger (synergistic, potentiating, supra-additive) or weaker (antagonistic, inhibitive, sub-additive, infra-additive) than expected from dose/concentration-addition or response-addition (changes of absorption, impaired inactivation, enzyme induction etc).

Based on the major principles and evaluating studies for which joint effects at or below individual NOEL(C)s have been suggested the opinion concludes:

Except for mixtures composed of substances with a similar mode of action, current evidence does not show significant mixture toxicity at exposures at or below zero-effect levels of the individual components.

However, NOELs or NOECs determined in experimental studies do not necessarily reflect a “true” no-effect level (see section 3.3). Safety factors are therefore applied to NOEL or NOECs for deriving the TDI, DNEL, PNEC or any other value. Under such conditions no unexpected effects will occur.

3.4.1 Effect assessment

Whole mixture approaches

Advantage: accounts for any unidentified materials and for any interactions among mixture components.

Disadvantage: no specific information on interactions or toxicity of individual components.

Component based approaches

- Knowledge of modes or mechanisms of action of individual components, dose-response information, concentrations
- Information on groups of similar or identical modes of action (assessment groups).

Grouping of mixture components
If (eco)toxicological data are lacking on the individual components or the mixture, read across, TTC or (Q)SAR-based approaches could be used for grouping on the basis of chemical structure e.g. using the OECD (Q)SAR Application Toolbox (OECD, 2009). For each group or individual chemical a limit value needs to be derived. This value can be based on the limit value of a representative substance in a group.

Grouping by toxicological or biological responses/ effects
Grouping of chemicals having similar endpoints including dose descriptors for critical effects such as benchmark doses, LOAELs or NOAELs.
The advantage is that for many chemicals such information is available.

Dose/concentration addition approaches

Methods for dose/concentration addition approaches:

- the Hazard Index (HI),
- the Reference Point Index (RfPI) or Point of Departure Index (PODI),
- the Relative Potency Factor (RPF)
- the Toxic Equivalence Factor (TEF)
- The toxic unit concept preferentially used in environmental toxicology

Terms of reference and Conclusions

1. Is there scientific evidence that when organisms are exposed to a number of different chemical substances, that these substances may act jointly in a way (addition, antagonism, potentiation, synergies, etc.) that affects the overall level of toxicity?

- Chemicals with <u>common modes of action</u> produce combination effects that are larger than the effects of each mixture component . These effects can be described by <u>dose/concentration addition</u>.
- For chemicals with <u>different (independent) modes of action</u> no robust evidence is available that exposure to a mixture is of health concern if the individual chemicals are present at or below their zero-effect levels.

- The examples, in which independent action has been expected, dose (concentration) addition slightly overestimated the actual mixture toxicity. This suggests that the use of the dose/concentration concept for unknown toxic mechanisms is sufficiently protective.

- For ecological effects, exposure to mixtures of dissimilarly acting substances at low but potentially relevant concentrations should be considered relevant, even if all substances are below the individual PNECs.

- Interactions (including antagonism, potentiation, synergies) usually occur at medium or high dose levels (relative to the lowest effect levels). At low exposure levels they are either not occurring or toxicologically insignificant.

2) If different chemical substances to which man/environment are exposed can be expected to act jointly, which affects their impact/toxicity, do the current assessment methods take proper account of these joint actions?

- Different chemical substances may act jointly in a way which affects their toxicity for man and the environment. Current assessment methods for mixtures can take account of joint actions, such as dose/concentration addition or response / effect addition generally only under specific circumstances. With these methods, effects of chemical mixtures composed of either dissimilarly or similarly acting substances can be reasonably well predicted.
- Interactions, are generally more difficult to assess and require expert judgement on a case-by-case basis.

3) Several approaches for the assessment of the mixture effects of chemicals already exist such as dose addition and independent action. What are the advantages and disadvantages of the different approaches and is there any particular model that could be considered as sufficiently robust to be used as a default option?

- In cases of similar mode of actions a dose/concentration addition approach is appropriate.
- Its application to mixtures with unknown modes of action may result in an over-prediction of toxicity, whereas the independent action approach may underestimate toxicity. Therefore, a dose/concentration addition approach is preferable to ensure an adequate level of protection.
- A significant limitation of component-based approaches is that they are only applicable to mixtures of which the major components are known.

