PTS THE PAPER TECHNOLOGY SPECIALISTS

RESOURCES | FIBRE COMPOSITES | SURFACES | ECOLOGICAL RELEVANCE

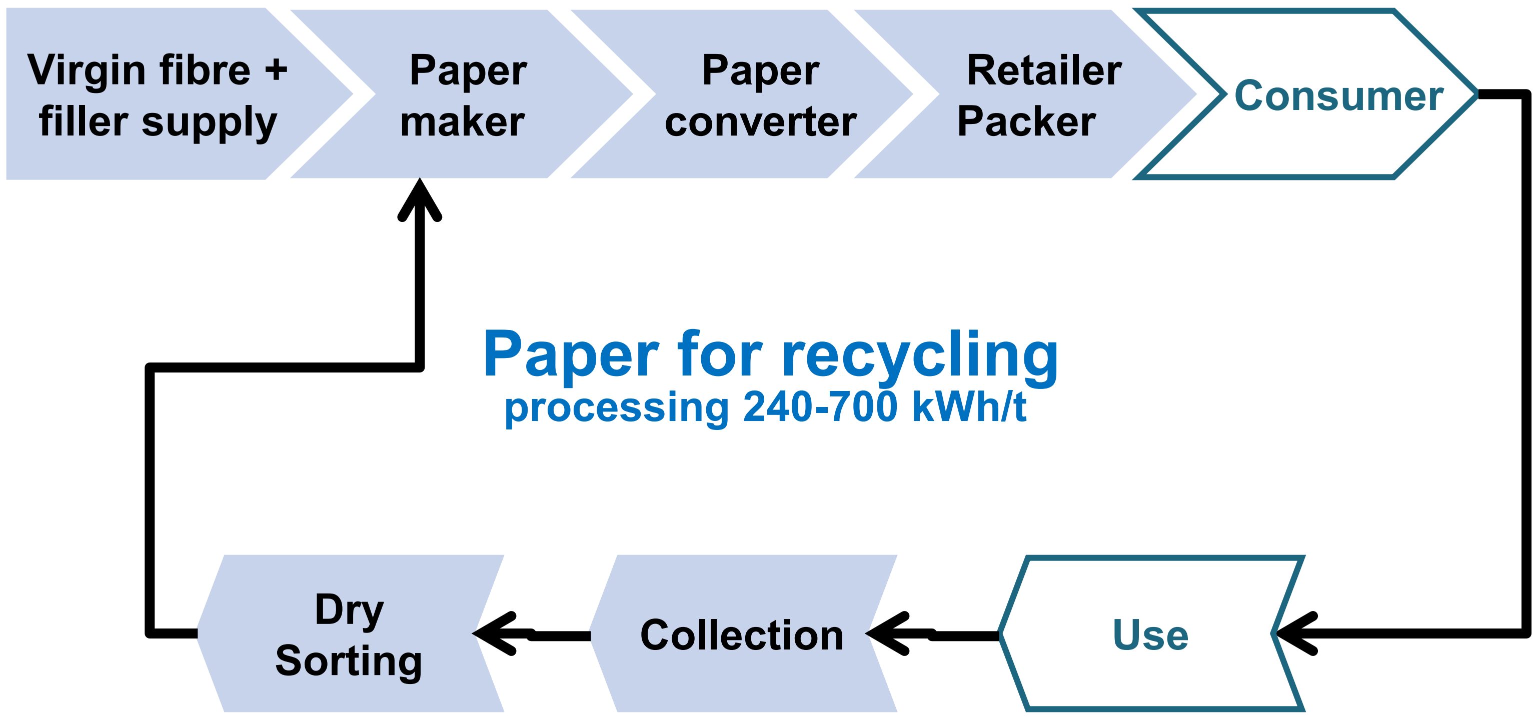
Sustainable paper recycling – Threats, needs and future opportunities

Johannes Kappen, Ingrid Demel, Mike Schiefer, Constanze Seidemann, Papiertechnische Stiftung (PTS) Heidenau

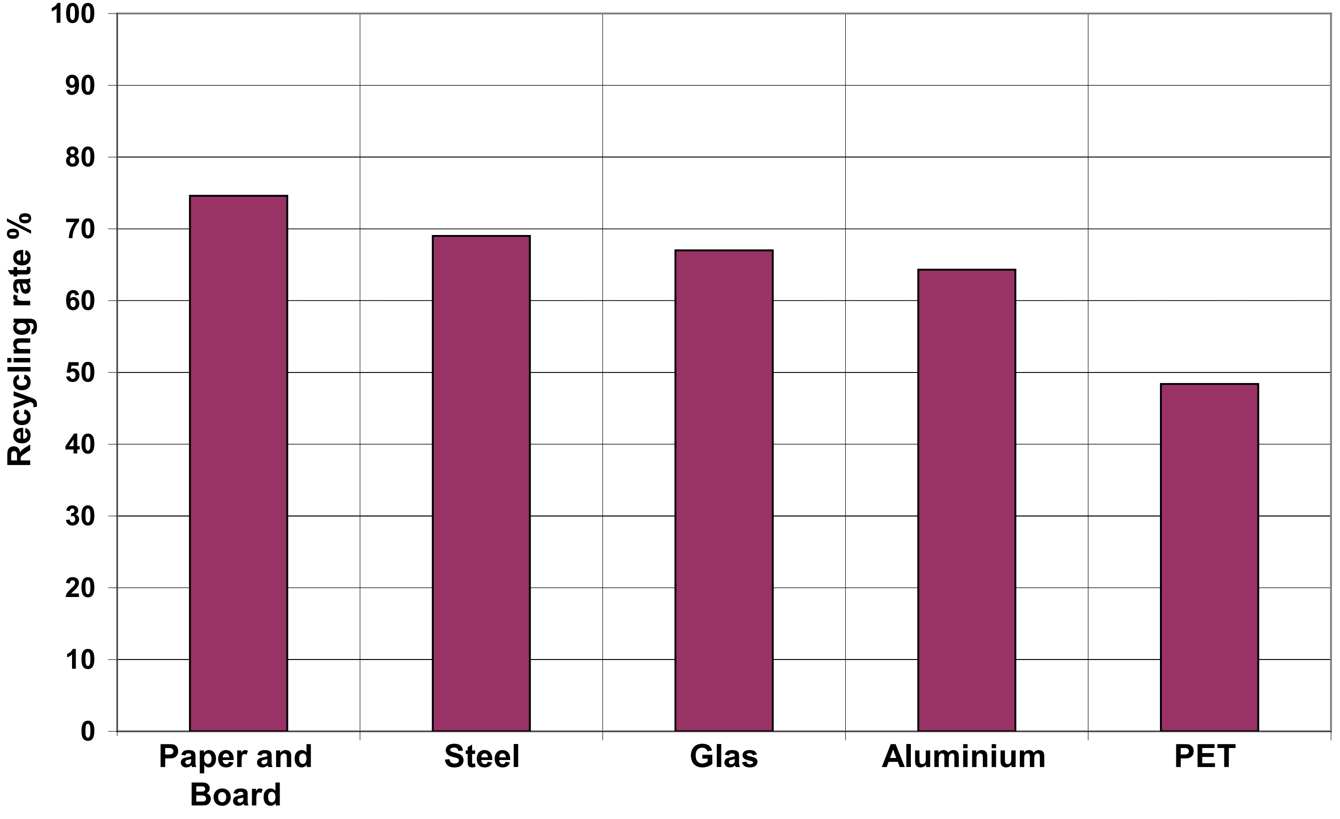
RISKCYCLE Conference, Dresden 8.-9.5.2012

The paper value chain

Mech/Chem. pulp
production 2250-3800 kWh/t
(gross energy demand)

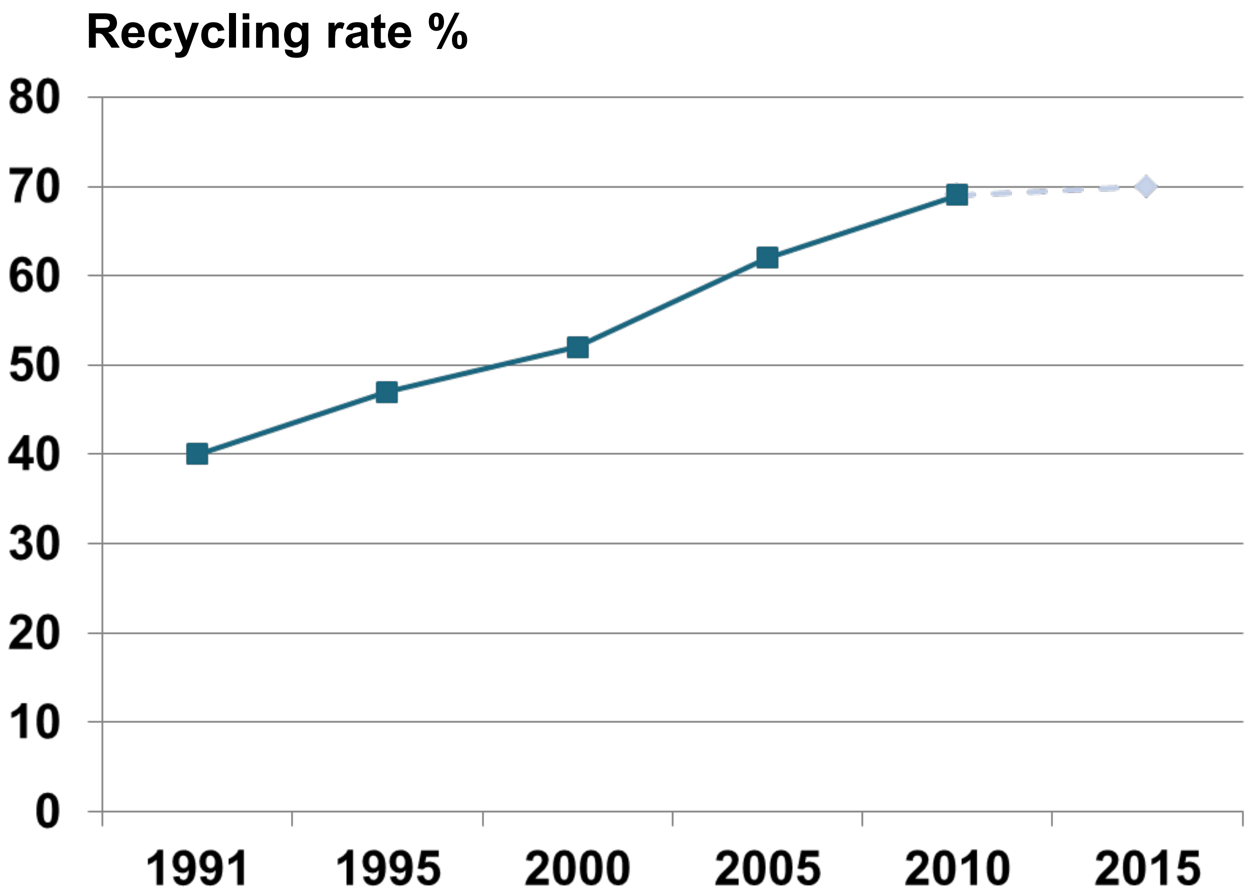


Recycling rates for various packaging materials



Europe 2008

European paper recycling rate
Continous efforts of the industry



CEPI 2012

Can go wrong? Risks implied in using paper for recycling

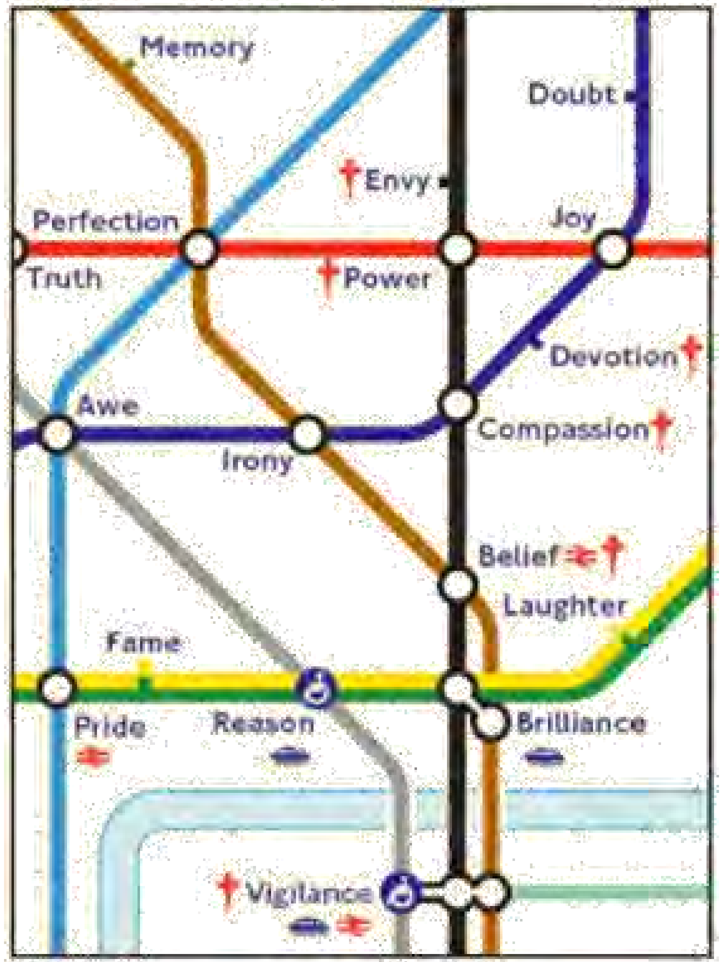
Paper is not collected.

Collected, but in bad quality.

Quality is not to our specifications.

Specs OK, but not affordable.

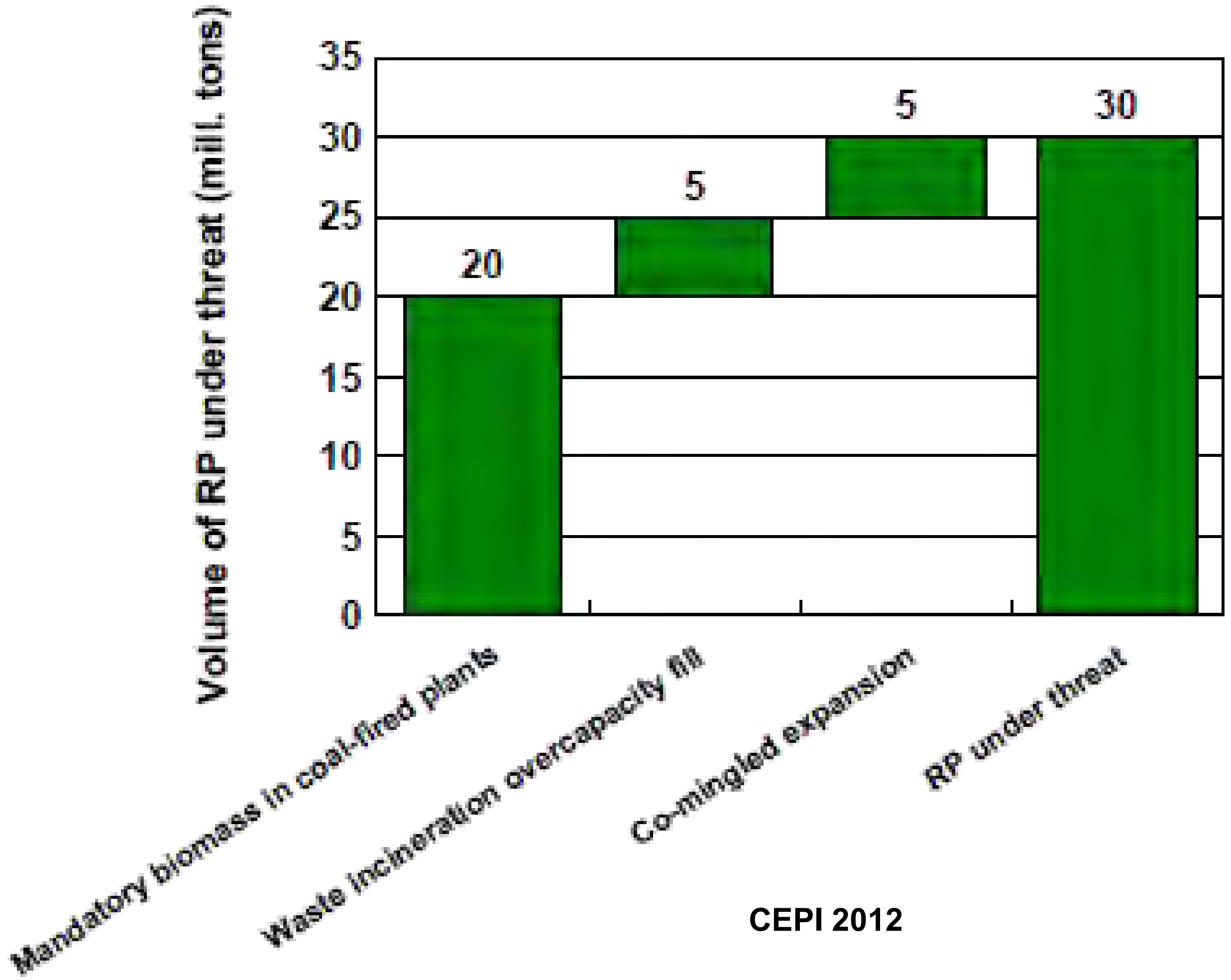
OK and affordable, but not recyclable.



