

Sources and congener profiles



Sources of PCBs

- Used as technical mixtures and may still be present in older equipment
 - Transformers
 - Heat exchange equipment
 - E.g. Arochlor, Kanechlor, Clophen
- Also used in certain paints and sealants
 - Flame retardant



Sources of dioxins (PCDD/Fs)

- Present as contaminants in e.g.:
 - PCB mixtures
 - Trichlorophenol
 - Pentachlorophenol
 - 2,4,5-trichlorophenoxyacetic acid (used in agent Orange)
- Kaolinic clay and other clays (ball clay, Mabele clay)
- Recycled minerals
- Formed during incineration of plastic waste (fires)

Burning of household waste, also at lower scale and some fires



Pattern database for dioxins

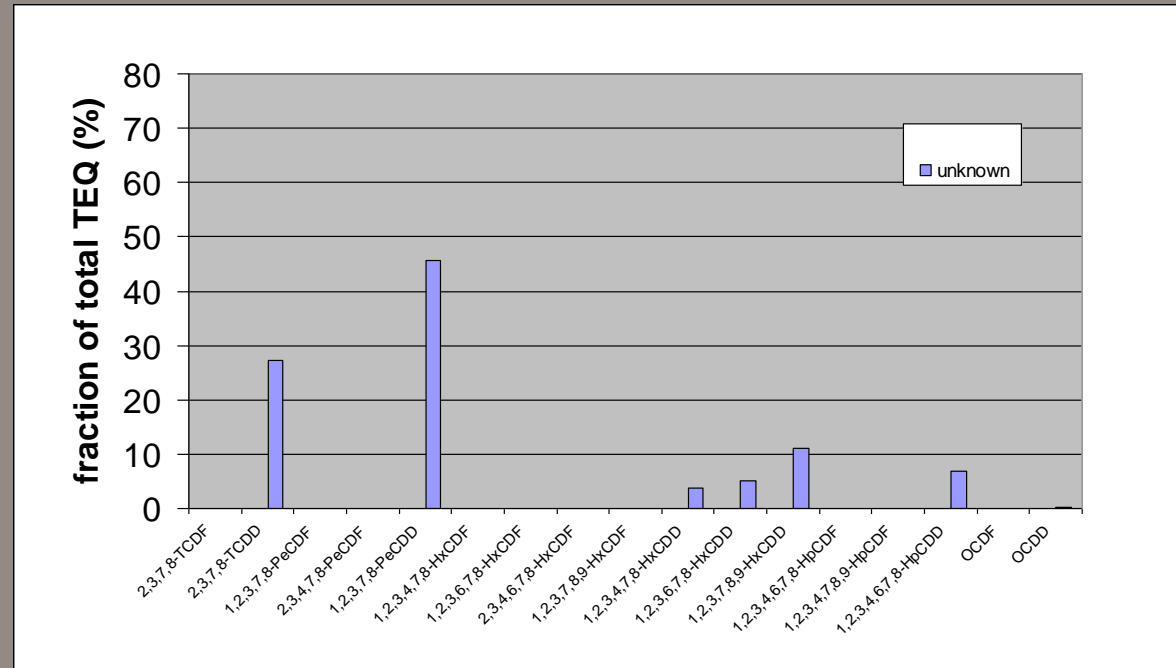
Ron Hoogenboom, Rainer Malisch, Guillaume ten Dam,
Stefan van Leeuwen, Helge Hove, Alwyn Fernandes,
Alexander Schächtele, Martin Rose (et al.)



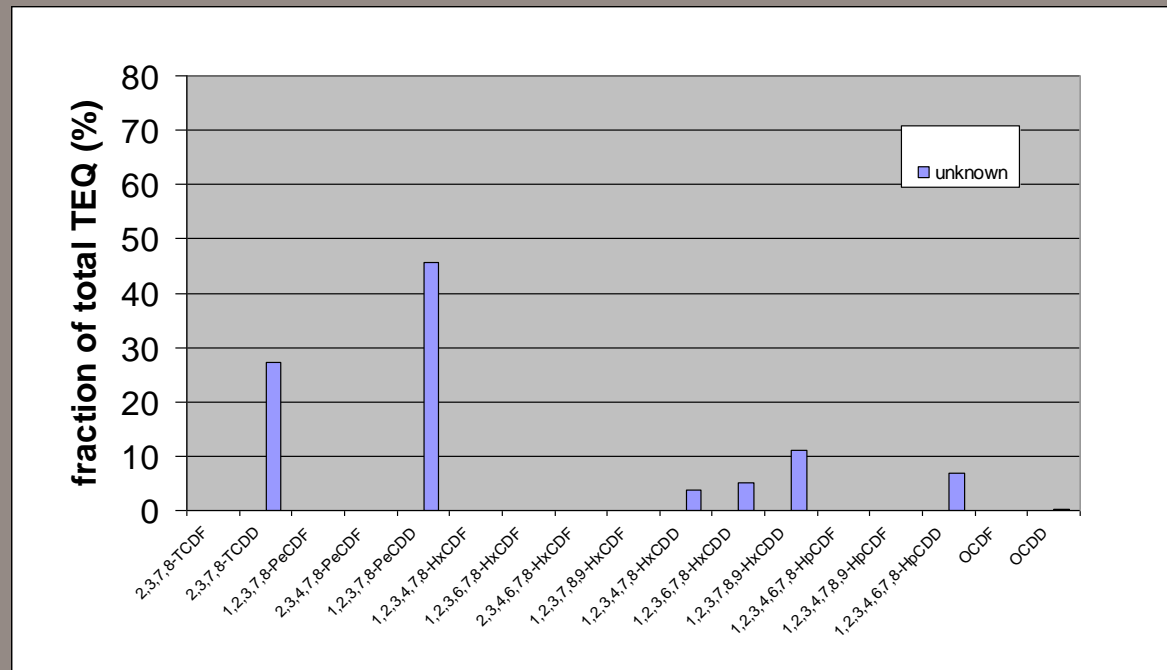
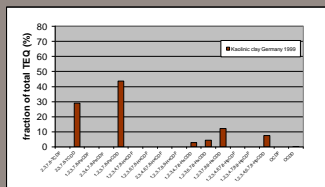
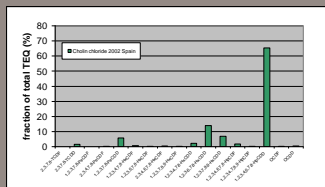
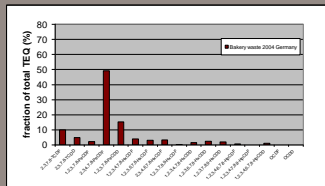
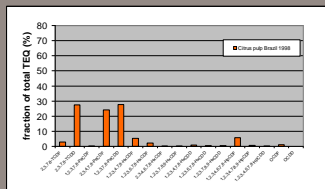
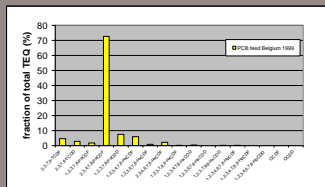
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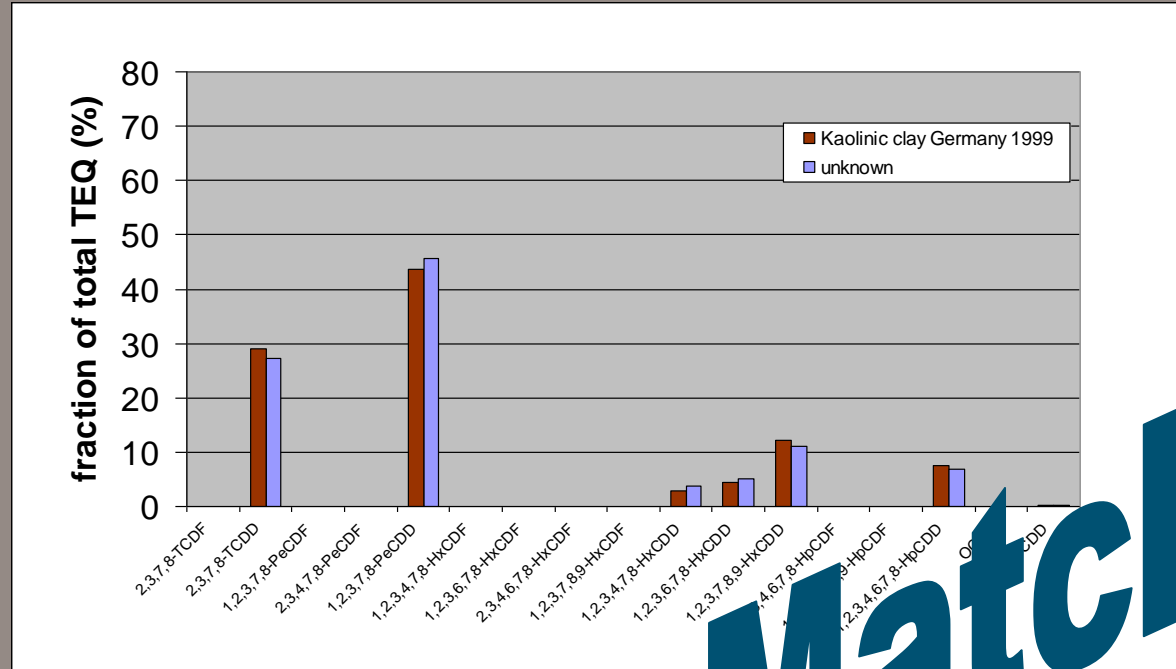
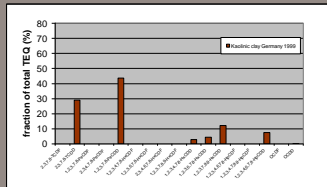
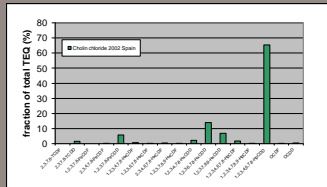
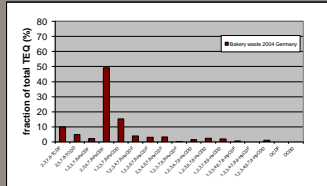
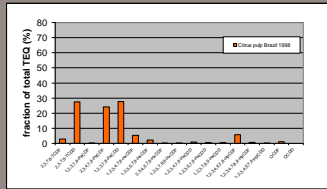
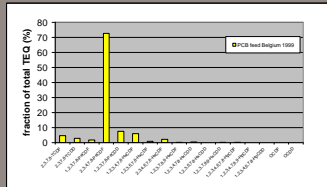
Unknown pattern in potato peels (2004)