4) Given that it is unrealistic to assess every possible combination of chemical substances what is the most effective way to target resources on those combinations of chemicals that constitute the highest risk for man and the environment?

- Exposure to one or more components approaching the threshold levels for adverse effects mean~~s~~ that the mixture should be given priority for assessment. A TTC like approach can be used to eliminate combinations that are of low or no concern.
- For the environment, attention should be paid to mixtures of chemicals, individual components of which approach the PNEC.
- In view of the difficulty to retrieve or generate an appropriate dataset for hazard characterisation and exposure estimates, a tiered approach may be considered.

5) Where are the major knowledge gaps with regard to the assessment of the toxicity of chemical mixtures?

- A major knowledge gap is the limited number of chemicals for which there is good mode of action information.
- In ecotoxicology knowledge of all possible modes of actions in the different types of organisms of a complex biological community is difficult (or impossible) to be attained. On the other hand, <u>ecologically relevant endpoints are generally broader</u> and not so specific (*e.g.* toxicity on specific organs, *etc.*) as in human toxicology.

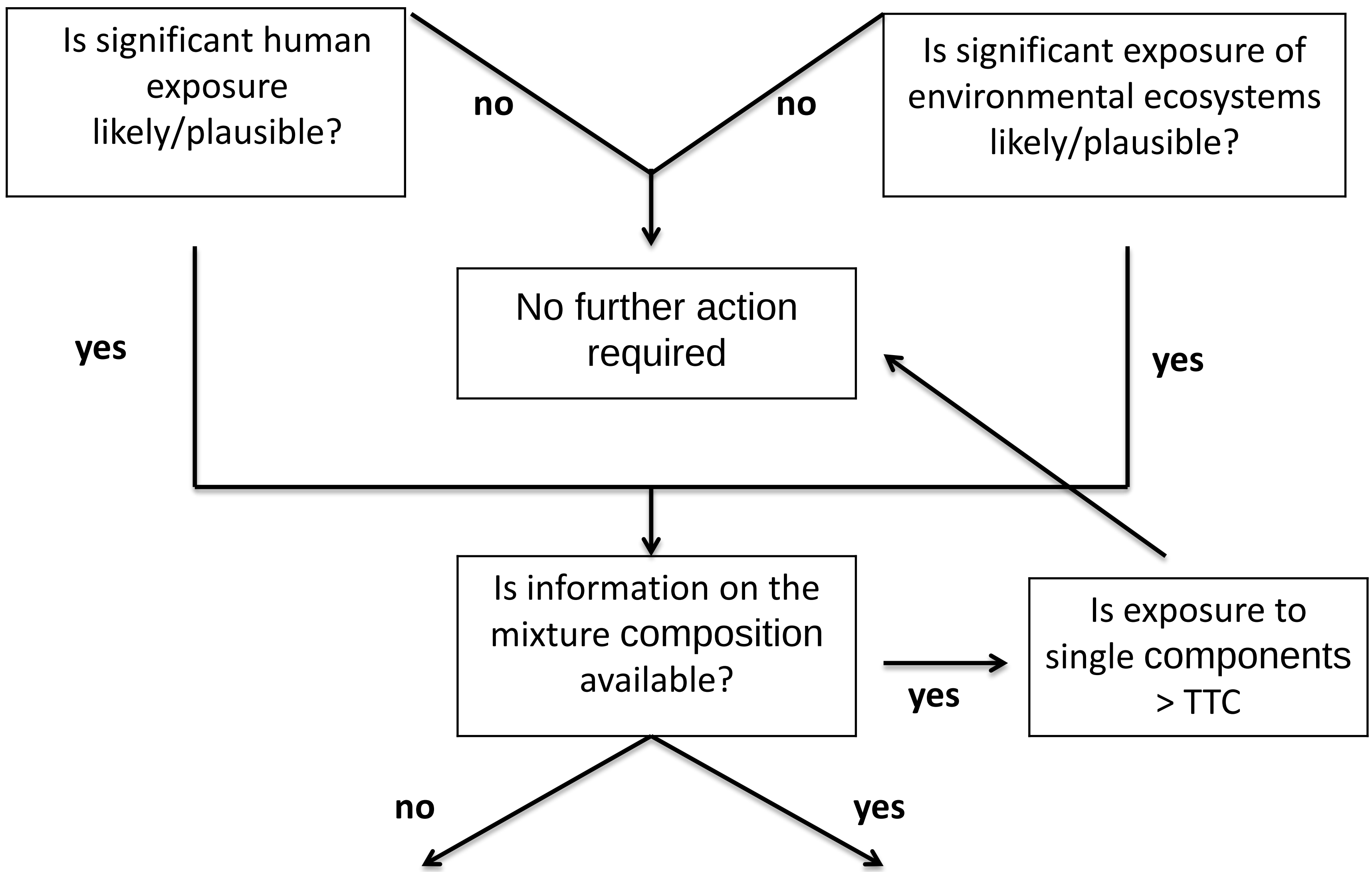
Other major knowledge gaps are:

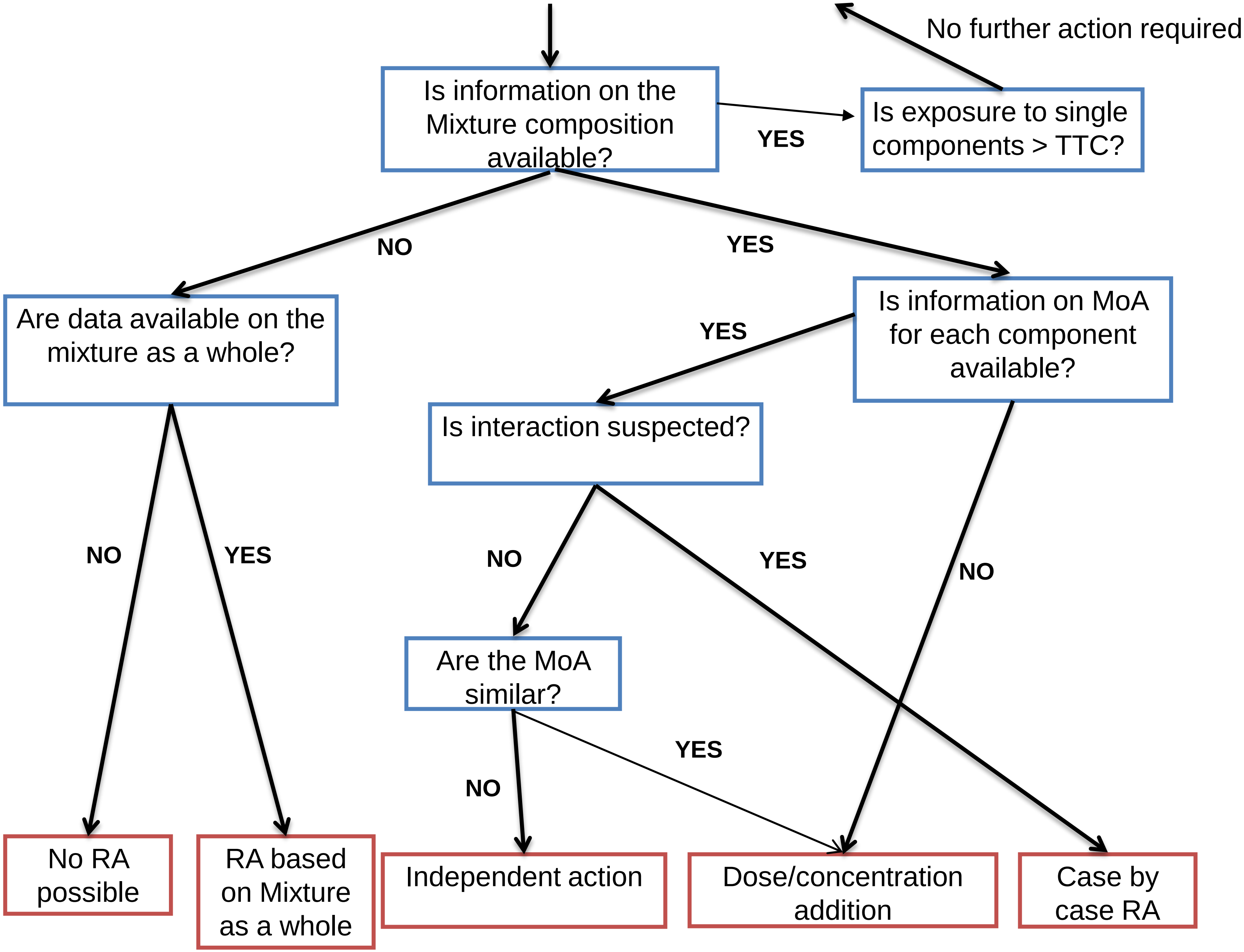
- The general lack of robust and validated tools for the prediction of interactions.
- How exposure and/or effects change over time