Barbara Kruger 2010

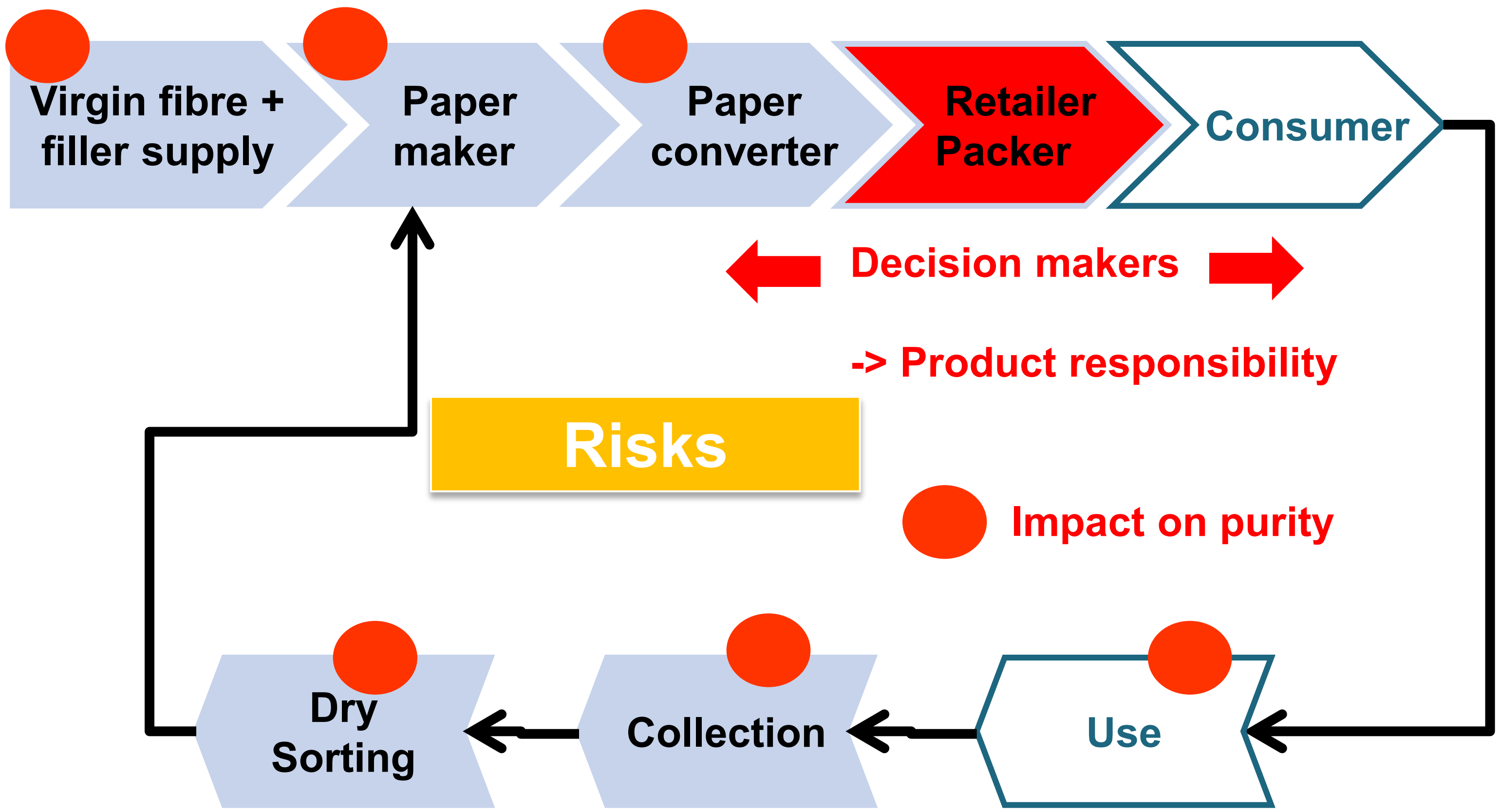
After: Jori Ringman-Beck, CTP-PTS Symposium, Grenoble 2012

Volumes of paper for recycling at risk



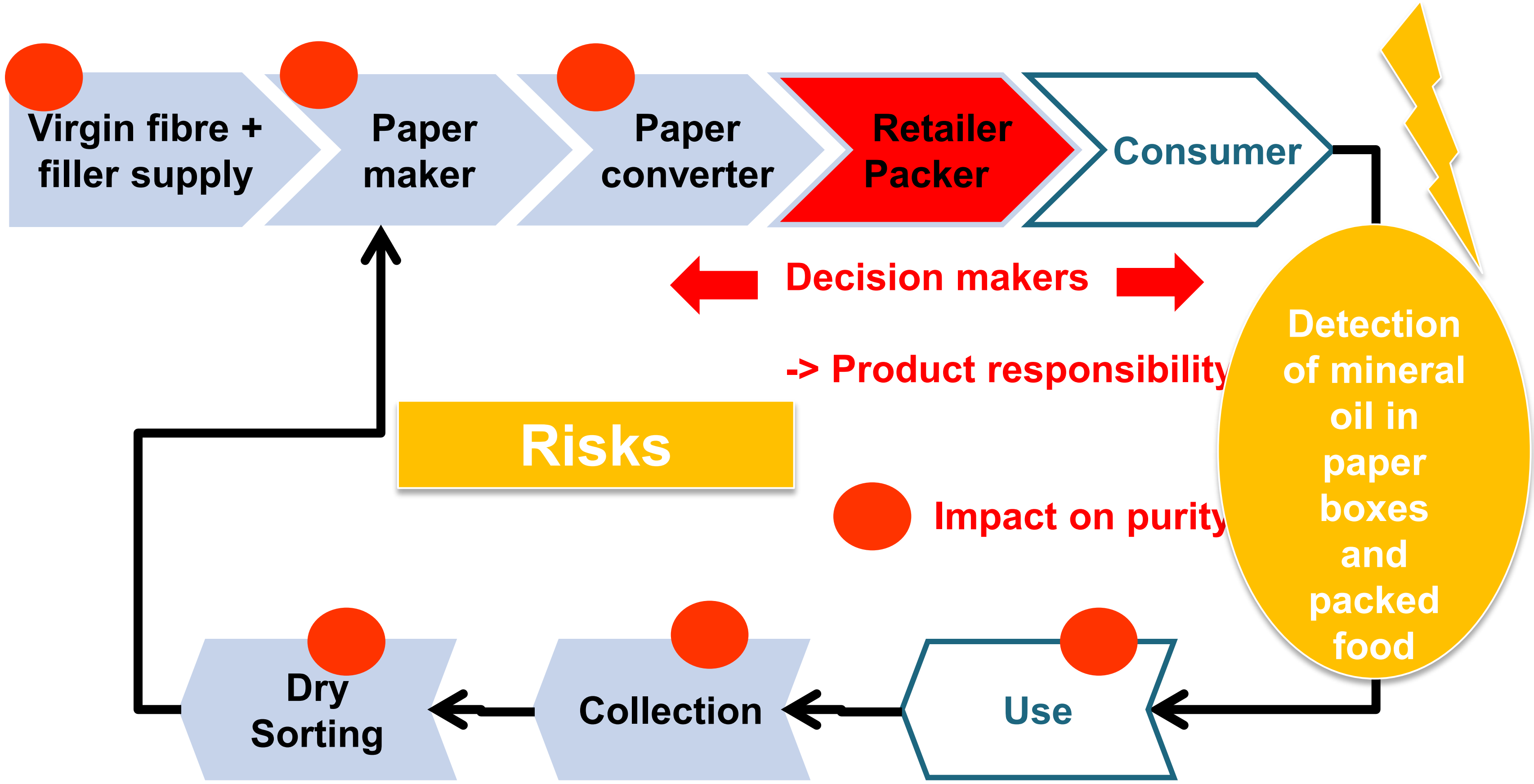
CEPI 2012

Influence on properties and purity of fibrous material within the paper value chain



PTS THE PAPER TECHNOLOGY SPECIALISTS

Influence on properties and purity of fibrous material within the paper value chain



Background (1)

- The problem of “mineral oil migration” from recycled-fibre based packages into food has been under discussion since 2009
- Sources:
  - Mineral-oil containing printing inks in package printing
  - Mineral-oil containing printing inks in newspaper printing
  - Additives used in paper production and converting
- BMELV (Federal Ministry of Food, Agriculture and Consumer Protection) has drafted a “Mineral oil ordinance 2.5.2011“ describing migration limits for saturated (MOSH) and aromatic (MOAH) hydrocarbons; the draft is currently under discussion
- There is insufficient toxicological data, no uniform methods available

Background (2)

- Measures taken so far in RCF-based packaging production
  - Use of recovered paper fractions with low mineral oil contents
  - Use of mineral oil-free printing inks in package printing
  - Replacement of mineral oil-containing additives
  - Development of barrier materials
- Conversion to mineral-oil free printing inks in newspaper printing
  - No activities known in Germany to date that would help solve the problem
- Several ongoing R&D projects at PTS Munich, PMV Darmstadt aim to find solutions to the mineral oil problem
- 4.5.12 BfR issues new method description (Messung von Mineralöl – Kohlenwasserstoffen in Lebensmitteln und Verpackungsmaterialien)

Mineral Oil

Mineral oil components in cartonboard made from recovered paper

Mineral Oil Saturated Hydrocarbons (MOSH)

- Open-chain, mostly branched alkanes and cycloalkanes
- Preliminary JECFA Classification of mineral hydrocarbons (medium and low viscosity) class III = ADI 0,01 mg/kg body weight (to be revised 04/12)

→ 0,6 mg/kg foodstuffs

Mineral Oil Aromatic Hydrocarbons (MOAH)

- Highly alkylated aromatic compounds
- Inseparable by chromatography
- Some substances with proved carcinogenic potential, other substances suspected of having carcinogenic effects

→ not detectable (to be defined) in foodstuffs

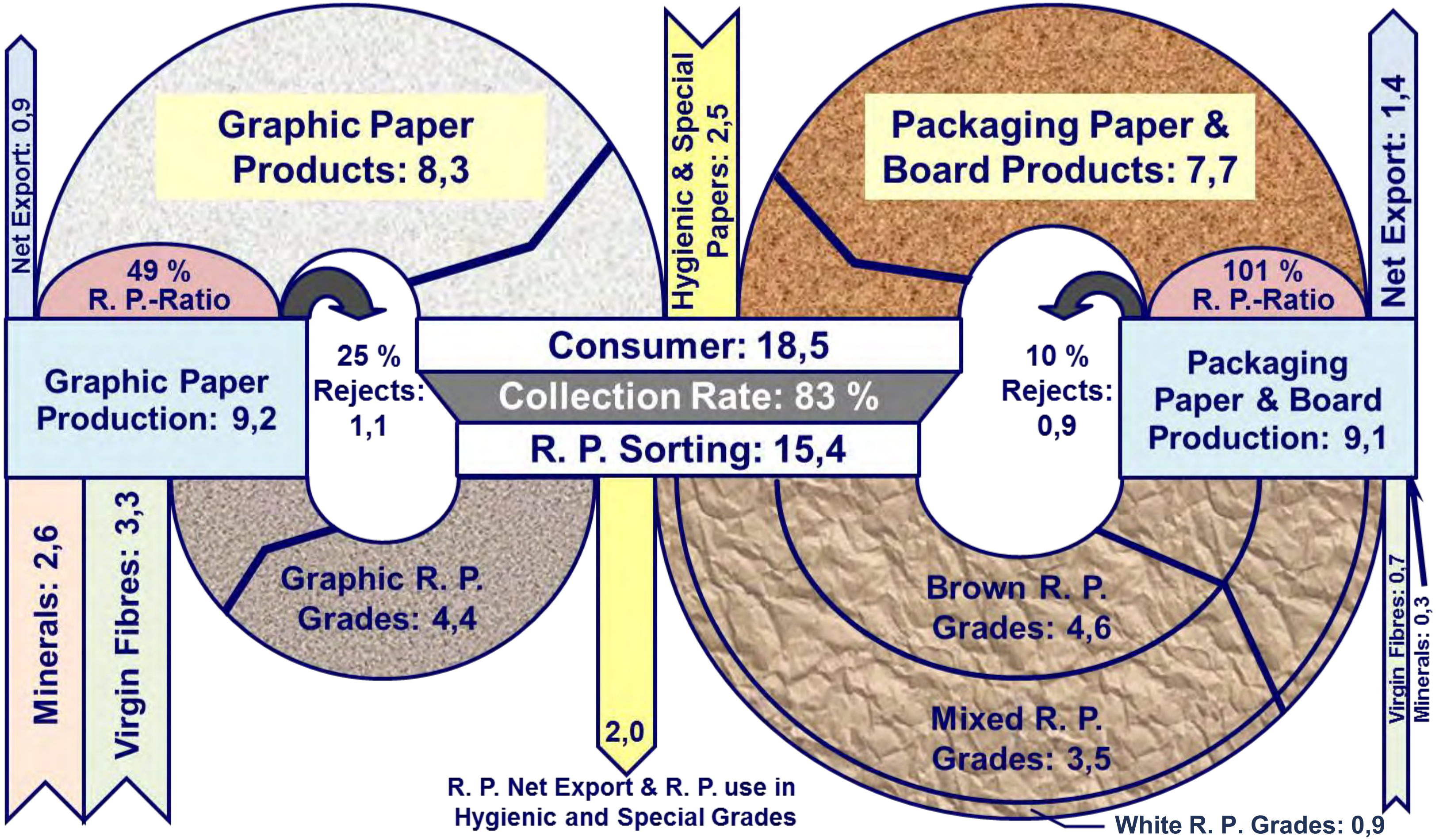
Problems: Migration from compounds ≤ C25 via gas phase into foodstuffs

Source: Printing inks from offset printed newspapers (coldset) and others

based on H.-J. Putz and A. Kersten; Migration of Mineral Oil; INGEDE Symposium; Munich 10.02.2011

Paper recycling happens within two interconnected cycles

numbers: Germany



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based on H.-J. Putz and A. Kersten; Migration of Mineral Oil; INGEDE Symposium; Munich 10.02.2011

Relevant Paper Products

Germany, 2008

Graphical Paper Total: 6.382 Mio. t (Germany 2008)	
Newsprint paper	**Magazine paper (SC/LWC)**
2.33 Mio. t	4,05 Mio. t

Packaging Paper Total 9.35 Mio. t (Germany 2008)										
Testliner and Fluting		**Board**					**Other packaging paper**			
		2,5 Mio. t								
		Folding boxboard				other board				
6.0 Mio. t		1,5 Mio. t					0.85 Mio. t			
thereof RCF		thereof RCF		virgin fibre			thereof RCF		davon Prim.	
6.0 Mio. t		1.4 Mio. t		0.1 Mio. t			0.82 Mio. t		0,03 Mio. t	
FO	BF	FO	NF	FO	NF		FO	NF	FO	NF
1.7 Mio. t	4.3 Mio. t	**0.7 Mio. t**	0.7 Mio. t	0.1 Mio. t		1,0 Mio. t	**0.48 Mio. t**	0.34 Mio. t	0.03 Mio. t	

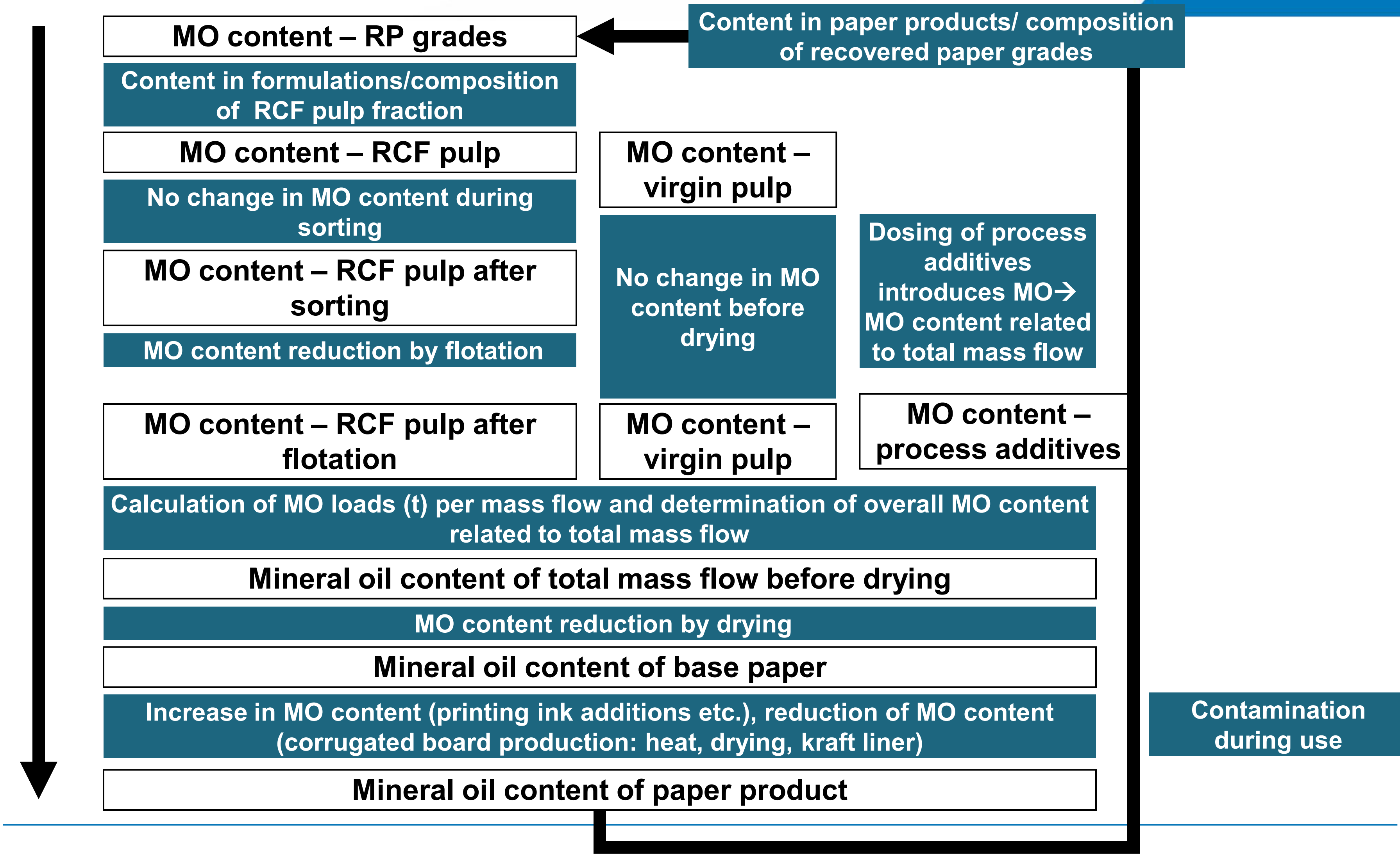
2.88 Mio t corrugated base paper, paperboard and other packaging paper from secondary pulps with food contact