Identification source



Identification source



Match!



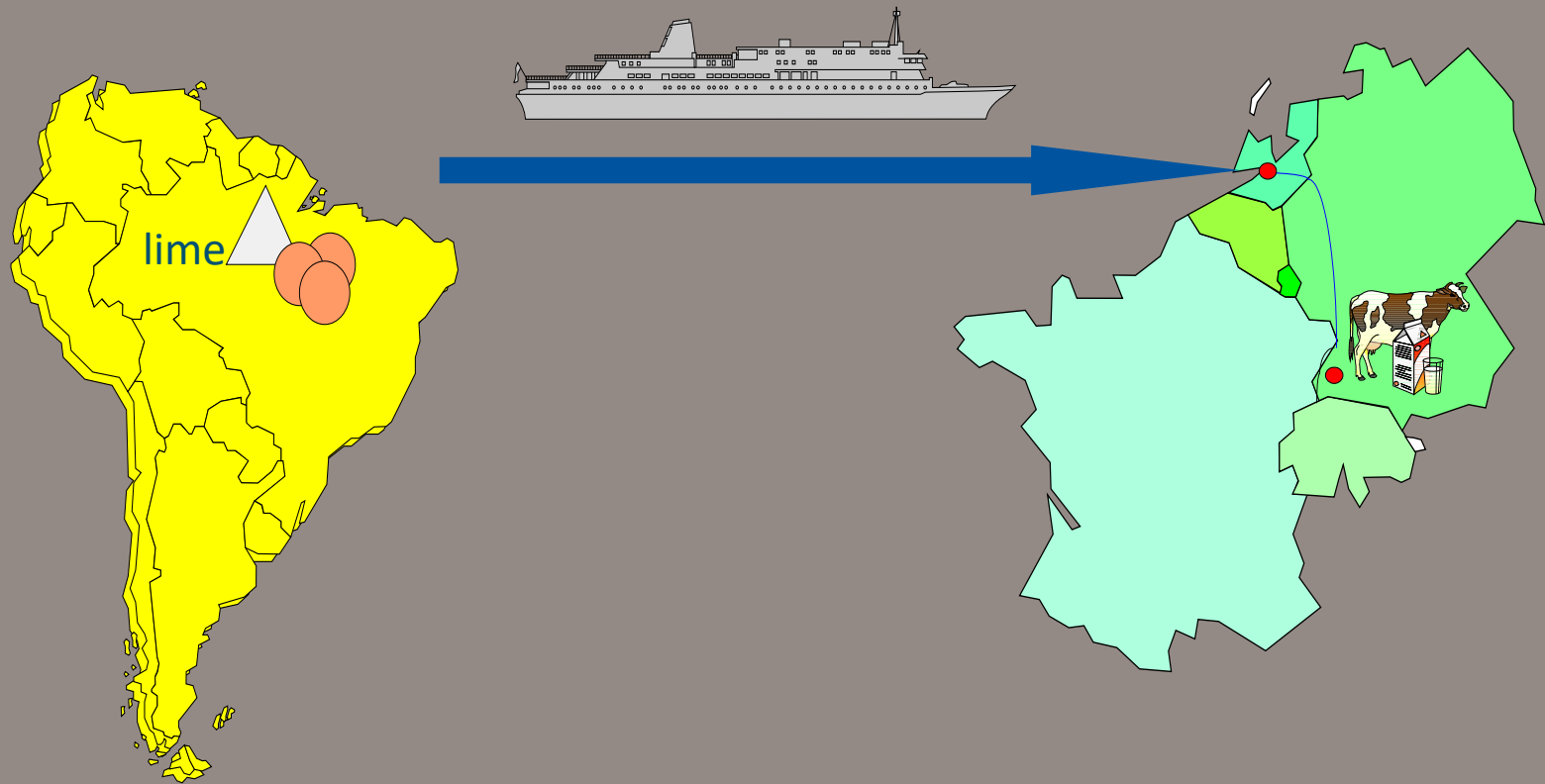
WG EURL/NRL congener patterns

- First phase:
 - To collect existing congener patterns
 - To develop a database
- Second phase:
 - To develop tools to analyze the patterns
- Third phase:
 - To include the role of kinetics

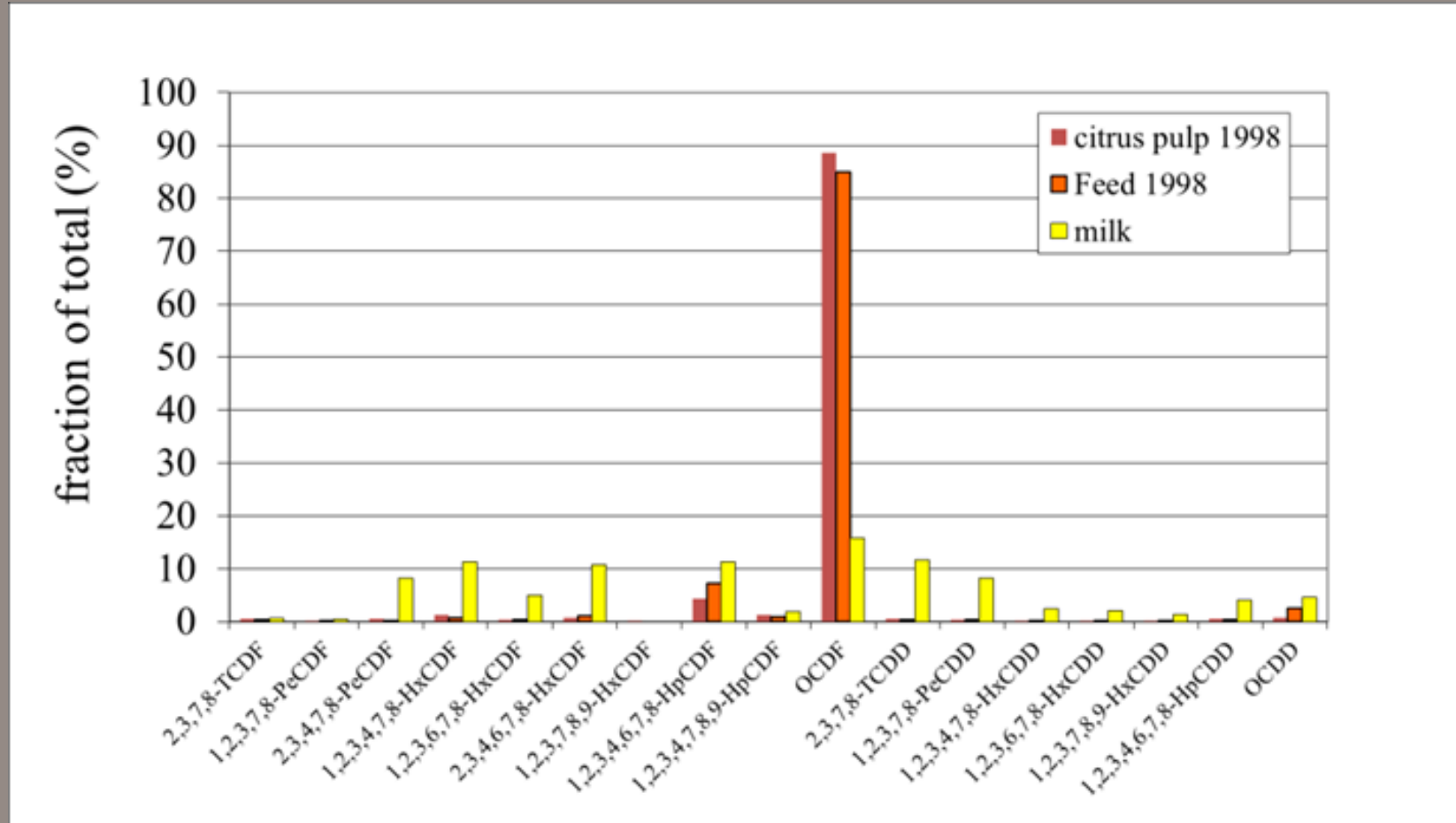
Which patterns?