6) Does current knowledge constitute a sufficiently solid foundation upon which to address the toxicity of chemical mixtures in a more systematic way in the context of EU legislations?

- In many cases, knowledge on concentration and effects of components is insufficient for a robust scientific analysis.
- If toxicologically significant interactions can be excluded, either a dose addition or independent action model should be applied.
- Grouping of chemicals into categories and assessment groups may cover insufficient information.
- In ecotoxicology the dose/concentration addition concept may be generally appropriate for predicting effects at the population level.

Decision tree for the risk assessment of mixtures





No further action required
Is information on the Mixture composition available?
YES
Is exposure to single components > TTC?
NO
YES
Are data available on the mixture as a whole?
Is information on MoA for each component available?
YES
Is interaction suspected?
NO
YES
NO
YES
NO
Are the MoA similar?
YES
NO
No RA possible
RA based on Mixture as a whole
Independent action
Dose/concentration addition
Case by case RA

The draft opinion has been published for public consultation
Deadline for submissions: September 9, 2011

There have been no major science based objections

Access: Toxicity and Assesssment of Chemical Mixtures

http://ec.europa.eu/health/scientific_committees/environmental_risks/opinions/index_en.htm#id9

SCHER-Opinions: others

Opinion of SCHER/SCCS/SCENIHR and institutions of the EC: EFSA, EEA, EMEA, ECHA

The TTC concept describes Levels of "no appreciable risk" (ug/person per day)

Structural alerts	microg/person and day
Alerts for genotoxicity	0.15
Any other compound without alerts for genotoxicity	1.5
Specific structural classes (e.g. organophosphates)	18
Cramer Class III	90
Cramer Class II Cramer Class I	540 1800

Structural classes see Toxtree 2008

Studies, which have been used to suggest joint effects of independently acting compounds:

Study with guppies (Hermens et al 1985): LD50 measured of mixtures, without determining the individual NOECs.

Studies with algae (reproduction) (Faust *et al.* 2003, Walter *et al.* 2002): The studies resulted in additive effects as predicted.

Study on human breast cells (Payne *et al.,* 2001): Although the individual concentration-response plots showed differences in shape and position, the combined effect could be predicted on the basis of dose-response.

Receptor-ligand interaction

Replacement of a physiological ligand, *i.e.* an oestrogen from the receptor by a competitor, i.e. a xenoestrogen, depends on its relative affinity to the receptor and its concentration. For example, replacement of the physiological ligand from the receptor by a compound of 1000-fold lower affinity requires a 1000-fold higher concentration than the endogenous compound.

Although this oversimplifies competitive interaction of compounds at a receptor, it demonstrates the need for information on the <u>relative binding affinities of the compounds in question and their concentration</u> in the organism.

Hazard Index (HI): the sum of the Hazard Quotients (HQ), *i.e.* the ratios between exposure and the Reference Value (RV) for each component to be evaluated.

Reference Point Index (RfPI): the sum of the exposures to each chemical expressed as a fraction of their respective RfPs (also known as Point of Departure) for the relevant effect (e.g., the dose that causes a 10% effect, or the NOAEL).

Relative potency factor methods/Toxic equivalency factor/ potency equivalency factor.

Toxic Units (TUs) concept: used in ecotoxicology, represents the ratio between the concentration of a component in a mixture and its toxicological acute (e.g. LC50) or chronic (e.g. long term NOEC) endpoint.