Source: **VDP** **UBA-Fachgespräch (MM)**

FO: used for food packing; NF: nonfood applications

Calculation model

Mineral oil (MOSH/MOAH) balance



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Model validation

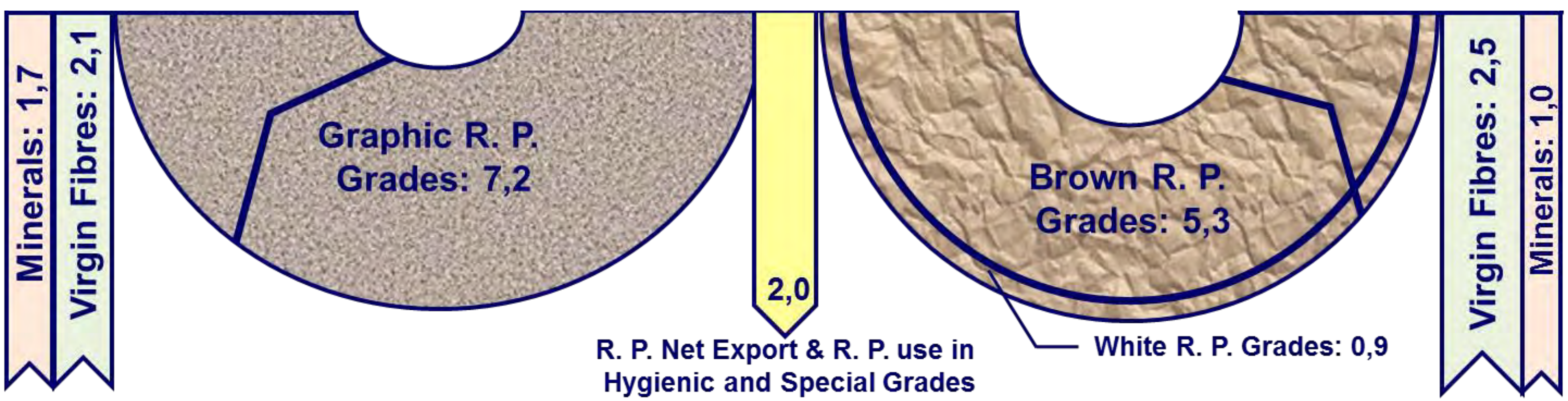
MOSH/MOAH content of paper products (printed)	Newspapers	Magazines (wood containing)	Corrugated board	Folding boxes made from RCP (food packaging)	Folding boxes made from RCP (non food applications)
Calculated [mg/kg]	**4.313**	**540**	**270**	**403**	**620**
Relation calculated vs. measured (=100 %)	108%	81 %	119 %	76 %	83 %
Measured (Avg) [mg/kg]	**3.988**	**667**	**226**	**527**	**744**
Measured (Min) [mg/kg]	1.870	189	64	177	433
Measured (Max) [mg/kg]	7.457	1.090	447	1826	1.967

Calculated scenarios

Option	Scenario	Description
As-Is scenario	**1**	
Replace 1.02 by high quality fibre stock	**2 a, b, c**	2 a: virgin fibre in folding box board only 2 b: grades 2.X, 3.X in folding box board only 2 c: virgin fibre (c) in folding bb + testliner/fluting
Separate collection of packaging RCP	**3 a, b**	3 a: to the feasible extent (INTECUS/PMV) 3 b: 100% separation (theoretical scenario)
Conversion to MOSH/MOAH free printing inks	**4 a, b, c**	4 a: reduction by 50% ; 4b: by 100% (b) (c) = 4b + replacement of all MOSH/MOAH containing papermaking additives
Protective measures	**5 a, b**	5 a bag in box, 5 b barrier coating
Apply flotation in stock prep.	**6**	efficiency 47%; losses 10%
"All paper makers could do"	**7**	= (6) + ban of all MOSH/MOAH in papermaking

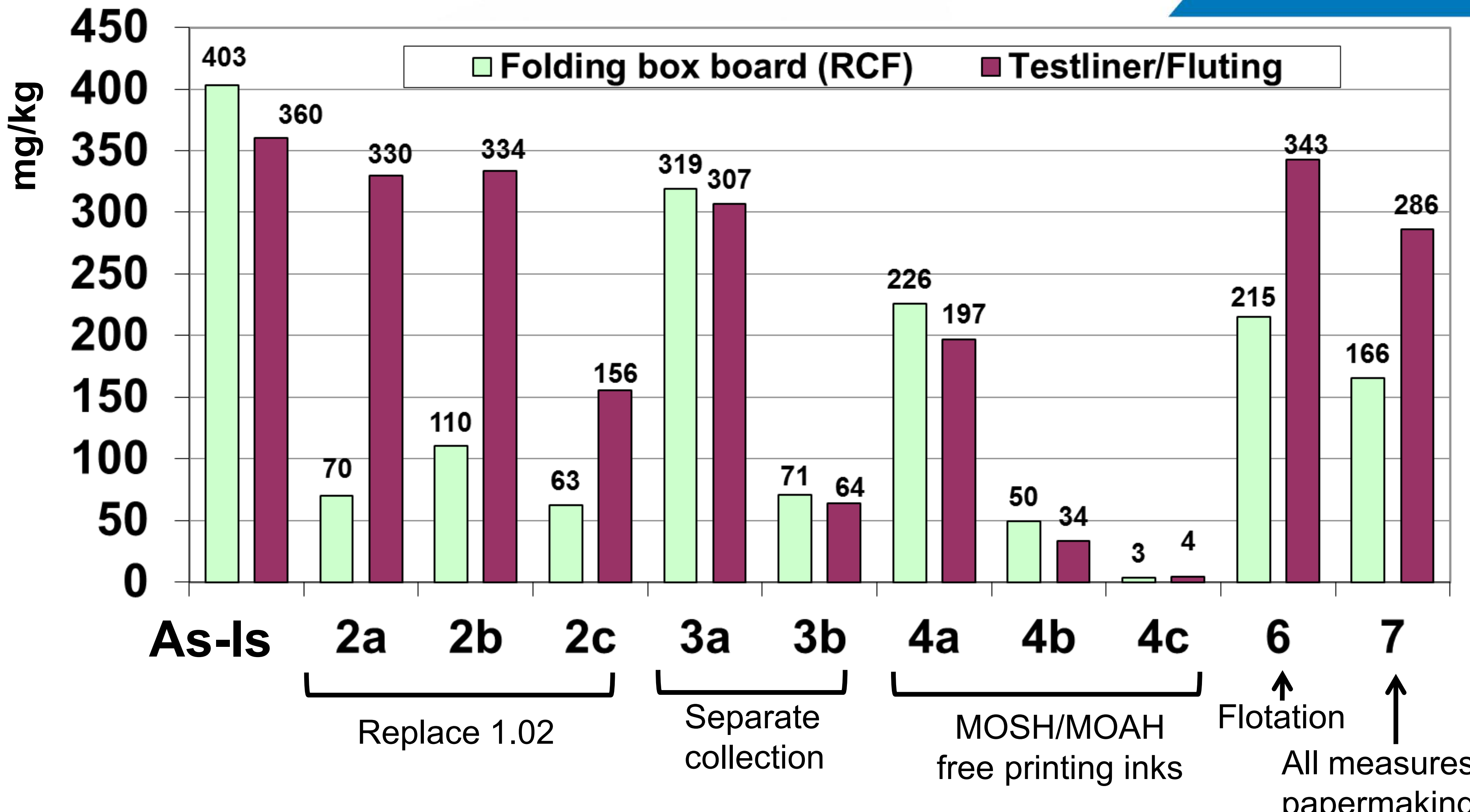
Separate collection? – Scenarios 3a and 3b

Achievable results of separate collection (INTECUS/PMV):
Reduction in News and Magazines by 46% in grade 1.01/1.02



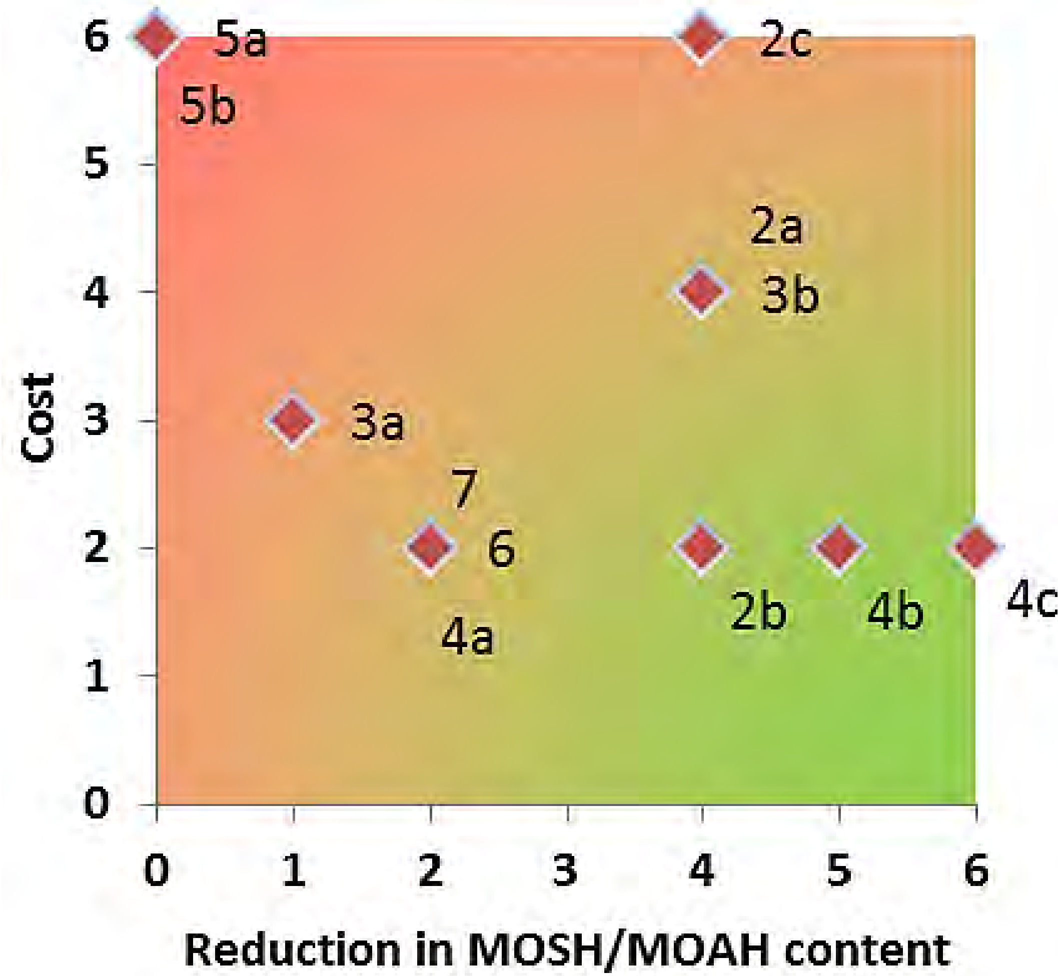
based on H.-J. Putz and A. Kersten; Migration of Mineral Oil; INGEDE Symposium; Munich 10.02.2011

Results – Mineral oil in paper



1: < 10 mn € **(Cost)**
2: 11 – 50 mn €
3: 51 – 100 mn €
4: 101 – 250 mn €
5: 251 – 500 mn €
6: > 501 mn €

As-Is scenario	1
Replace 1.02 by high quality fibre stock	2 a, b, c
Separate collection of graphical and packaging RCP	3 a, b
Conversion to MOSH/MOAH free printing inks	4 a, b, c
Protective measures	5 a, b
Apply flotation in stock prep.	6
“All papermakers could do“	7

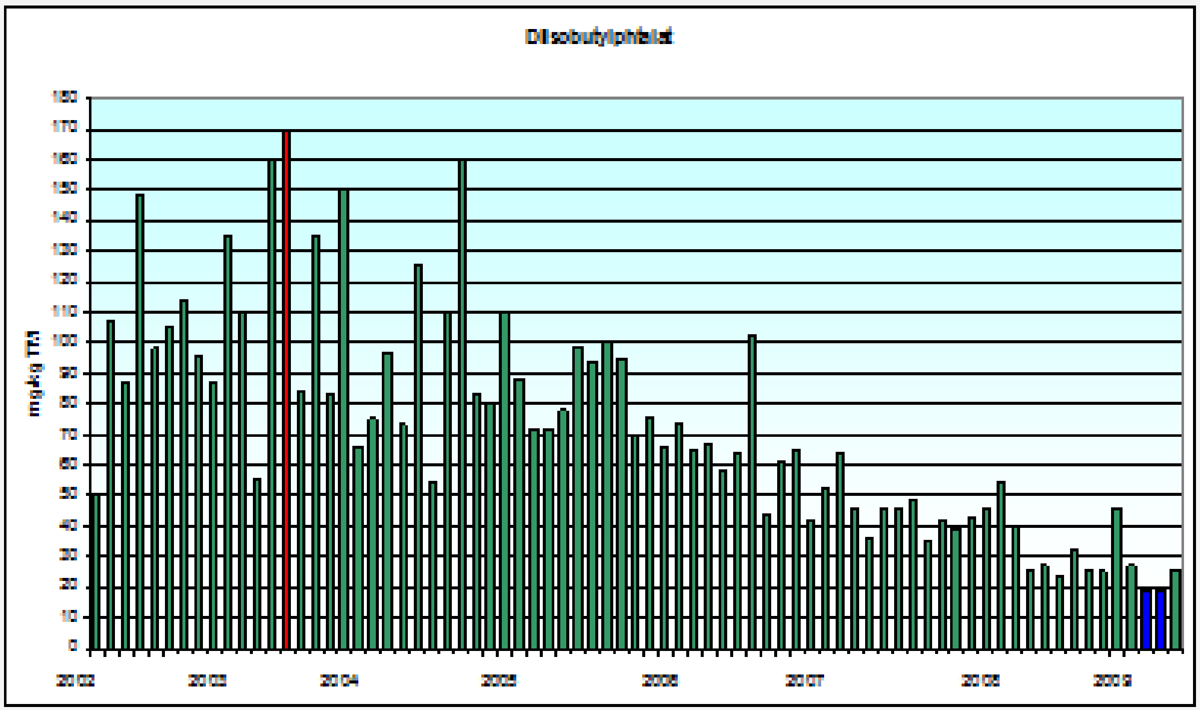


1: > 300 mg/kg) **(MOSH/MOAH content)**
2: 200 – 299 mg/kg
3: 100 – 199 mg/kg
4: 50 – 99 mg/kg
5: 10 – 49 mg/kg
6: < 10 mg/kg

And how long may it take?

sustainable board solutions

Reduction of DIBP in recycling board by aligned actions of the involved industries



Source MMK

Example:

Diisobutyl-phthalat (DiBP)

50 % reduction within 5 years

Up to 90% reduction within 10 years

Everything solved anyway?

PRINT | AUDIO/VIDEO | ONLINE | MOBILE

cpwissen home | wettbewerbe | technik | studien | best practice | termine | ex

Das führende Medienportal für Unternehmen

.: Technik

Ökologisch veredelt

Coop und Migros drucken jetzt mineralölfrei

Die Schweizer Einzelhändler Coop und Migros führen vor, wie man Kundenmaga nicht nur mit ökologisch einwandfreiem Papier, sondern auch mit umweltfreundl Druckfarben den grünen Anstrich verpasst - und eine Verunreinigung von Leben über die Recyclingkette ausschließt.

Mineralöl raus: Vor allem bei Magazinen mit Millionenauflagen im Handel

Mineralölfreie Druckfarbene sind im Handel schon läng Thema. Vor allem seit klassische, mineralölhaltige Druckfarben in Lebensmitteln nachgewiessen wurden. Übertragungswege stehen Recyclingkartons am Prang verwendete Altpapier, vor allem Zeitungen, beinhaltet Mineralöl, das zur Trocknung der Farben eingesetzt w

"Grüne" Händler sind starke Händler

Kundenmagazine sind, solange man nicht seinen Sala einpackt, zwar unbedenklich, können aber über die Recyclingkette letztlich ebenfalls Lebensmittel kontam Coop und Migros wollen nun, auf dieses Thema sensit das Mineralöl heraus- und das "grüne" Händlerimage hereinholen. Bei mineralölfreien Druckfarben wird Min durch pflanzliches Öl ersetzt.