- Primary focus on dioxins (PCDD/Fs)
 - No specification in PCB source
- Single sources, incidents with feed:
 - not mixed patterns
 - Not pure chemicals
 - Ideally with known source
- Primary patterns: so not in animal derived products
 - Third phase?
- Expressed on contribution to absolute or TEQ levels?

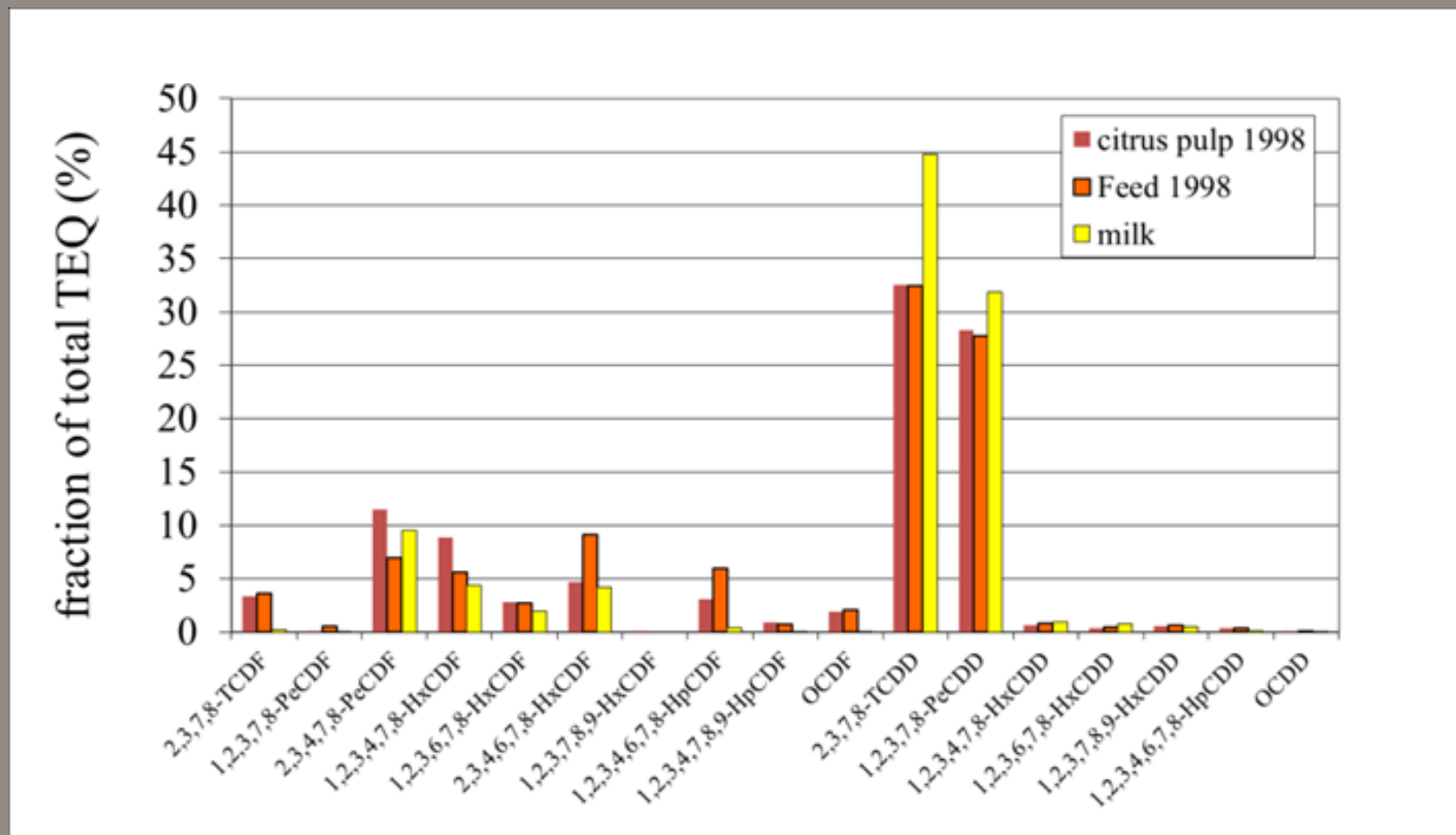
Dioxins in Brazilian citrus pulp (1998)



Expression of patterns, absolute levels or ..

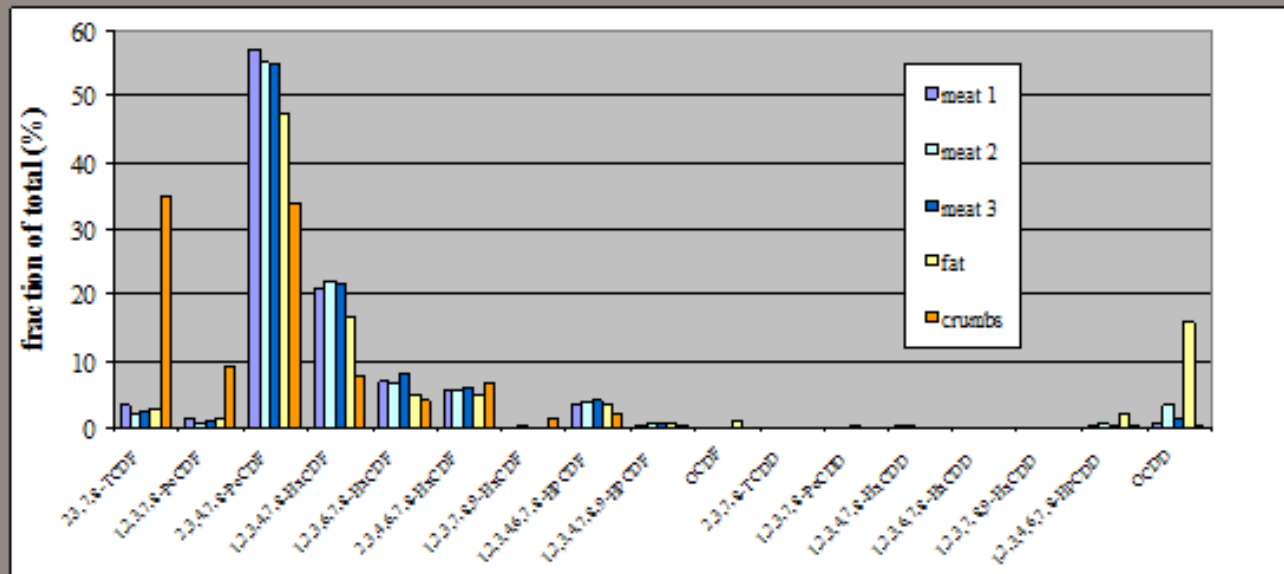


TEQ contribution?



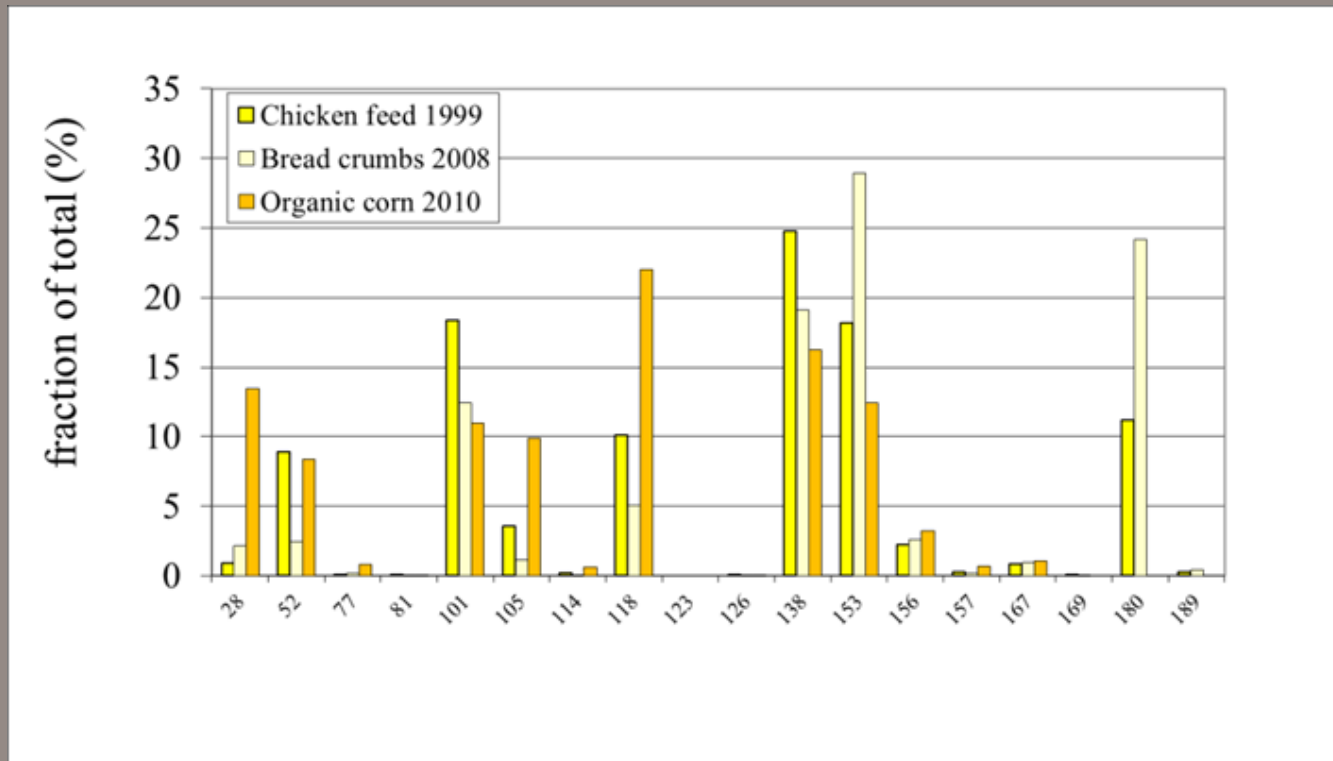
Comparison feed vs animal product

- Better comparison when based on TEQ contribution
- Reasonable correlation between transfer rate and TEFs
- Does not apply to all congeners
 - TCDF and 1,2,3,7,8-PeCDF metabolized by pigs and cows



What about PCBs?

- If based on TEQ, PCB 126 will dominate the pattern
- When based on absolute levels, ndl-PCBs can be included



Patterns collected



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Food and feed incidents (PCBs)