Coop hat zunächst eine Teilauflage seiner *Coop-Zeitu* 500.000 Exemplare von insgesamt 1,7 Millionen - mit mineralölfreien Zeitungsdruckfarben hergestellt. Auch Migros testet mineralölfreie Farben in einer Teilauflage des *Migros-Magazins*. Coop Partner bei der

Presse-Information

BASF The Chemical Company

BASF bietet der Verpackungsindustrie innovative Barrierelösungen gegen Mineralölrückstände

- **Lösungen für alle Verpackungsarten und Herstellprozesse**

Die BASF bietet der Verpackungsindustrie verschiedene Barrierelösungen an, die eine hohe Wirksamkeit gegenüber Mineralölrückständen zeigen, die aus Lebensmittelkartons in die Nahrung gelangen können. Das haben Messreihen mit den BASF-Produkten Ultramid®, Epotal® A 816, Ecovio® FS Paper sowie speziell entwickelten Dispersionen ergeben, die vom Kantonalen Labor in Zürich durchgeführt wurden. Damit stehen insgesamt vier verschiedene Lösungen zur Verfügung, mit denen alle Formen von Lebensmittelverpackungen beschichtet werden können, sowohl

03. Mai 2011
P252/11

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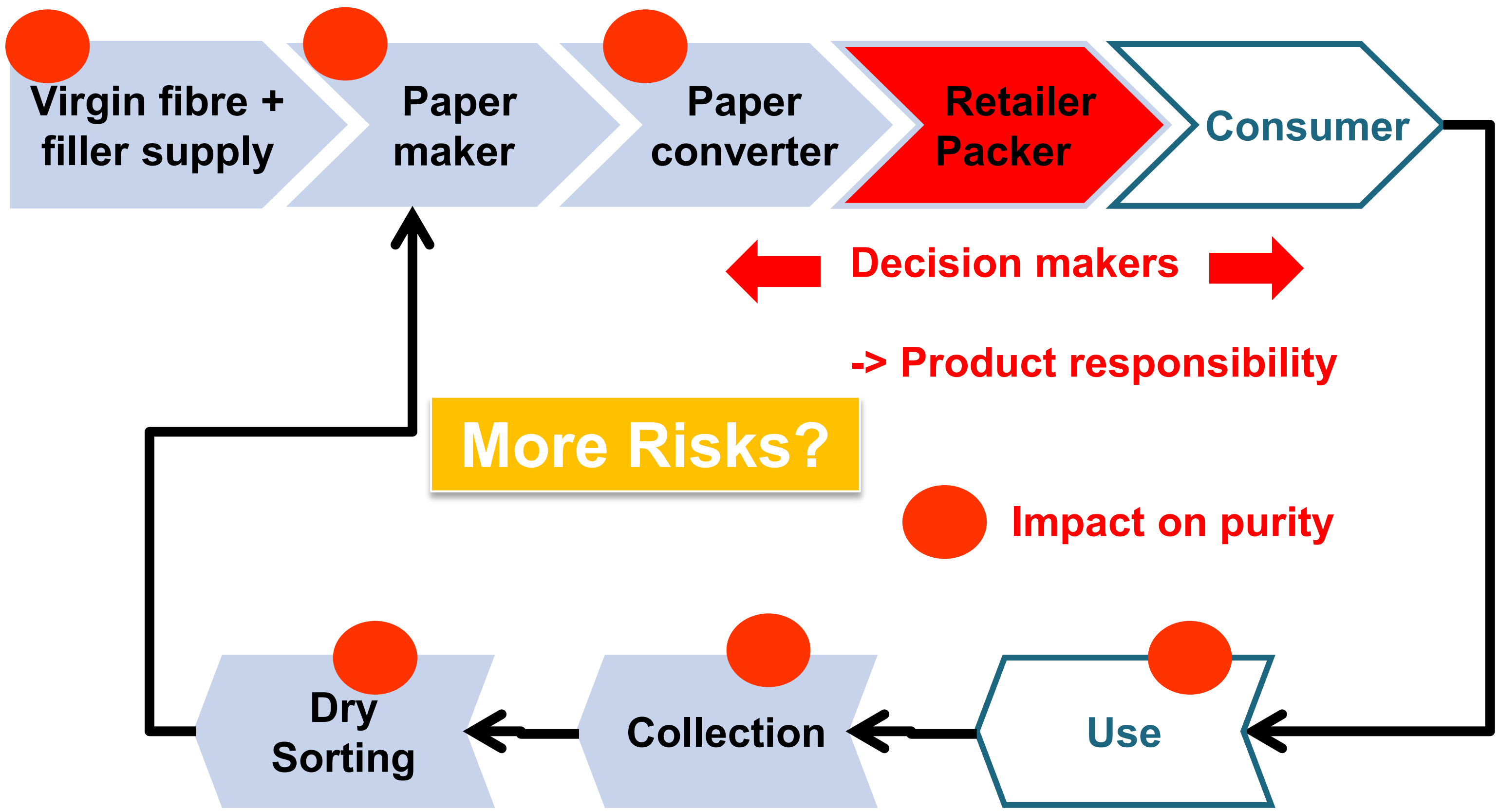
Influence on properties and purity of fibrous material within the paper value chain



Conclusions

- Paper for recycling is a valuable raw material to be preserved
- Paper recycling is exposed to various and significant risks
- Risks are coming from the outside and from the inside of the value chain

Lessons learned from the mineral oil case:

- Uncompromising conversion to mineral oil-free in all processes of the paper value chain is needed
- Barriers may support transition temporarily
- Recyclability of barrier coated material has to be safeguarded
- A closer collaboration between all players within the value chain can help to reduce risks
- Product responsibility may foster further value chain performance increase

Acknowledgement

The mineral oil related work presented here has been elaborated within the frame of the INFOR Project 155 that has been funded by:

- INFOR [the Research and Technology Board of Trustees of the Pulp and Paper Industry in the German Pulp and Paper Association (VDP)]
- INREKA [Association of Interests Recycling Cardboard]
- VPWP [Association of the German Producers of Packaging and Corrugated Papers]

We greatly appreciate the very good collaboration with Hans-Joachim Putz and Antje Kersten from PMV Darmstadt within the project.

Tracking E-waste Trade to China: A Global Perspective

H.Tien[1], S. Heise[1], R.M. Darbra[2], X. Segui[2], J. Casal[2], N. Suciu[3], M. Trevisan[3], E. Capri[3], M. Schuhmacher[4], J. Rovira[4], M. Nadal[4]

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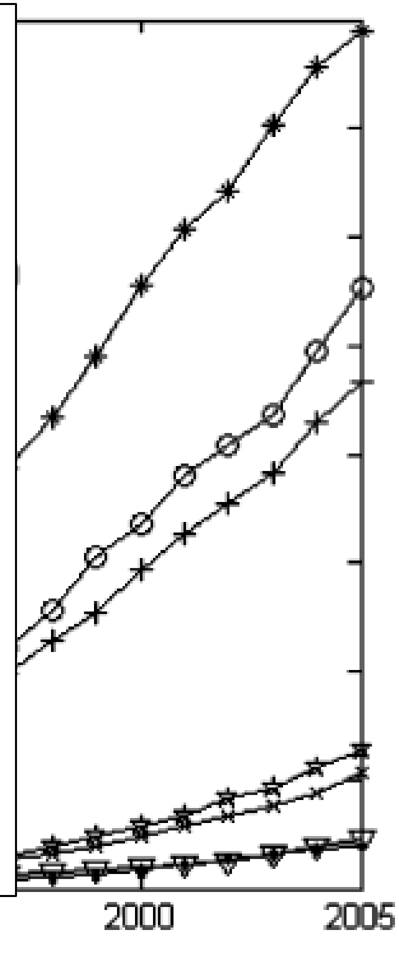
EUROPEAN COMMISSION
Community Research
SEVENTH FRAMEWORK PROGRAMME
RISKCYCLE
Hochschule für Angewandte Wissenschaften Hamburg
Hamburg University of Applied Sciences

Objectives of the Study

Objectives:

- Where does the growing e-waste volume end up?
- How is e-waste composed?
- Distribution of contamimants at the end of use stage and recycling



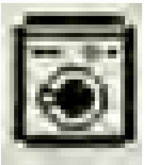
Yu 2010

Known and Suspected Routes of e-waste Dumping

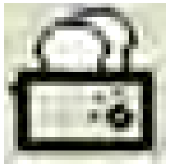
PCIJ 2008

Categories of Interest?

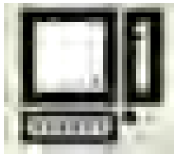
Cat 1:Large household appliances



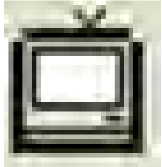
Cat 2: Small hh. Appl.



Cat 3: IT and telecommunication equipment

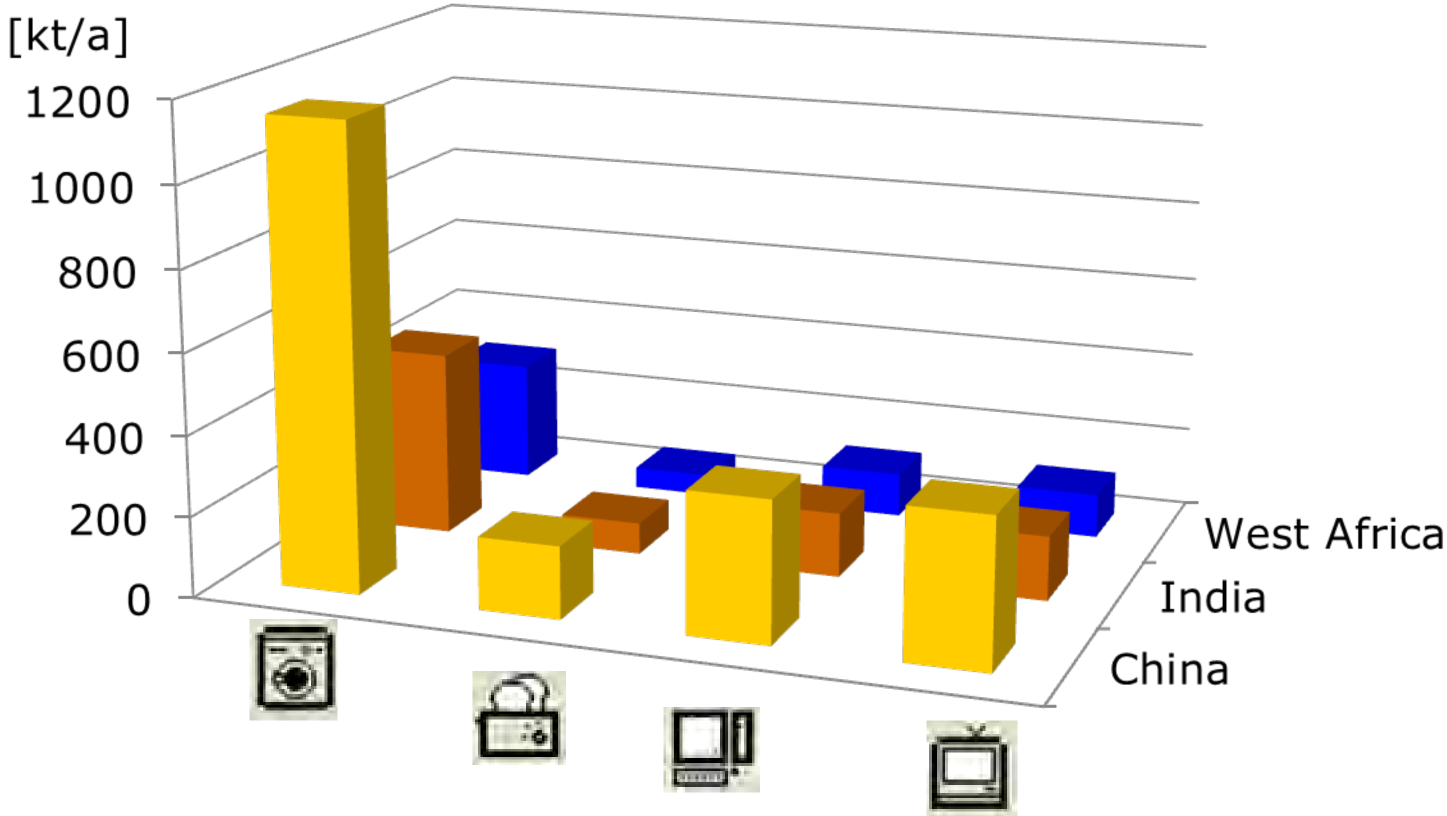


Cat 4: Consumer equipment



An Estimation of Shipped Electric and Electronic Waste

Estimation on the total import of WEEE 2005 [kt]



Based on Zoeteman 2010

Hazardous Substances in Electronics

Ionoregulatory effects,
biomagnification
Anaemia,
Kidney damage,
depression of thyroid activity,
Special hazard to children

Pb

Cr (VI)

Cd

Hg

PCB

Bioaccumulation
Persistent
Carcinogenic (promotor?)
endocrine disruption

Brominated flame retardants

European Commission
RESEARCH
SEVENTH FRAMEWORK PROGRAMME
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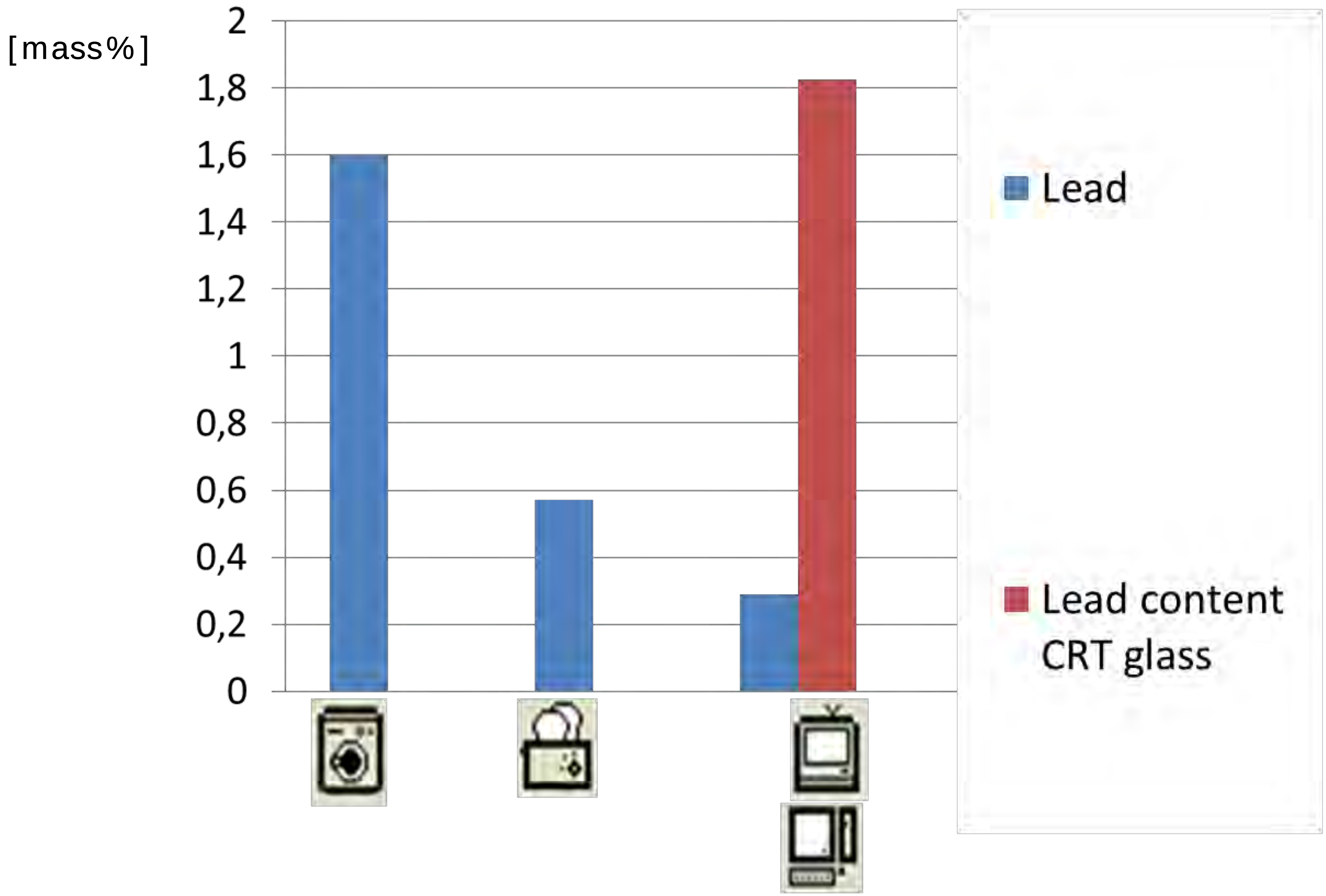
Lead Distribution in e-Waste [mass%]



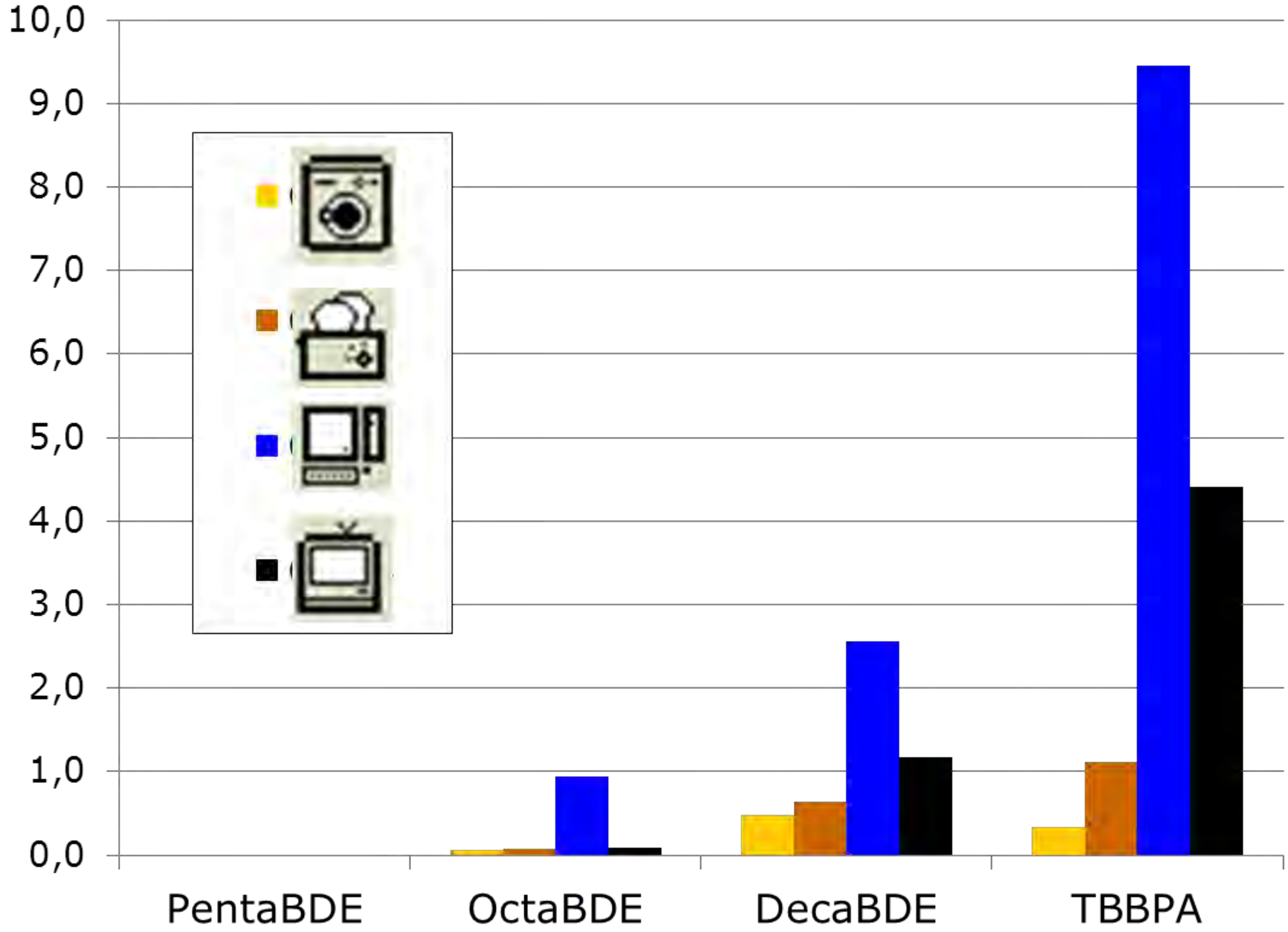
Based on Ewasteguide 2009 and Townsend 1999