MWI milk 1989

Brazilian citrus pulp 1998

Belgian PCB fat 1999

German kaolinic clay 1999

Mozzarella Italy 2001-2004

Belgian choline chloride 2002

German bakery waste 2003

Potato peels/kaolinic clay 2004

Gelatin fat/Hydrochloric acid 2006

Indian Guar Gum 2007

Minerals (Zinc) Chile 2008

Bakery waste Ireland 2008

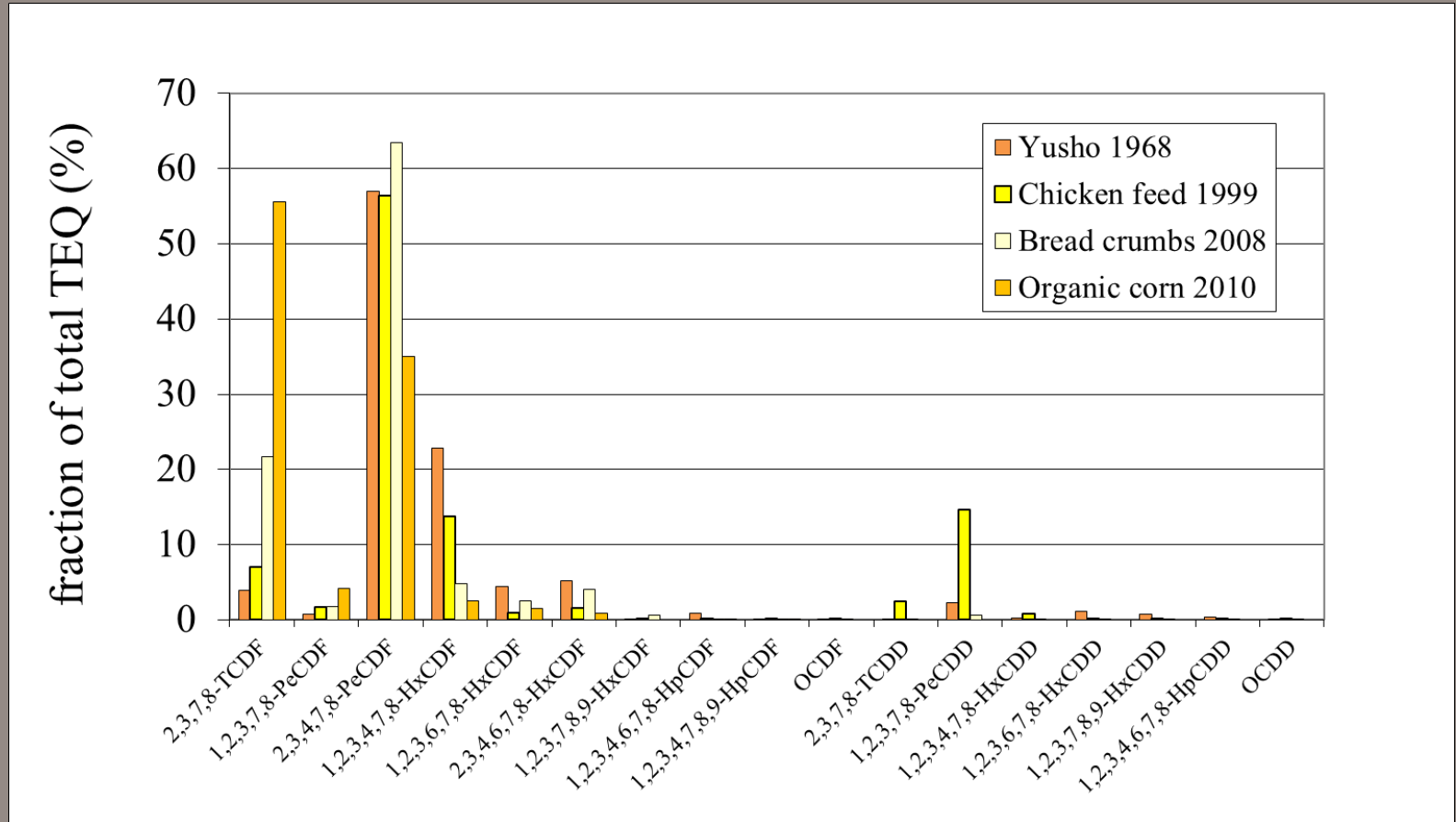
Organic corn Ukraine 2010

Fatty acids Germany 2011

Beet pulp Germany 2011

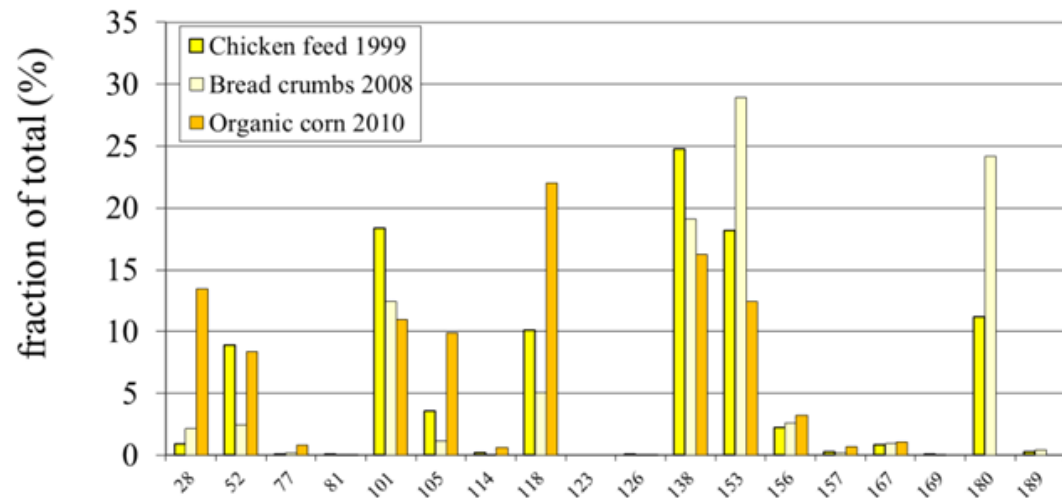
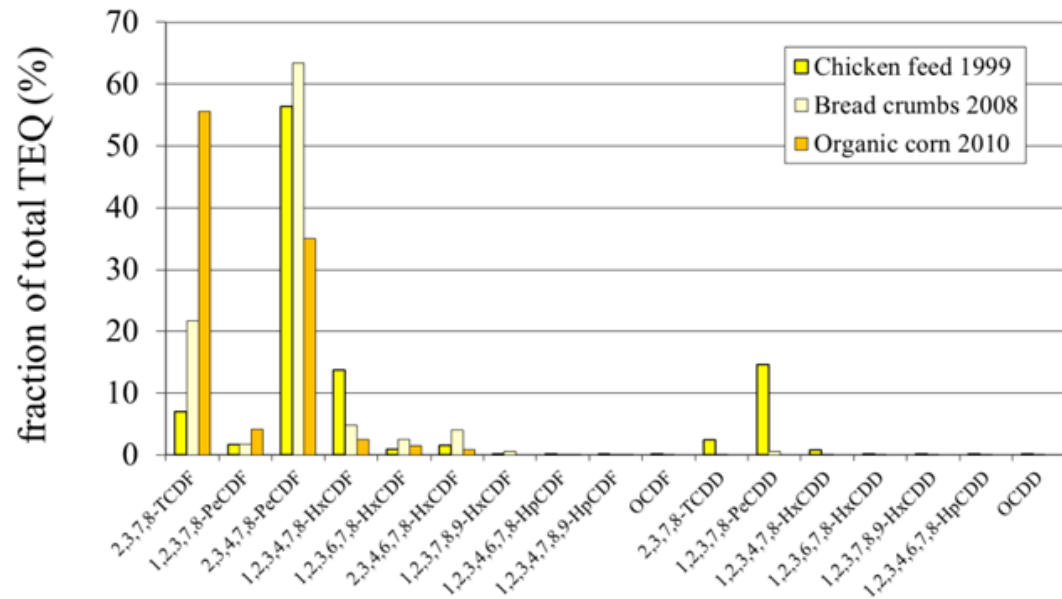
Free range eggs

PCBs



Primarily PCDFs; pattern depends on mixture

PCBs



Food and feed incidents (chlorophenols)

MWI milk 1989

Brazilian citrus pulp 1998

German kaolinic clay 1999

Mozzarella Italy 2001-2004

Belgian choline chloride 2002

German bakery waste 2003

Potato peels/kaolinic clay 2004

Gelatin fat/Hydrochloric acid 2006

Indian Guar Gum 2007

Minerals (Zinc) Chile 2008

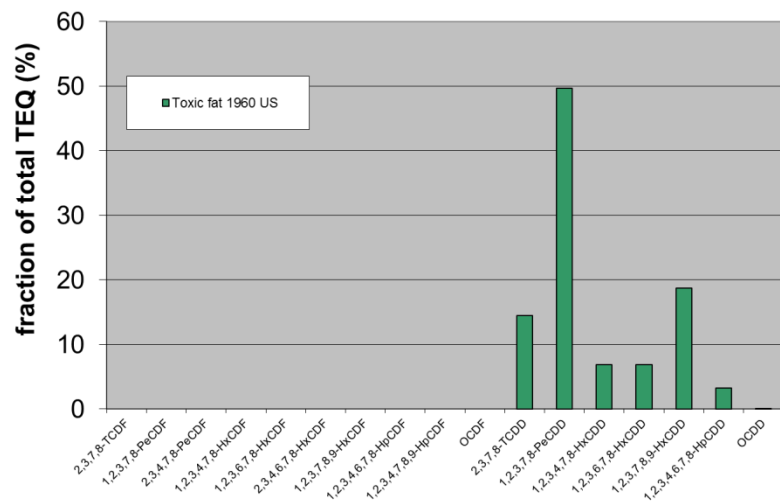
Free range eggs

Fatty acids Germany 2011

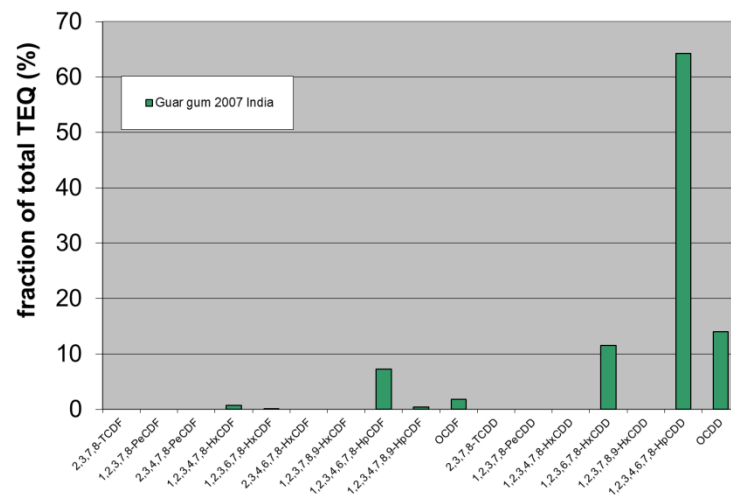
Beet pulp Germany 2011

Chlorophenols (PCDDs)

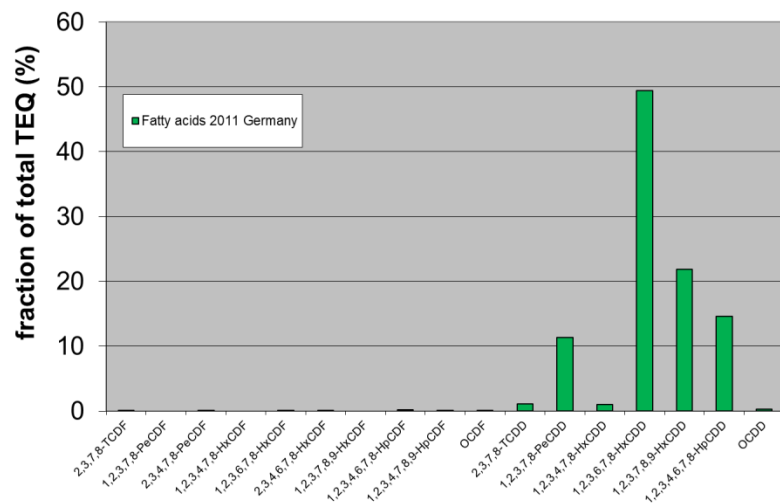
Toxic fat 1960 US



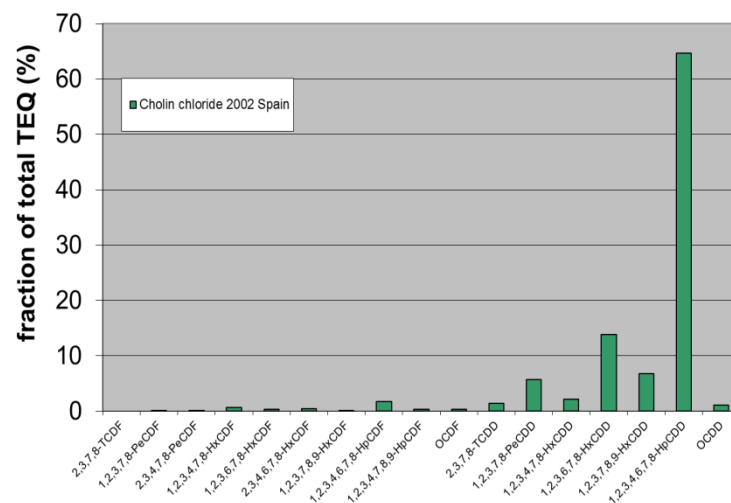
Guar gum 2007 India



Fatty acids 2011 Germany



Cholin chloride 2002 Spain



Food and feed incidents (clays)