European Commission RESEARCH

SEVENTH FRAMEWORK PROGRAMME

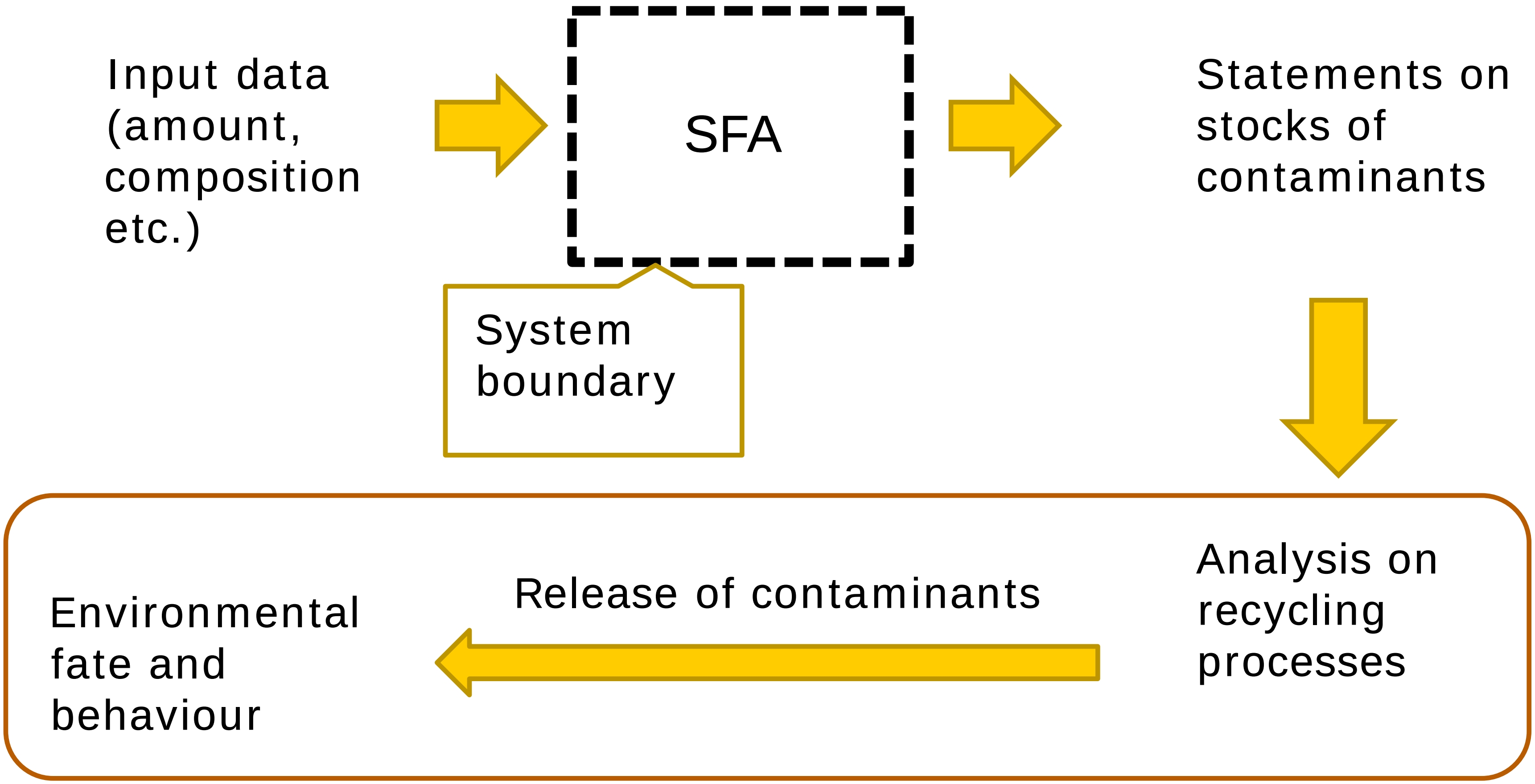
RISKCYCLE

BFR-Distribution in e-Waste

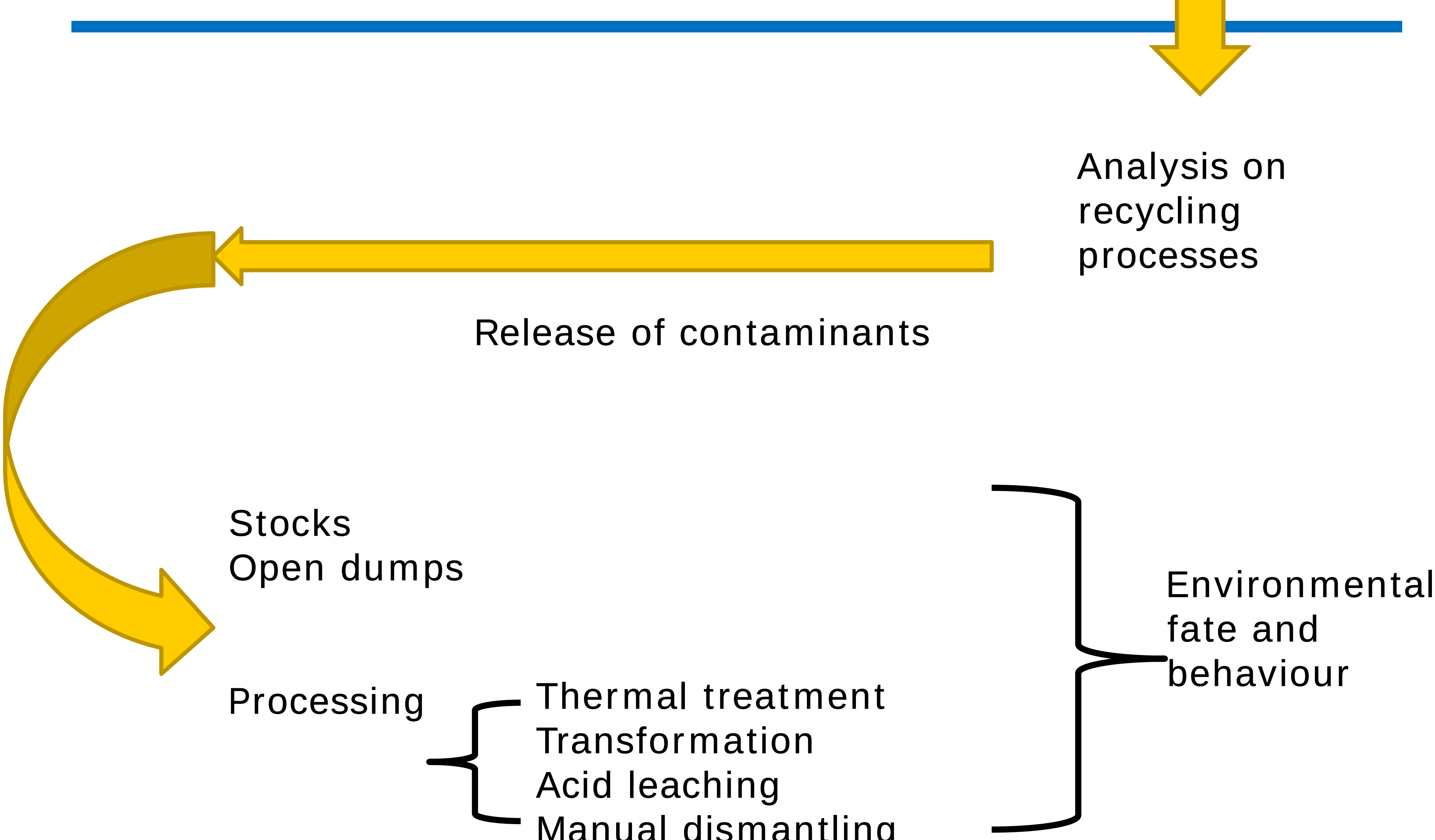


Derived from Morf et al. 2002

The Approach



Input=Release?

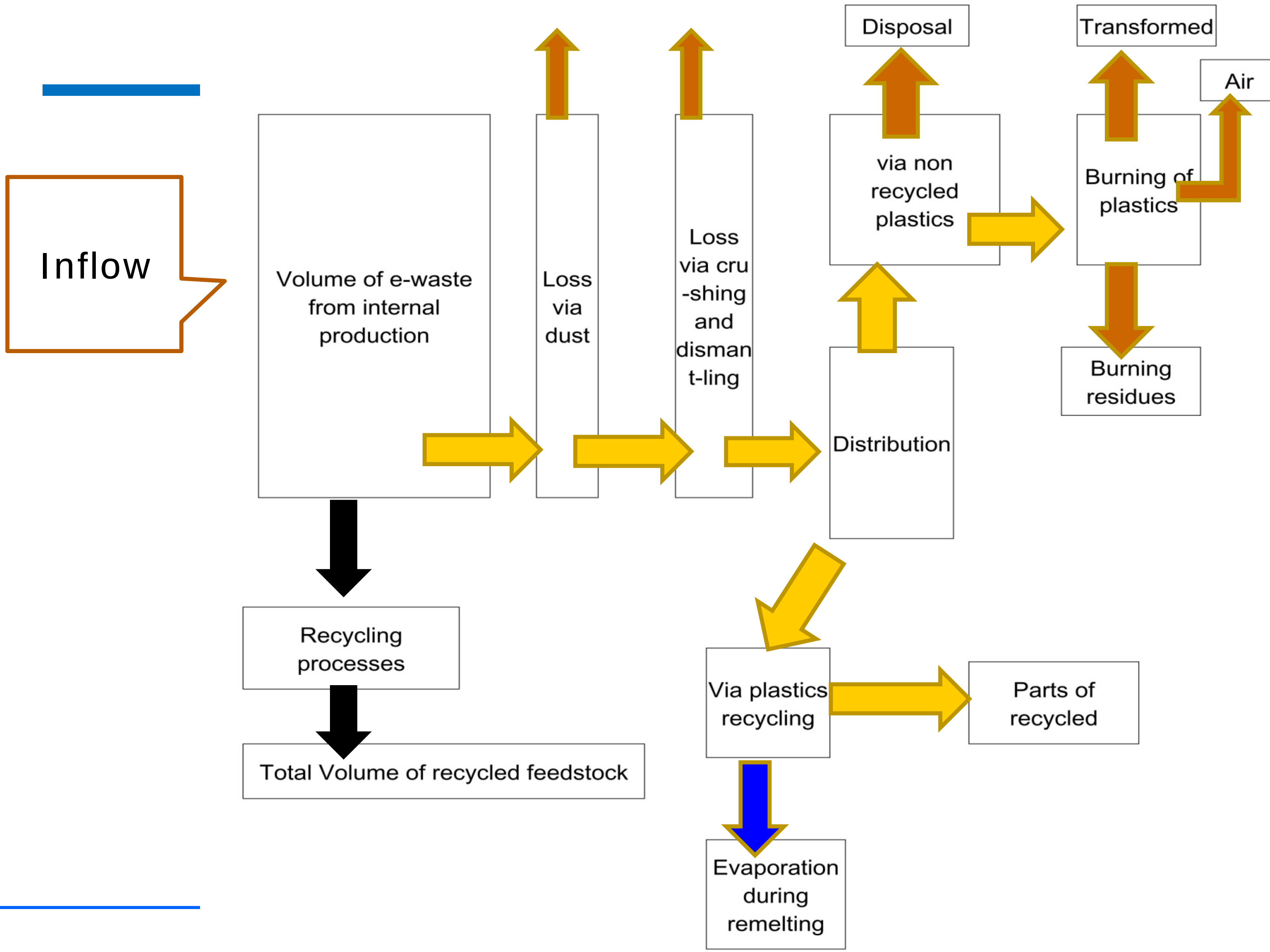


Conceptual Diagram

Flow data
- Statistical data or estimations

Compo-sition
- Analysis, literature data

Distribu-tion
- Observation, literature data


Inflow
Volume of e-waste from internal production
Loss via dust
Loss via cru -shing and disman t-ling
Distribution
via non recycled plastics
Disposal
Burning of plastics
Transformed
Air
Burning residues
Recycling processes
Total Volume of recycled feedstock
Via plastics recycling
Parts of recycled
Evaporation during remelting

Another Point of View: Single Appliance Approach

Consider single appliances (TVs and PCs) instead of categories:

- Information more accurate for specific appliances
- Knowledge of the different parts of the e-waste devices

<u>Printed Circuit Boards</u>:
Lead (PCs):13900 mgPb/kg

<u>Metals</u>:
Lead (PCs & TVs): 16000 mgPb/kg

<u>Plastics</u>:
Lead (PCs & TVs): 230 mgPb/kg
PBDE: 28000 (PCs) and 24500 (TVs) $mgPBDE/kg_{plastics}$

<u>CRT glass</u>:
Lead (PCs & TVs): 80000 mgPb/kg

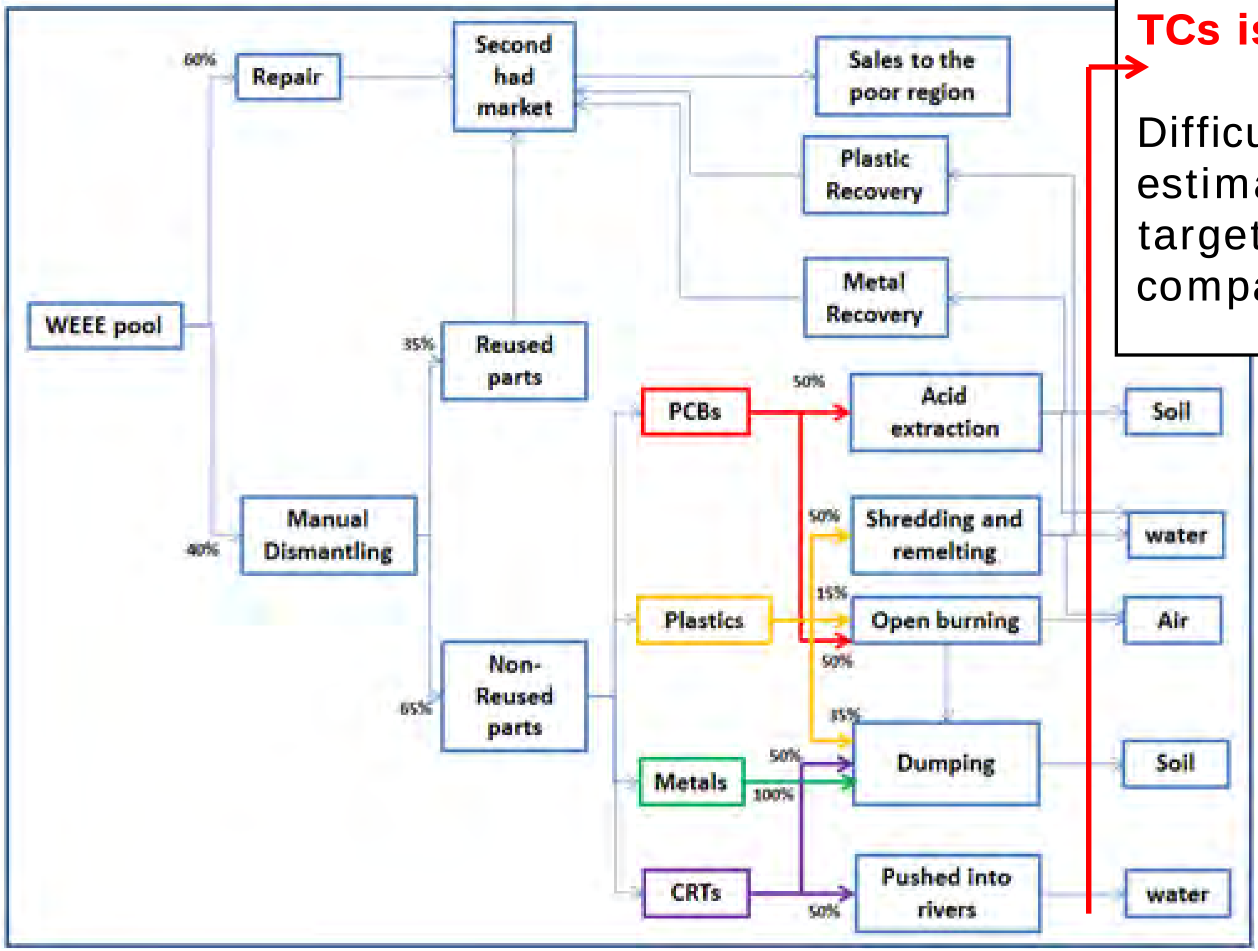
Another Point of View: Single Appliance Approach