MWI milk 1989

Brazilian citrus pulp 1998

German kaolinic clay 1999

Mozzarella Italy 2001-2004

German bakery waste 2003

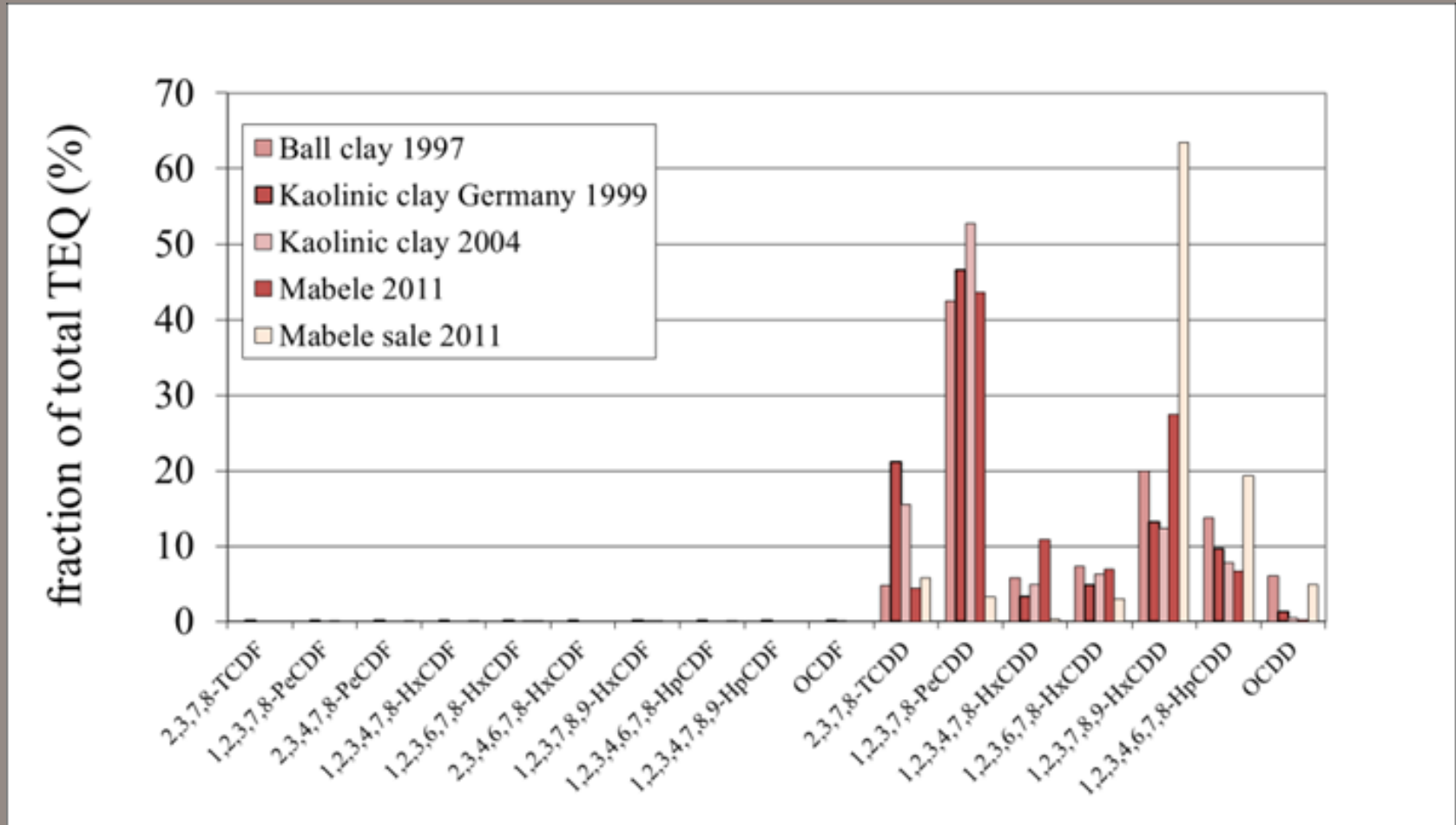
Potato peels/kaolinic clay 2004

Gelatin fat/Hydrochloric acid 2006

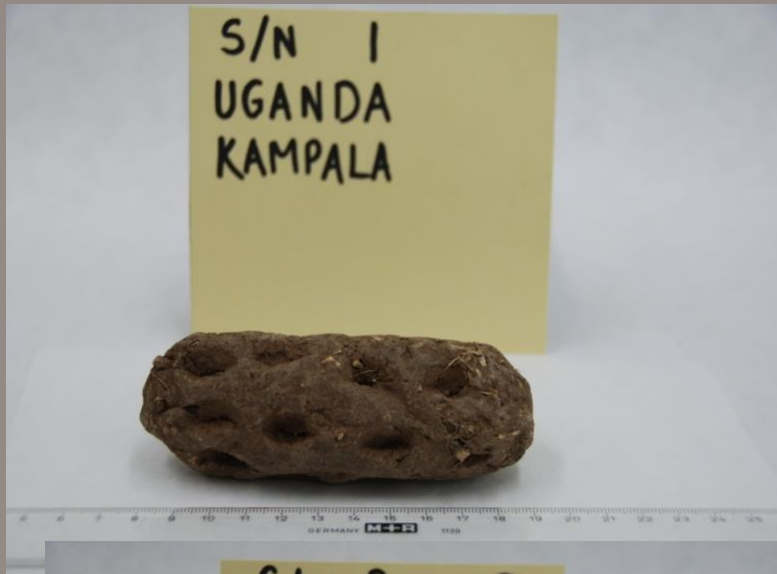
Free range eggs

Minerals (Zinc) Chile 2008

Clays (also PCDDs)