- The distribution of the different parts of an appliance is normally well-known

Inflow Input

19,57 Mio. PCs

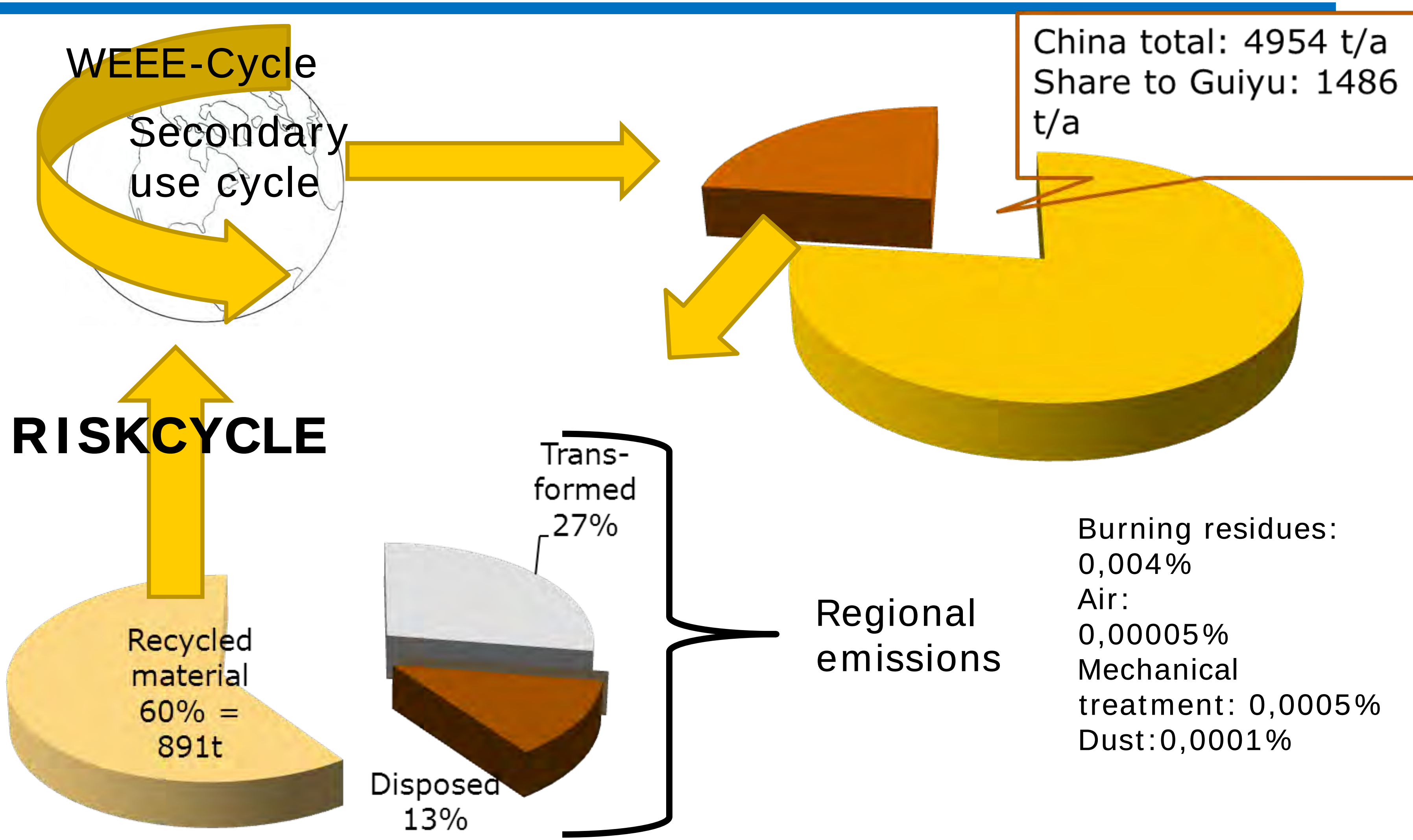
55,73 Mio. TVs



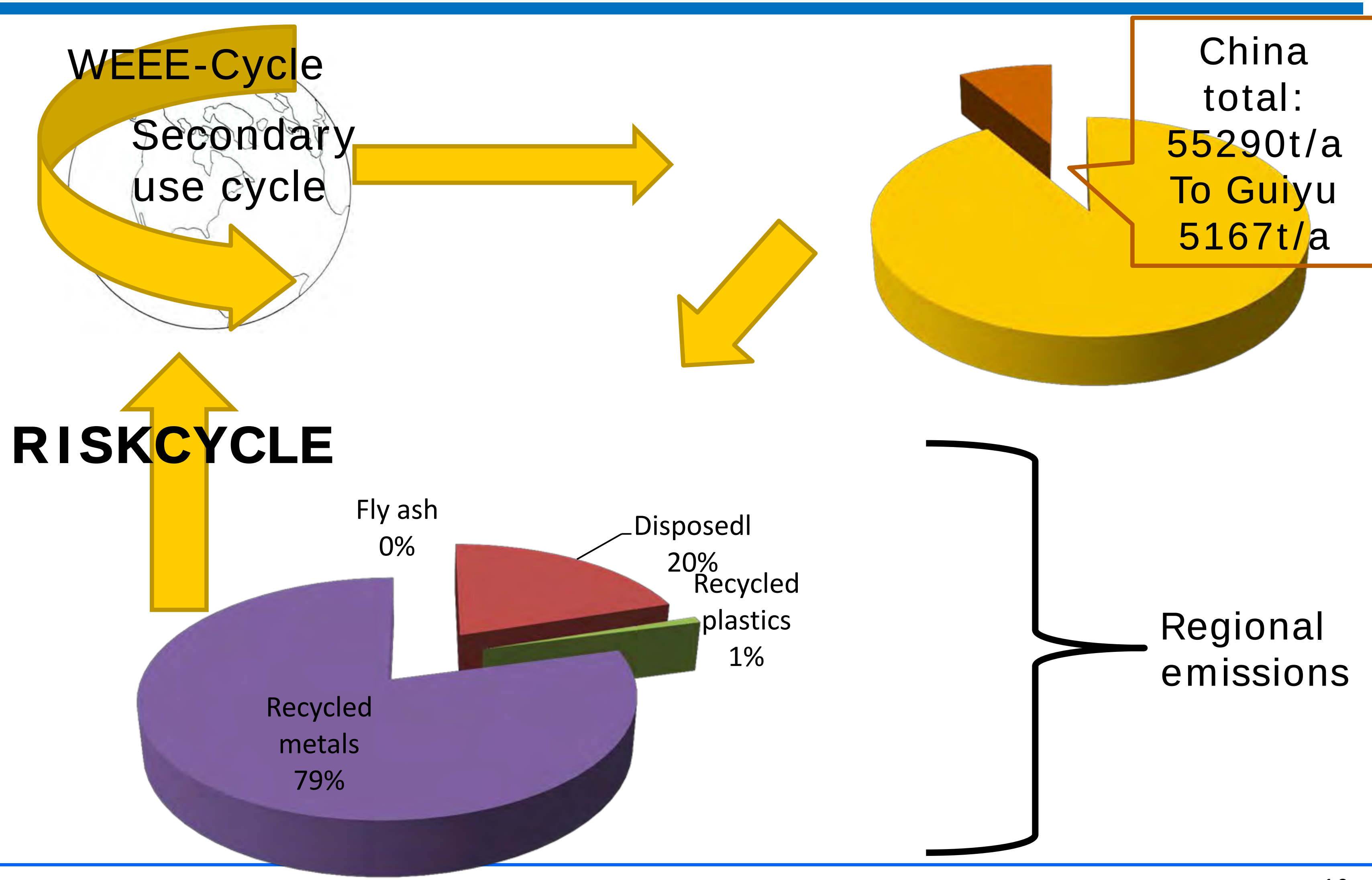
TCs issue !!

Difficulties on estimating the target comparments

BDE-209 on Continental and Regional Scale

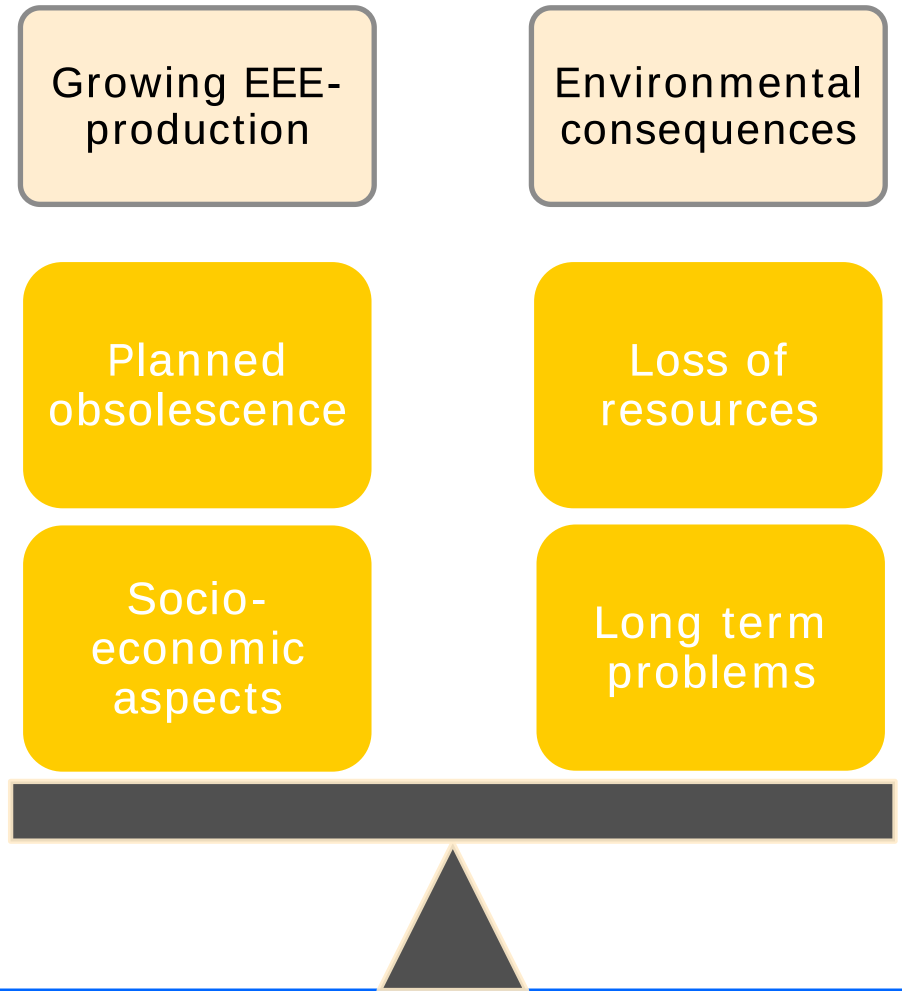


Lead (w/o CRTs) on Continental and Regional Scale



Formal and Informal Recycling

Balancing the Needs of a Globalized World



Suggested Mitigation Measures

- Reduction of illegal exports
  - Enforcement of Basel Convention
- Production of greener electronics
  - Discussion on planned obsolescence
- Improving of working and environmental conditions
  - Risk perception

Thank you for your attention!

Please find the subsequent use of this SFA's results in the presentation of Nicoleta Suciu, Wednesday 10.20 am

ht@henning-tien.com

Hochschule für Angewandte Wissenschaften Hamburg
Hamburg University of Applied Sciences

Substance flow analysis of plastic additives in the Swedish waste management system

Jenny Westerdahl, Katarina Hansson,
Hanna Andersson & Eva Brorström-Lundén

IVL Swedish Environmental Research Institute

IVL Svenska Miljöinstitutet

Overview

- About the study
- Metod
- Results
- Conclusions
- Future work

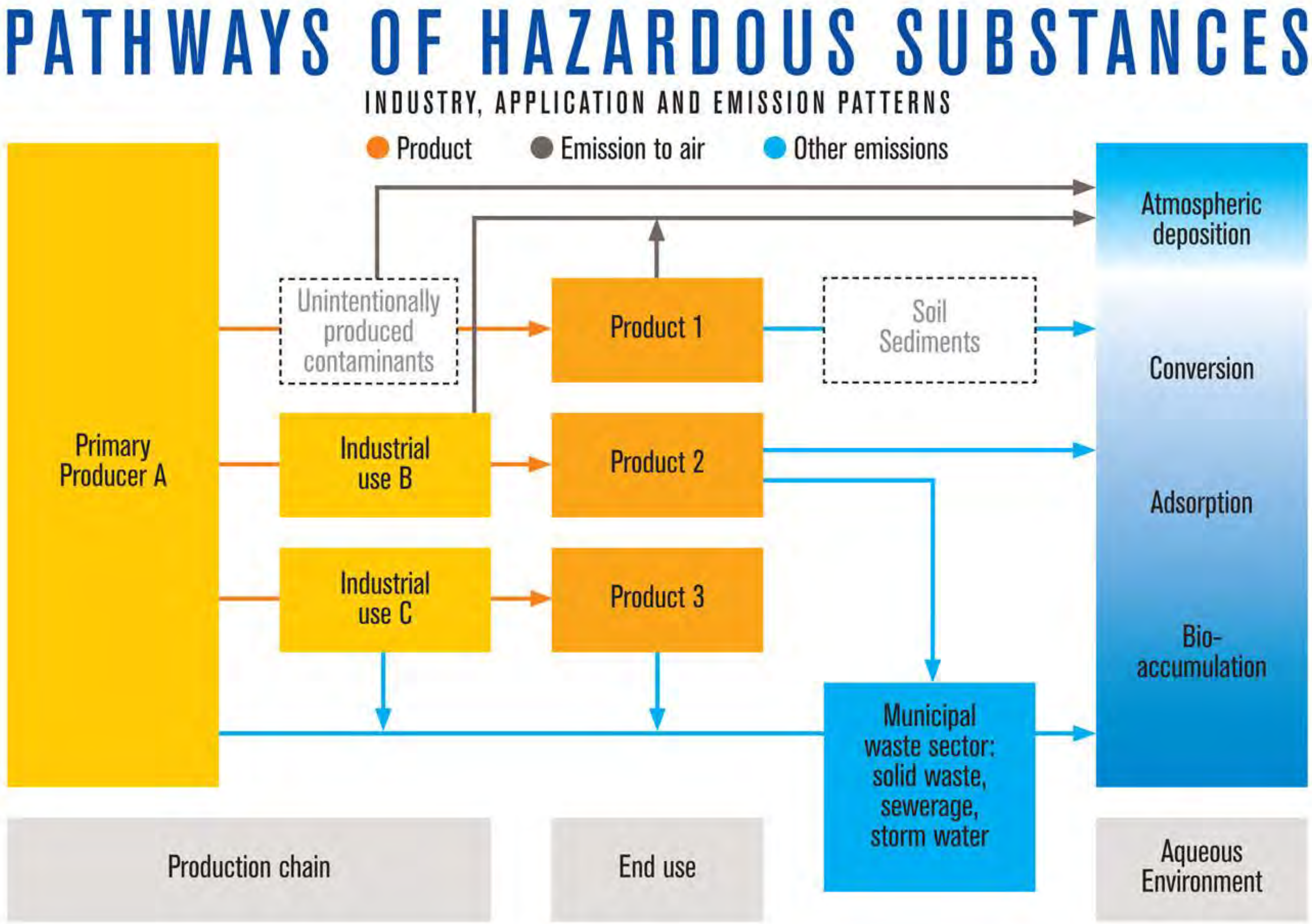
About the study

- This study was performed within the research programme ChEmiTecs
- The aim of the study was to map the flows of plastic additives within the Swedish society in order to answer the following question:
  - How big is the problem with emissions from use and waste management of articles?

Substance Flow analysis (SFA)

- Systematic assessment of the flows of a substance, including **inflow, emissions** and **outflow**, within a **defined system** during a **specified time**

- Sometimes a SFA also includes **stock** and **environmental distribution**



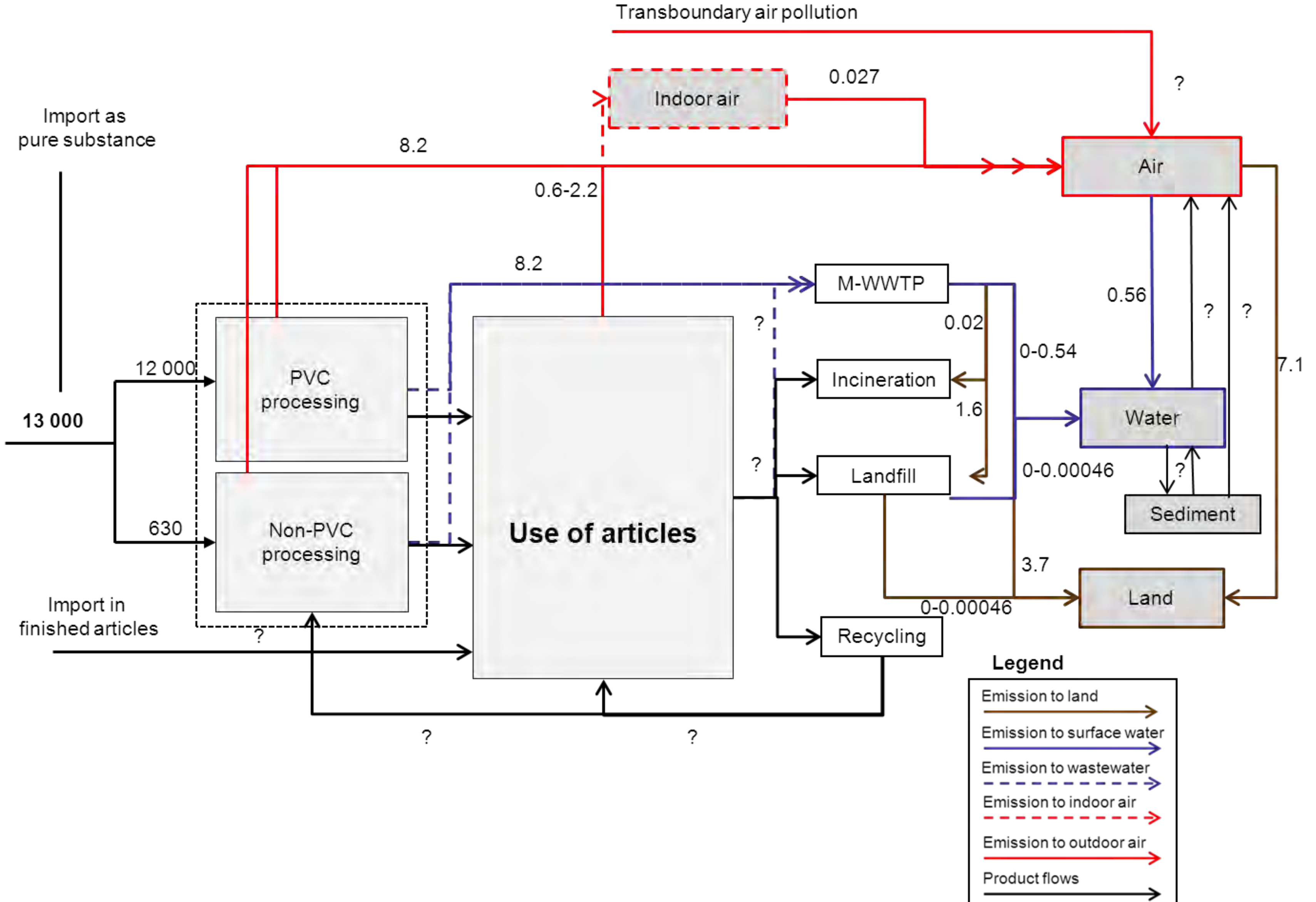
Part-financed by the European Union (European Regional Development Fund)

Source: COHIBA project

Information about DINP

- DINP – diisononyl phthalate
- Main use is as a plasticiser in PVC (95%)
- DINP a substitute for DEHP
- One of the main phthalate plasticisers used in the EU