Pregnancy clays collected from Africa




Risk communication

In the Netherlands advice not to use these clays



Zwanger?
Gebruik geen pimba of mabele

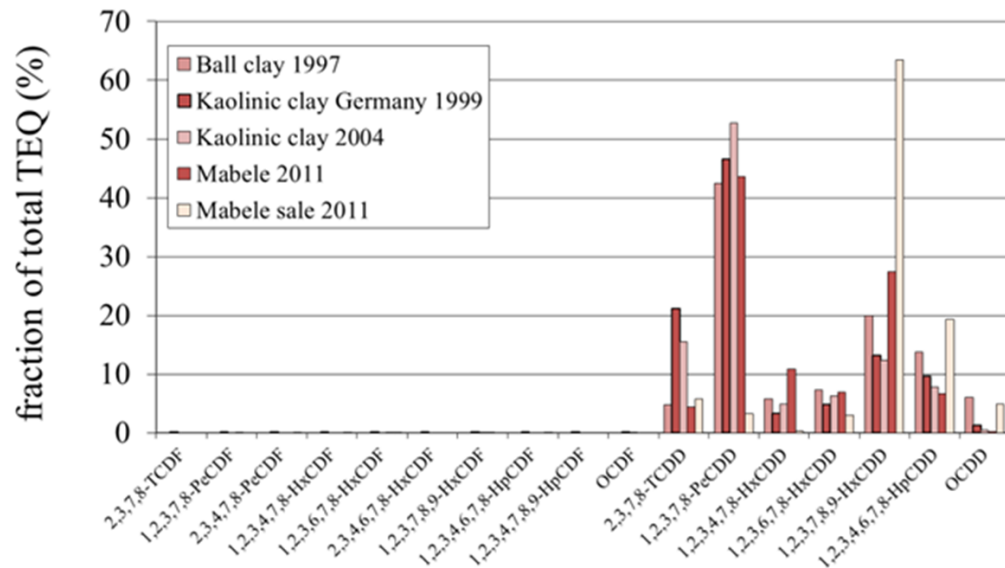
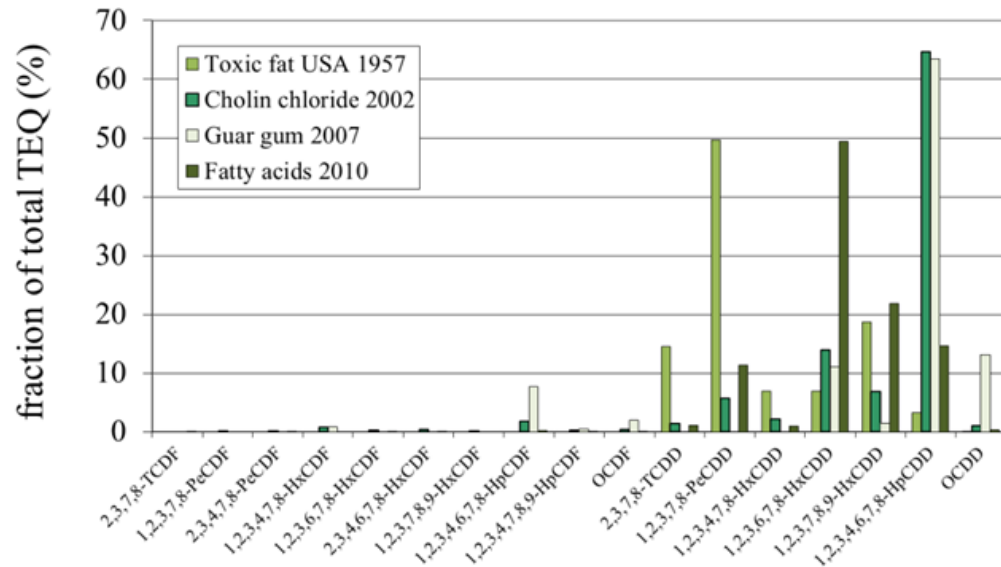
Pregnant? **Do not use shilie**
Enceinte? **La craie déconseillée**



kalebaskalk	nzu
shilie	úlo
calabash chalk	mabele
argile	white clay
pimba	ebumba
la craie	calabar steen

Voedingscentrum.nl
eerlijk over eten

chlorophenols vs clays



Food and feed incidents (minerals)

MWI milk 1989

Brazilian citrus pulp 1998

Mozzarella Italy 2001-2004

German bakery waste 2003

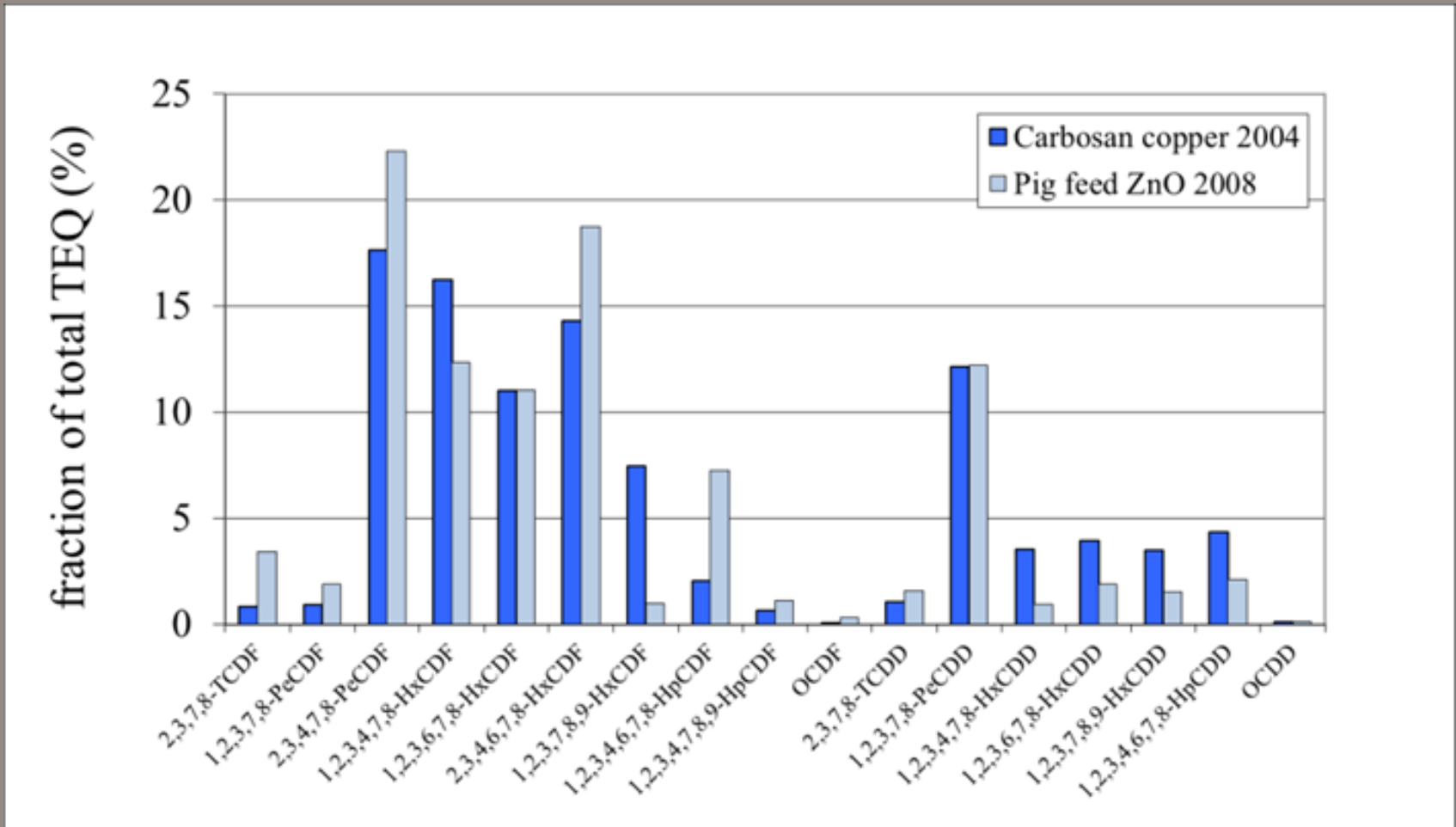
Free range eggs

Gelatin fat/Hydrochloric acid 2006

Minerals (Zinc) Chile 2008

Minerals

(dominated by PCDFs but also some PCDDs)



Food and feed incidents (burning of plastics)

MWI milk 1989

Brazilian citrus pulp 1998

Mozzarella Italy 2001-2004

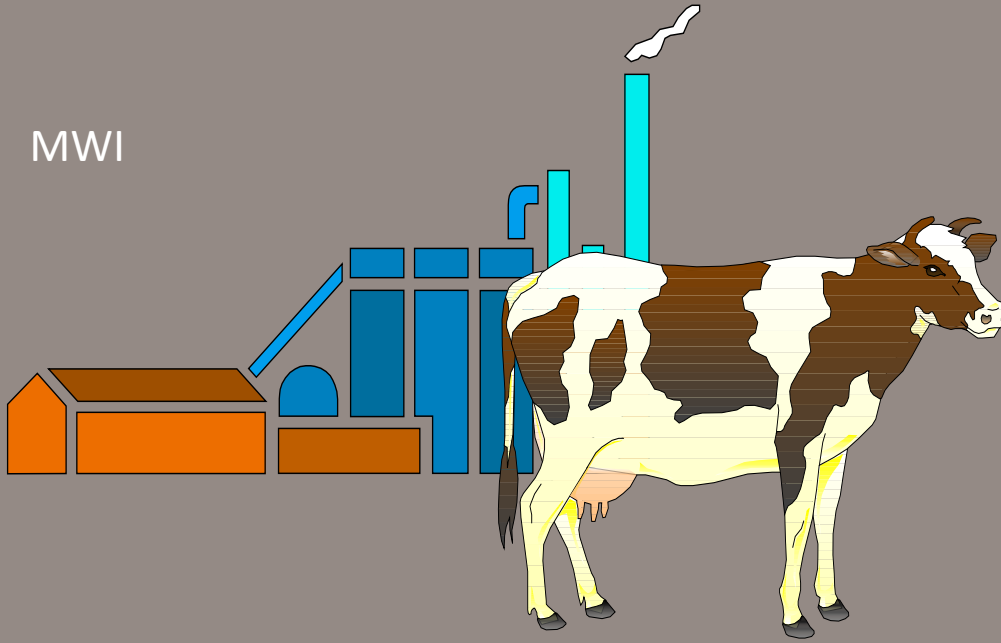
German bakery waste 2003

Free range eggs

Gelatin fat/Hydrochloric acid 2006

Waste incineration (1989)