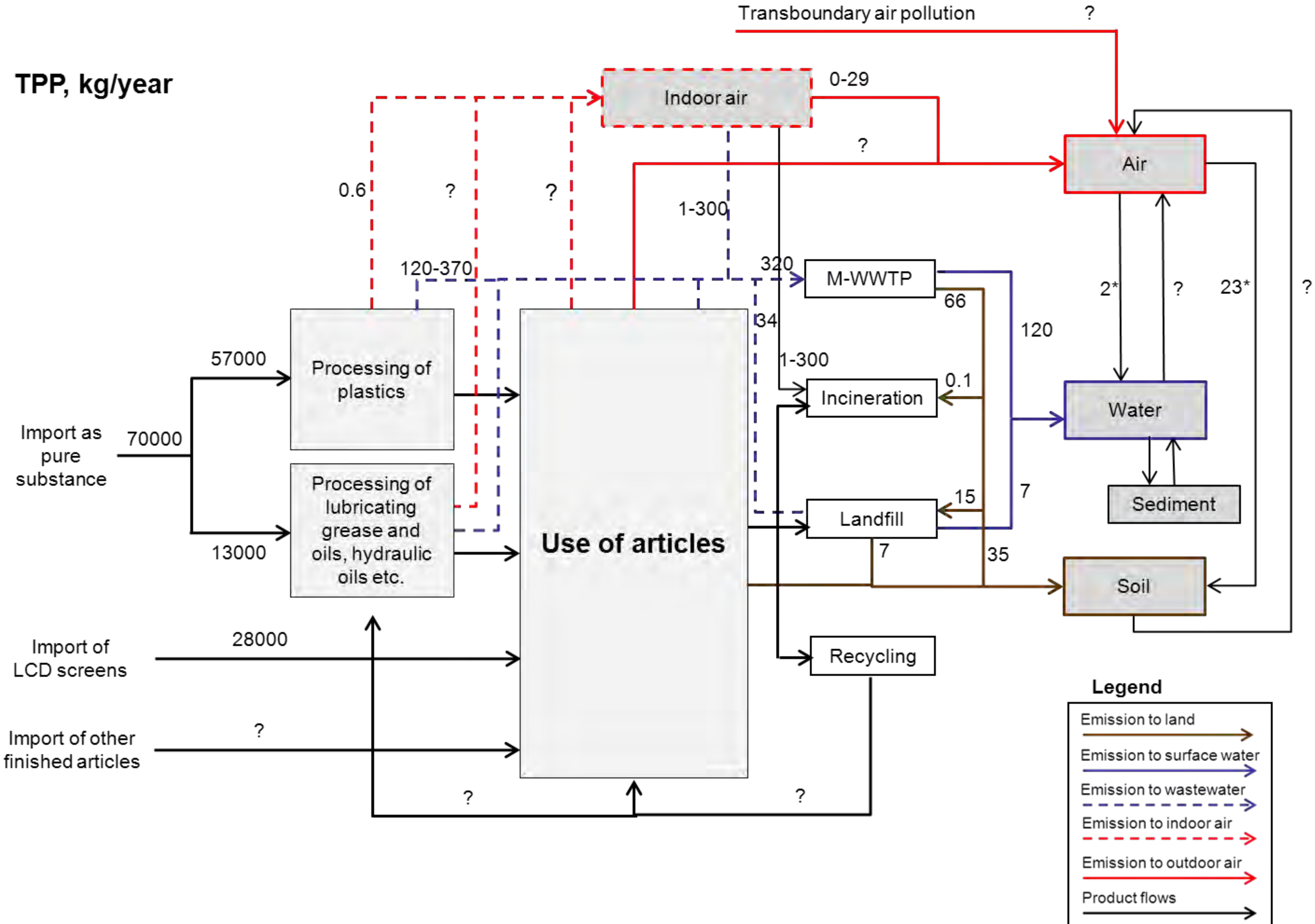
DINP, tonnes/year



Information about TPP

- TPP – triphenyl phosphate
- Main use is as a flame retardant in plastics such as PVC and in printed circuit boards
- TPP is also used in hydraulic fluids, adhesives, inks and coatings

TPP, kg/year



Transboundary air pollution
?
Indoor air
0-29
?
Air
0.6
?
?
1-300
120-370
320
M-WWTP
66
34
120
2*
?
23*
?
1-300
Incineration
0.1
Water
57000
Processing of plastics
Import as pure substance
70000
Processing of lubricating grease and oils, hydraulic oils etc.
13000
Use of articles
15
Landfill
7
7
35
Sediment
Soil
Import of LCD screens
28000
Recycling
Import of other finished articles
?
?
?
Legend
Emission to land
Emission to surface water
Emission to wastewater
Emission to indoor air
Emission to outdoor air
Product flows

Conclusions

- The majority of data that exist is regarding:
  - Use of chemicals within the Swedish industry
  - Environmental concentrations in different matrices such as wastewater, sludge, landfill leachate etc.

- Very little on no data exist for:
  - Chemical content in finished products
  - Import of chemicals in finished products
  - Emissions from use and waste management

Conclusions

- The import of these substances as pure substances and within finished articles is much larger than the sum of all emissions quantified here.
- →The majority of the additives appear to remain in the articles when they reach waste management
- However, emissions of plastic additives during use and waste management can vary greatly due to chemical properties

Future work

- Develop declarations of contents for articles
- Develop models that describe emission processes during use and waste management (ChEmiTecs)
- Develop fate models that take indoor environment into consideration (ChEmiTecs)
- Screen for more substances in the environment so that emissions models and fate models can be verified
- All articles consist of a mixture of chemical substances – develop/improve risk assessment methodology for mixtures

Thank you.

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Chemicals in leather – International trends on risk based control and management

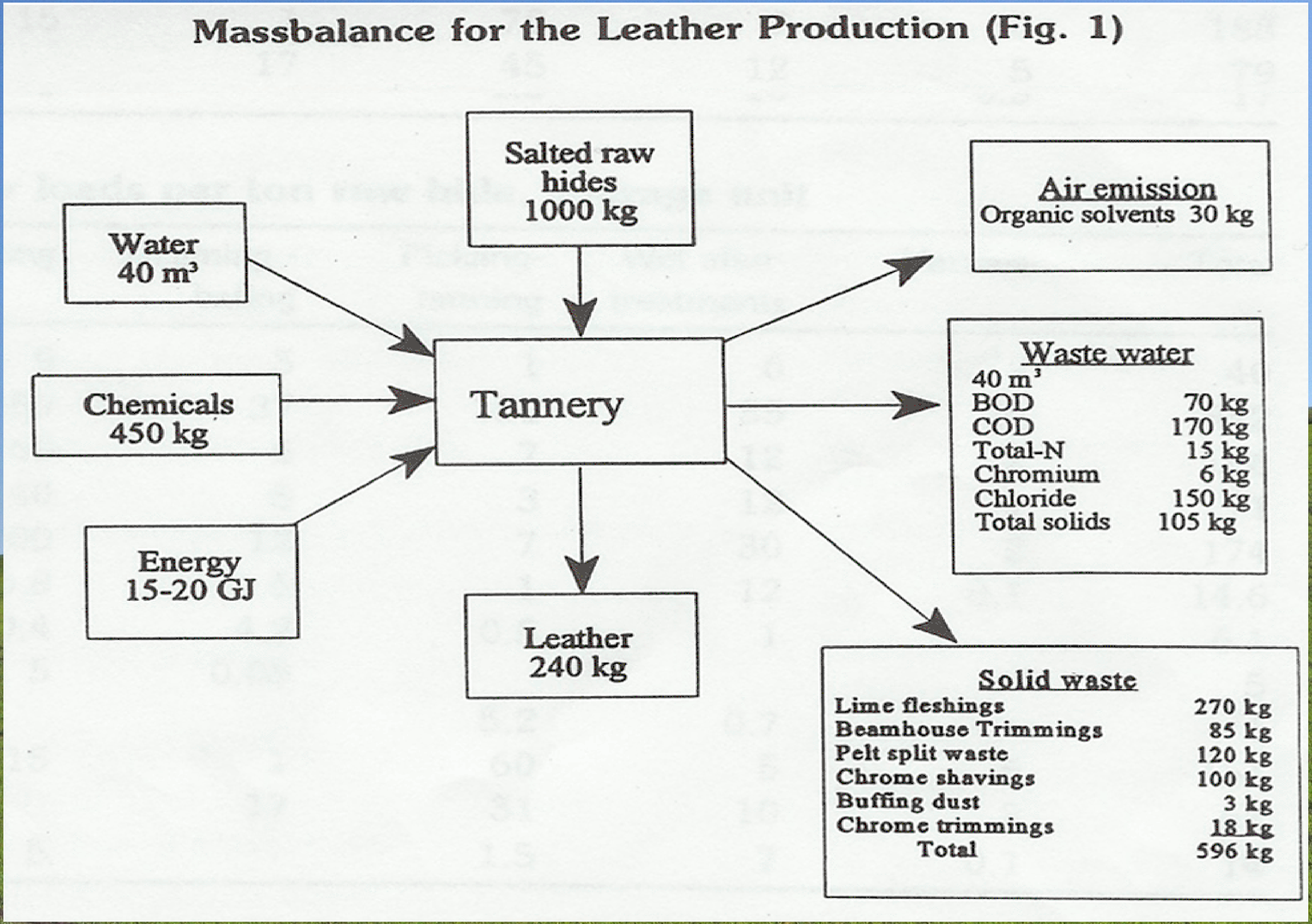
Stefan Rydin

Nordeconsult Sweden AB

DRESDEN , 8 MAY 2012

Contents

- Use of chemicals in leather sector
- Drivers and barriers for chemical management
  - National/European regulations
  - Eco-labels
  - Manufacturers and brands
- Chemicals in products


Massbalance for the Leather Production (Fig. 1)
Salted raw hides 1000 kg
Water 40 m³
Chemicals 450 kg
Energy 15-20 GJ
Tannery
Leather 240 kg
Air emission
Organic solvents 30 kg
Waste water
40 m³
BOD 70 kg
COD 170 kg
Total-N 15 kg
Chromium 6 kg
Chloride 150 kg
Total solids 105 kg
Solid waste
Lime fleshings 270 kg
Beamhouse Trimmings 85 kg
Pelt split waste 120 kg
Chrome shavings 100 kg
Buffing dust 3 kg
Chrome trimmings 18 kg
Total 596 kg

LEATHER INDUSTRY

- Traditional industrial sector
- Leather Industry – chemically intensive industry
- 3 kg chemicals / kg leather produced
- Approximately 300-400 different chemicals used
- 20-25 % weight of hides becomes leather
- Use by-product from meat industry as raw material

Chemical consumption

Chemical	Kg/ton salted rawhide
Inorganic standard chemicals	215
Organic standard chemicals	35
Chromium tanning agents	80
Vegetable/synthetic tanning agents	40
Fatliquoring agents	40
Finishing chemicals	46
Organic solvents	25
Detergents, enzymes	8
Dyes	9
Others	25
TOTAL	450 - 500

Use of Inorganic Chemicals

Chemical	Kg/ton salted rawhide
Sodium chloride	85
Calcium hydroxide	35
Sodium sulphide/hydrosulphide	29
Ammonia and ammonium salts	23
Sulphuric acid	14

Drivers for Chemical Management

– Drivers

- National/European regulations and laws
- Eco-Labels for consumer items
- Manufacturers and brands

– Barriers

- Traditional sector
- Not enough knowledge

National/European legislation

- EU IED (Industrial Emissions Directive)
- EU REACH
- USA – EPA and Consumer Product Safety Commission (CPSC)
- Japan – Harmful Substance (Law 112)
- China – ”China Reach” (October 2010)

Eco-Labels

- High number – test-institute – textile oriented
- Oeko-Tex
- SG Label
- Blue Angel
- Nordic Ecolabel (svanen)
- EU Footwear Eco-Label

Manufacturers and brands

- Adidas, H&M, IKEA, Gant and others – Restricted Substances List (RSL)
- Automotive Industry (2732 substances)
- Sweden Textile Water Initiative
- Swedish Shoe Environmental Initiative

Chemicals in products

- Aromatic amines from Azo-dyes (22 amines forbidden, detection limit EU regulation 30 mg/l)
- Short-chained chlorinated paraffins
- Chlorinated phenols
- Chromium (VI)
- Formaldehyde (e.g. automotive industry, eco-labels)
- Dimethylfumarate
- Nonylphenol

Chromium (VI)

- Chromium (VI) not used by tanneries
- Can be formed during certain process conditions
- Investigations started 10-15 years ago
- Recent investigations in Sweden (gloves) and Denmark (shoes)
- Chromium allergy in DK increased due to leather
- Danish proposal for REACH regulation

Final remarks

- Many chemicals used by tanneries (300-400 different chemicals)
- Drivers for chemical management
  - Customer requirements
  - Legislation
- Barriers
  - Difficult to get information
  - Mainly SMEs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Evangelos Gidarakos

John Hahladakis

Assessment of released heavy metals from the MS "Sea Diamond" shipwreck

Contents

- Introduction
- Sea Waste (sources and effects)
- The “Sea Diamond” shipwreck
- The environmental study of TUC in the “Sea Diamond” shipwreck
- Safety limits criteria for heavy metals in Seawater and Sediments
- Results
- Conclusions

Introduction

- The involuntarily influx of heavy metals of the third category ("unnecessary" e.g. Hg, Cd, Pb) in the marine environment is considered, by definition, **contamination.**
- Furthermore, when metals of the secondary category (e.g. Zn, Cu) exist in elevated concentrations, may lead to disturbance of the mechanisms of intake-excretion of the living organisms in the aquatic environment.

Heavy metals come with two significant characteristics :

They are not biodegradable

(Persistent pollutants)

They tend to bioaccumulate

Sea Waste (1)

- **Sea Contamination** occurs when harmful, or potentially harmful effects, can result from the entry into the ocean of chemicals, particles, industrial, agricultural and residential waste, noise, or the spread of invasive organisms.
- Most sources of sea contamination are land based.
- Toxic metals can also be introduced into marine chain food. These can cause a change to tissue matter, biochemistry, behaviour, reproduction, and suppress growth in marine life.

Sea Waste (2)

There are many different ways to categorize, and examine the inputs of pollution into our marine ecosystems but generally, there are four main types of inputs of pollution into the ocean:

- direct discharge of waste into the oceans
- runoff into the waters due to rain
- pollutants that are released from the atmosphere
- ship pollution

Sea Waste (3)

- **Direct discharge**

Pollutants enter rivers and the sea directly from urban sewerage and industrial waste discharges, sometimes in the form of hazardous and toxic wastes.

- **Land runoff**

Polluted runoff from roads and highways can be a significant source of water pollution in coastal areas.

- **Atmospheric pollution**

Wind blown dust and debris, including plastic bags, are blown seaward from landfills and other areas.

Sea Waste (4)

- **Ship Pollution**

Ships can pollute waterways and oceans in many ways. Oil spills can have devastating effects. While being toxic to marine life, polycyclic aromatic hydrocarbons (PAHs), found in crude oil, are very difficult to clean up, and last for years in the sediment and marine environment. Heavy metals existing both in the hulk and cargo of a ship are also one of the major contaminants of seawater, especially in a **shipwreck case Scenario**.

The «Sea Diamond» shipwreck (1)

On April 5, 2007 the MS “Sea Diamond” ran aground a reef, at the east side of Nea Kameni, an area within the caldera of the Greek island of Santorini.

Fig. 1

The «Sea Diamond» shipwreck (2)

The «Sea Diamond» shipwreck (3)

Keeping in mind the volcanic activity of the area, it is feared that the hulk would either brake or slide deeper and sink into the submerged caldera of the island, as shown in Figure 2

Fig. 2

Environmental Study of TUC (1)

Qualitative and quantitative characterization of hazardous and toxic substances released from the sinking of "SEA DIAMOND"

Environmental Study of TUC (2)

PARTS

- Part A:

  “Qualitative and quantitative characterization of hazardous and toxic substances from the sinking of SEA DIAMOND’’
- Part B

  ‘’Evaluation of impacts of SEA DIAMOND’s antifouling paints in the Santorini’s marine environment’’
- Part C

  ‘’Petroleum Hydrocarbons: Sampling and Analysis’’
- Part D

  ‘’Environmental impacts of influx of heavy metal contaminants into the marine environment of Caldera’’
- Part E

  ‘’Determination of heavy metals in fish tissues into the Santorini’s marine environmental’’
- Part F

  ‘’Release of heavy metals from the sinking of SEA DIAMOND- Evaluation of current and long term impacts’’
- Part G

  ‘’Final results’’

Environmental Study of TUC (3)

Table 1. *Estimated quantities of metals and heavy metals existing in "Sea Diamond" according to the Green Passport of the MS and the part F of the environmental study of TUC in the wreck area ([a] The quantities are in tons).*

Element	Estimated quantity (kg)[a]
Iron (Fe)	[a]14.625-14.629
Manganese (Mn)	58.562-104.595
Copper(Cu)	7.652,5-11.657,3
Zinc (Zn)	1.169-6.751,7
Lead (Pb)	1.140-1.260
Chromium (Cr)	372,4-886
Cadmium (Cd)	0,63-1,05
Nickel (Ni)	38,43-1.497,4
Aluminum (Al)	134-1.598,6
Vanadium (V)	262
Magnesium (Mg)	47-81,2
Molybdenum (Mo)	67-180
Mercury (Hg)	0,075-0,080

Safety limits criteria for heavy metals in Seawater and Sediments (1)

US EPA (US Environmental Protection Agency) has set a series of concentration limits for heavy metals in seawater based on their effects on aquatic living organisms. These are:

- Criterion Maximum Concentration (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect
- Criterion Continuous Concentration (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect

Safety limits criteria for heavy metals in Seawater and Sediments (2)

Similarly, and originally intended for use by NOAA (National Oceanic and Atmospheric Administration) SQG's (Sediment Quality Guidelines) provide concentrations limits of contaminants (heavy metals and pahs) in sediments in order to ensure safe living of organisms in or near them. Two sets of guidelines are commonly used, the ERL/ERM and TEL/PEL.

- The low range values (**E**ffects **R**ange **L**ow or **T**hreshold **E**ffect **L**evel) represent concentrations below which adverse effects upon sediment dwelling organisms are not likely to occur.

- Upper range values (**E**ffects **R**ange **M**edian or **P**robable **E**ffects **L**evel) represent concentrations above which adverse effects are expected to appear.

Safety limits criteria for heavy metals in Seawater and Sediments (3)

- The ERL/ERM indicators use percentiles of the 10th and 50th of metal concentrations that create adverse biological effects respectively.

- On the other hand, TEL/PEL indicators use the geometric mean of the aforementioned percentiles of concentration values that create or not adverse effects respectively

Table 2. *Safety limits (criteria) set by the US EPA for concentrations of heavy metals in seawater*

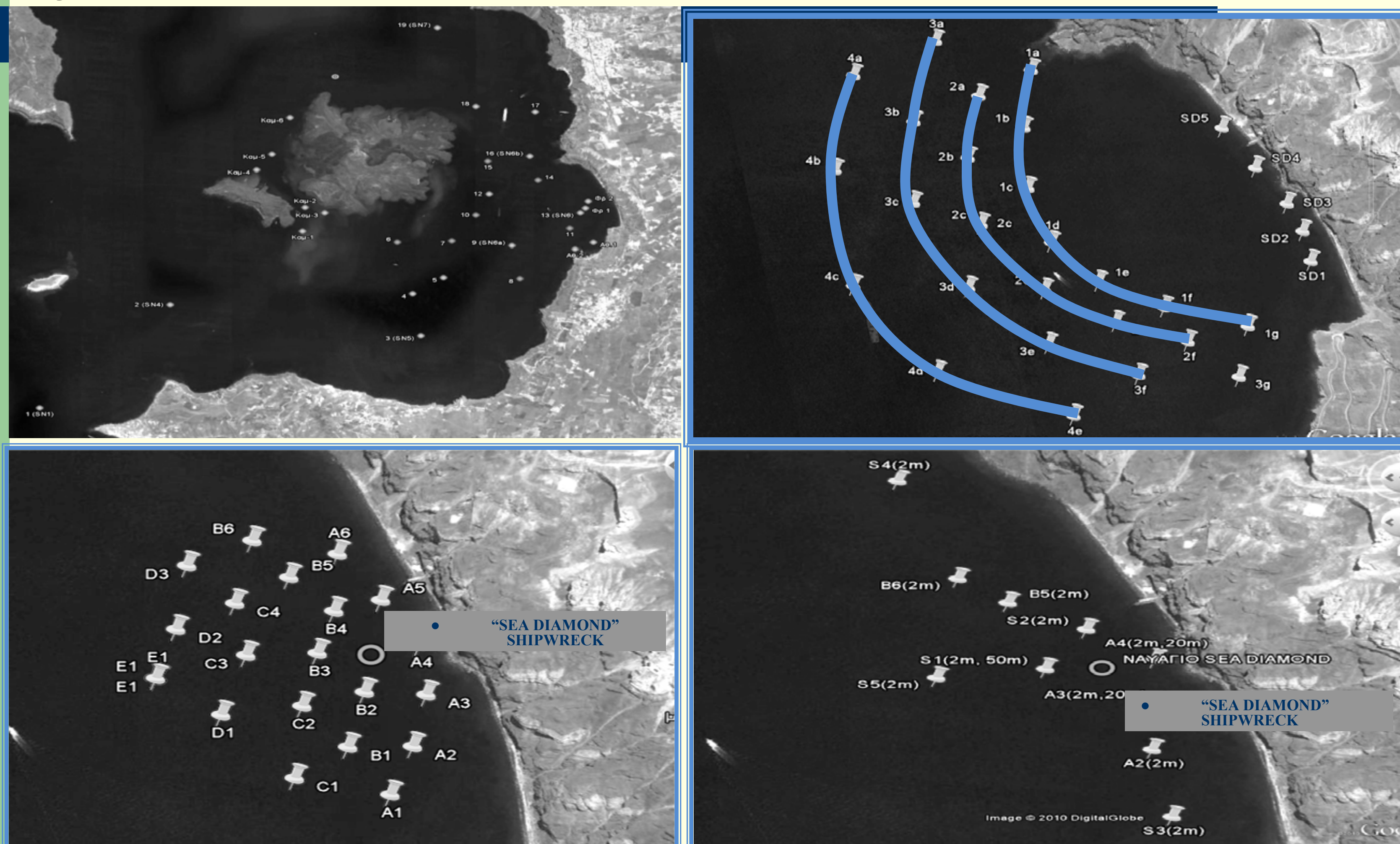
Element	Criterion of maximum concentration (CMC, μg/l)	Criterion of continuous concentration (CCC, μg/l)
Cadmium (Cd)	40,0	8,8
Copper (Cu)	4,8	3,1
Lead (Pb)	210,0	8,1
Nickel (Ni)	74,0	8,2
Chromium (Cr (VI))	1.100,0	50,0
Zinc (Zn)	90,0	81,0
Mercury (Hg)	1,8	0,94
Arsenic (As)	69	36

Table 3. *ERL/ERM, TEL/PEL limit values for sediments*

Element	ERL (mg/kg dw)	ERM (mg/kg dw)	TEL (mg/kg dw)	PEL (mg/kg dw)
Pb	46,7	218	30,2	112
Cd	1,2	9,6	0,68	4,21
Cr	81	370	52,3	160
Ni	20,9	51,6	15,9	42,8
Hg	0,15	0,71	0,13	0,7
Zn	150	410	124	271
Cu	34	270	18,7	108

Sampling sites of all the four series of seawater sampling (1)

Fig. 3



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Laboratory of Toxic & Hazardous Waste Management

Sampling sites of all the three series of sediment sampling (2)

Fig. 4

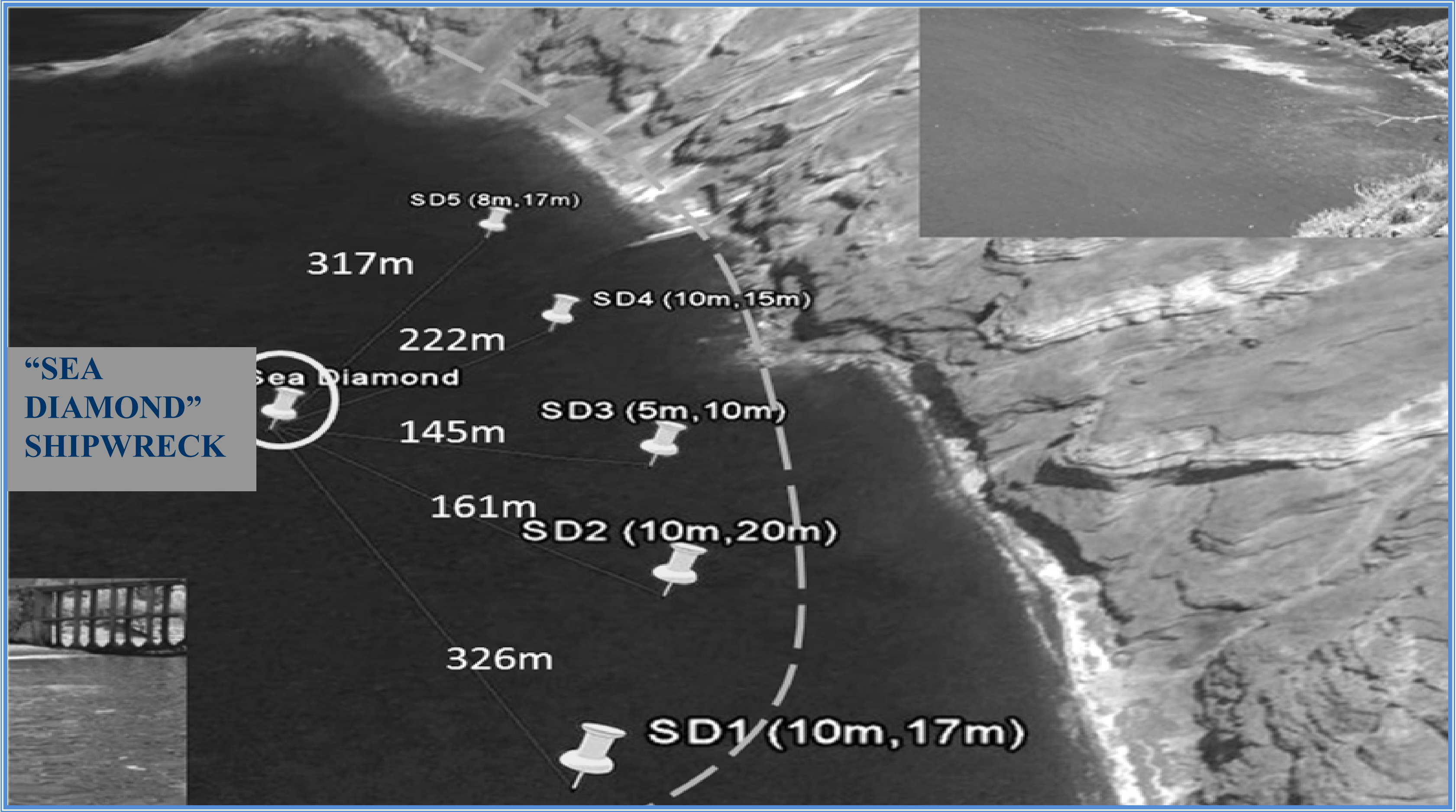


***Table 4.** Comparison of heavy metals concentration results in all seawater samples (n=85) with EPA criteria*

Element	Criterion maximum concentration (CMC, μg/l)	Criterion continuous concentration (CCC, μg/l)	Limits exceeded $1^{η}$ sampling (%)	Limits exceeded $2^{η}$ sampling (%)	Limits exceeded $3^{η}$ sampling (%)	Limits exceeded $4^{η}$ sampling (%)
(Cd)	40,0	8,8	0/29 (0%)	0/25 (0%)	**5/18 CMC (28%)**	0/13 (0%)
(Cu)	4,8	3,1	**1/29 CMC (3%)**	0/25 (0%)	0/18 (0%)	0/13 (0%)
(Pb)	210,0	8,1	0/29 (0%)	0/25 (0%)	**5/18 CMC (28%) & 3/18 CCC (17%)**	0/13 (0%)
(Ni)	74,0	8,2	0/29 (0%)	0/25 (0%)	0/18 (0%)	0/13 (0%)
Cr (VI)	1.100,0	50,0	0/29 (0%)	0/25 (0%)	0/18 (0%)	0/13 (0%)
(Zn)	90,0	81,0	0/29 (0%)	0/25 (0%)	0/18 (0%)	0/13 (0%)
(Hg)	1,8	0,94	0/29 (0%)	0/25 (0%)	0/18 (0%)	0/13 (0%)

Table 5. *Mean values of metal concentrations from all sediment samples (n=31)*

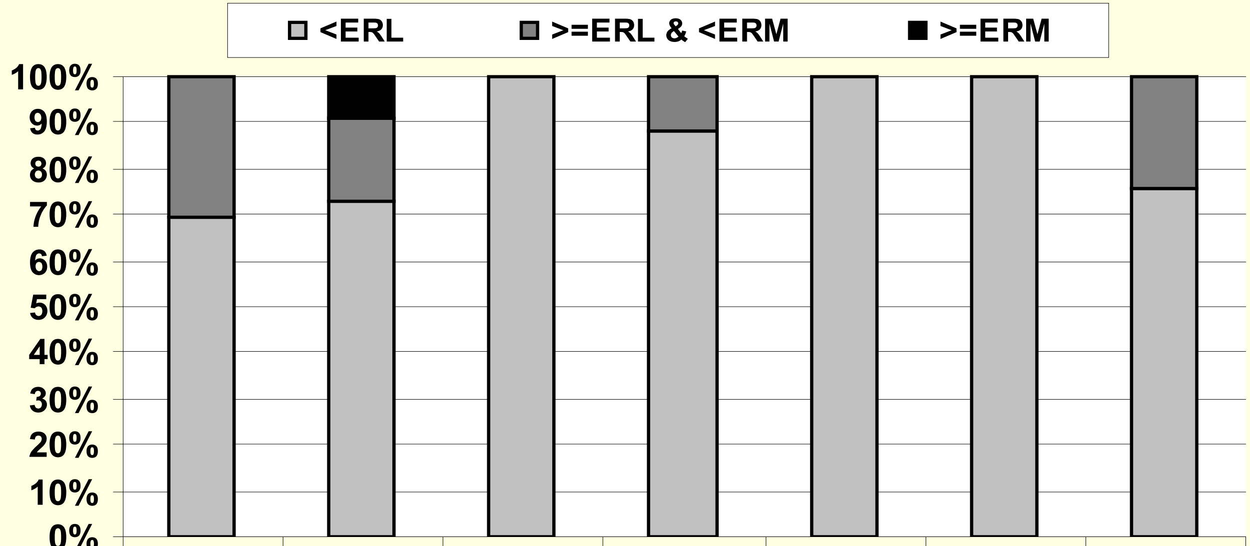
Element	Mean Value (ppm) First sampling series (n=10)	Mean Value (ppm) Third sampling series* (n=10)	Mean Value (ppm) Fourth sampling series (n=11)
Lead (Pb)	63,4	24,9	27,4
Cadmium (Cd)	-	10,7	2,1
Iron (Fe)	23.300	19.300	18.180
Copper (Cu)	48,8	18	14,3
Chromium (Cr)	-	4,9	4.5
Manganese (Mn)	370	275,7	265,5
Nickel (Ni)	22,3	6,25	6,3
Mercury (Hg)	-	-	-
Zinc (Zn)	53	52,1	46,7

**** No sediment samples were collected during the second series of sampling***

Application of SQGs (Sediment Quality Guidelines) for the contamination assessment of sediments from the wreck area in accordance with (a) the ERL/ERM values and (b) the TEL/PEL values (1)

Fig. 5 (a)

Sediment is rarely **(<ERL)**, occasionally **(>ERL & <ERM)** and frequently **(>ERM)** associated with adverse biological effects

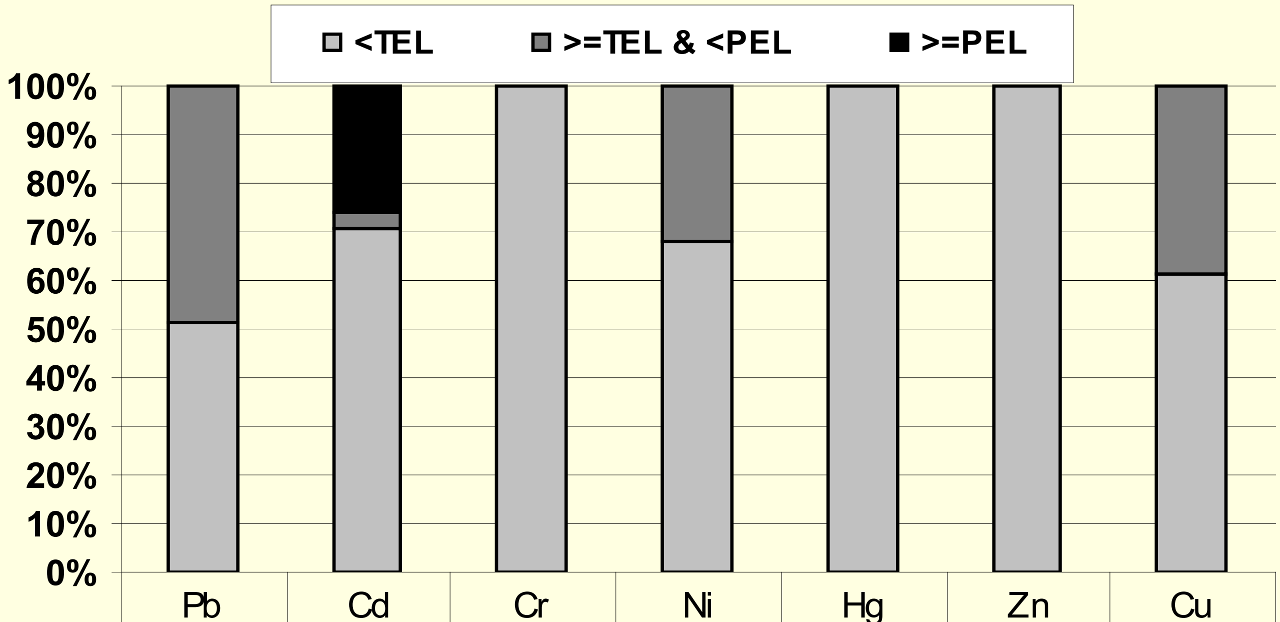


	Pb	Cd	Cr	Ni	Hg	Zn	Cu
>=ERM	0,0%	9,1%	0,0%	0,0%	0,0%	0,0%	0,0%
>=ERL & <ERM	30,3%	18,2%	0,0%	12,1%	0,0%	0,0%	24,2%
<ERL	69,7%	72,7%	100,0%	87,9%	100,0%	100,0%	75,8%

Application of SQGs (Sediment Quality Guidelines) for the contamination assessment of sediments from the wreck area in accordance with (a) the ERL/ERM values and (b) the TEL/PEL values (2)

Fig. 5 (b)

Sediment is rarely **(<TEL)**, occasionally **(>TEL & <PEL)** and frequently **(>PEL)** associated with adverse biological effects



	Pb	Cd	Cr	Ni	Hg	Zn	Cu
>=PEL	0,0%	25,8%	0,0%	0,0%	0,0%	0,0%	0,0%
>=TEL & <PEL	48,4%	3,2%	0,0%	32,3%	0,0%	0,0%	38,7%
<TEL	51,6%	71,0%	100,0%	67,7%	100,0%	100,0%	61,3%

Conclusions (from Seawater samples)

- The first and the second sampling series of the water column showed low concentration values for all metals.
- The third revealed the abundant presence of Pb and Cd in concern levels (up to 1000% for Cd and 800% for Pb above the EPA limits for seawater).
- The sampling sites of the above measurements were very near the wreck area and the results, therefore, can be associated with the shipwreck.
- Other heavy metals (such as Hg, Ni, Cr) were found in concentrations below 1-3 ppb and raise no concern at all.
- In general, it is expected that whatever heavy metals may be released in the water column from the shipwreck of “Sea Diamond”, will eventually end up to their final recipient, the seawater sediments.

Conclusions (from Sediment samples)

- According to SQGs significant percentage of the sediment samples could be associated to occasional **toxic effects** to aquatic organisms. The percentages in accordance with ERL/ERM and TEL/PEL limits are higher for **Cu** (24,2% -38,7%) and **Pb** (30,3% -48,4%) and lower for **Ni** (18,2% -32,3) respectively.
- **Cd** more than any other heavy metal can be held responsible for toxic effects upon sediments dwelling fauna since 18,2% of the samples can be associated with frequent observation of adverse effects and 9,1% with occasional.
- Cr, Ni and Hg, according to SQGs, can be rarely associated with toxic effects.

Thank you all for your attention!

CRETE2012

3RD INTERNATIONAL CONFERENCE ON INDUSTRIAL AND HAZARDOUS WASTE MANAGEMENT

12-14 September 2012
Chania, Crete, Greece

www.hwm-conferences.tuc.gr

Important Deadlines:

Full paper submission:
15th May 2012

Early registration:
15th May 2012

TOPICS

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  - Regulation / legislation
  - Characterization
  - Management Practices
  - Production, Minimization and Recycling
  - Treatment and Disposal
- Hazardous Waste Toxicology - Risk assessment
- Treatment of Hazardous Waste landfill and Mine leachates
- Contaminant Release and Transport
- Toxic substances in the food Chain
- Management of Contaminated sites
- Special Topics on Environmental Management and Remediation (sediment sites – characterization and risk assessment, munition and explosives production sites, etc.)
- Radioactive Waste (management, environment, health and safety, nuclear explosions, etc.)
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- Case studies
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