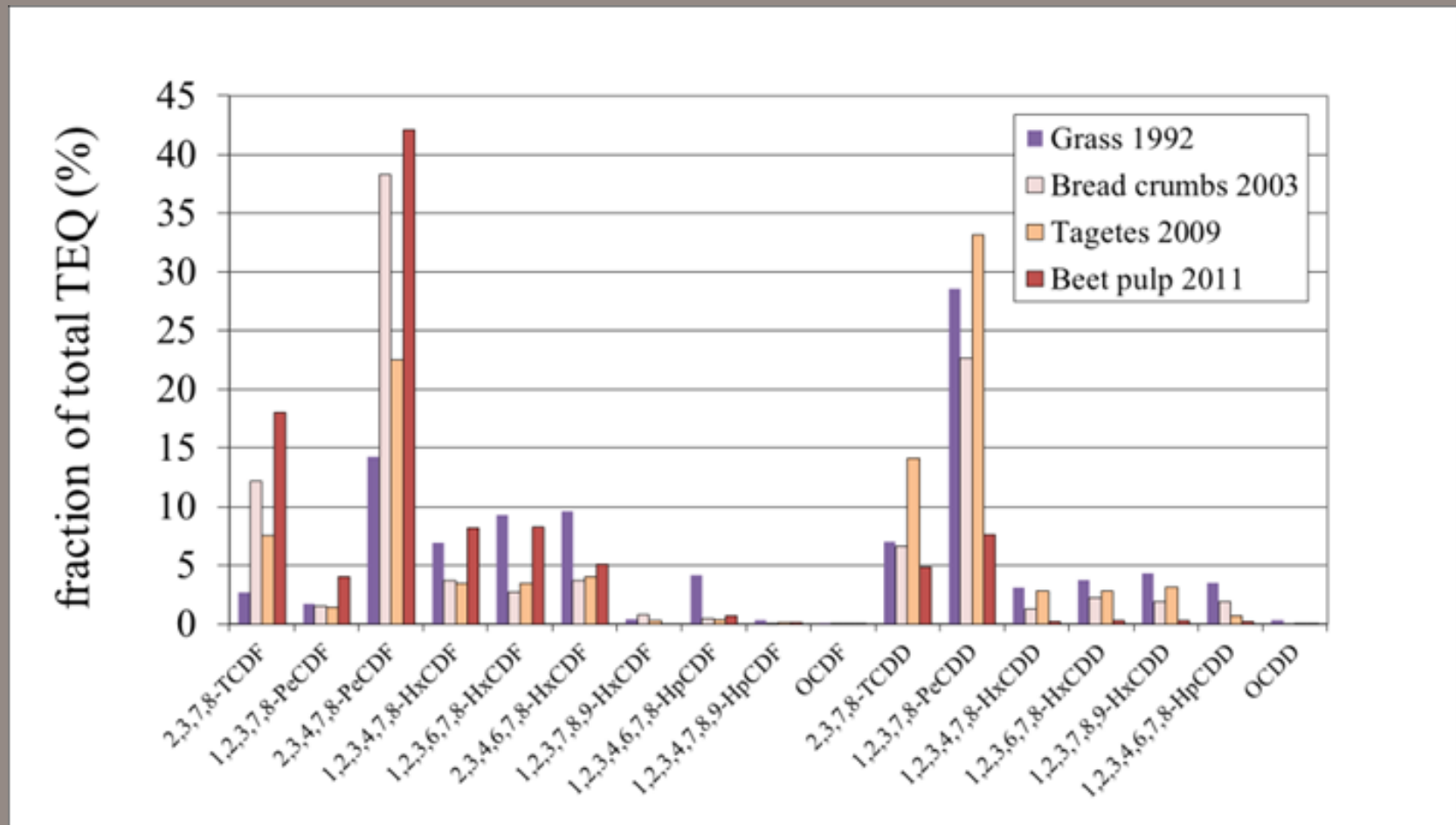
MWI



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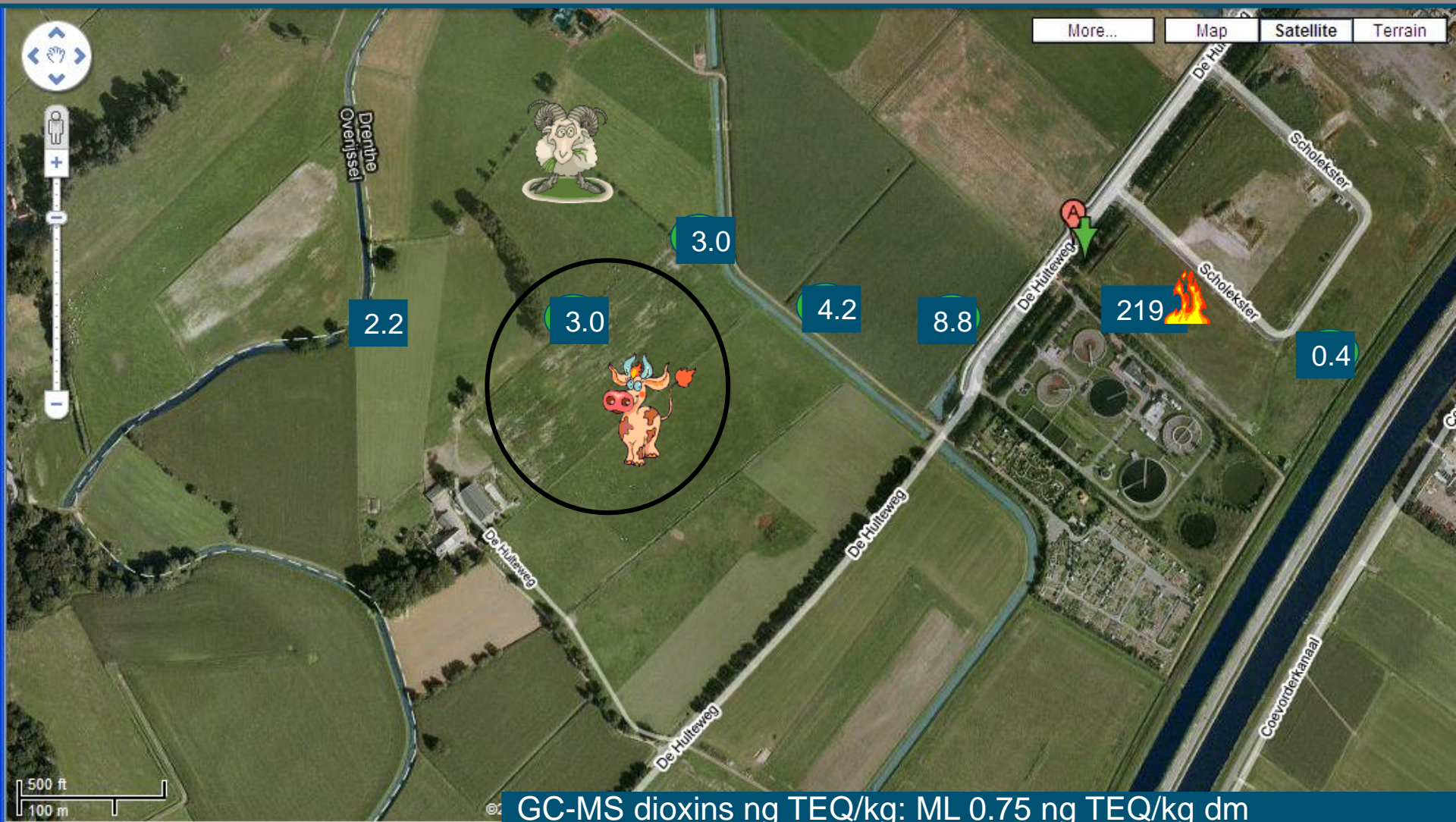
Burning (waste, fires, drying)



- Dominated by 23478-PeCDF/PeCDD/TCDF/ TCDD

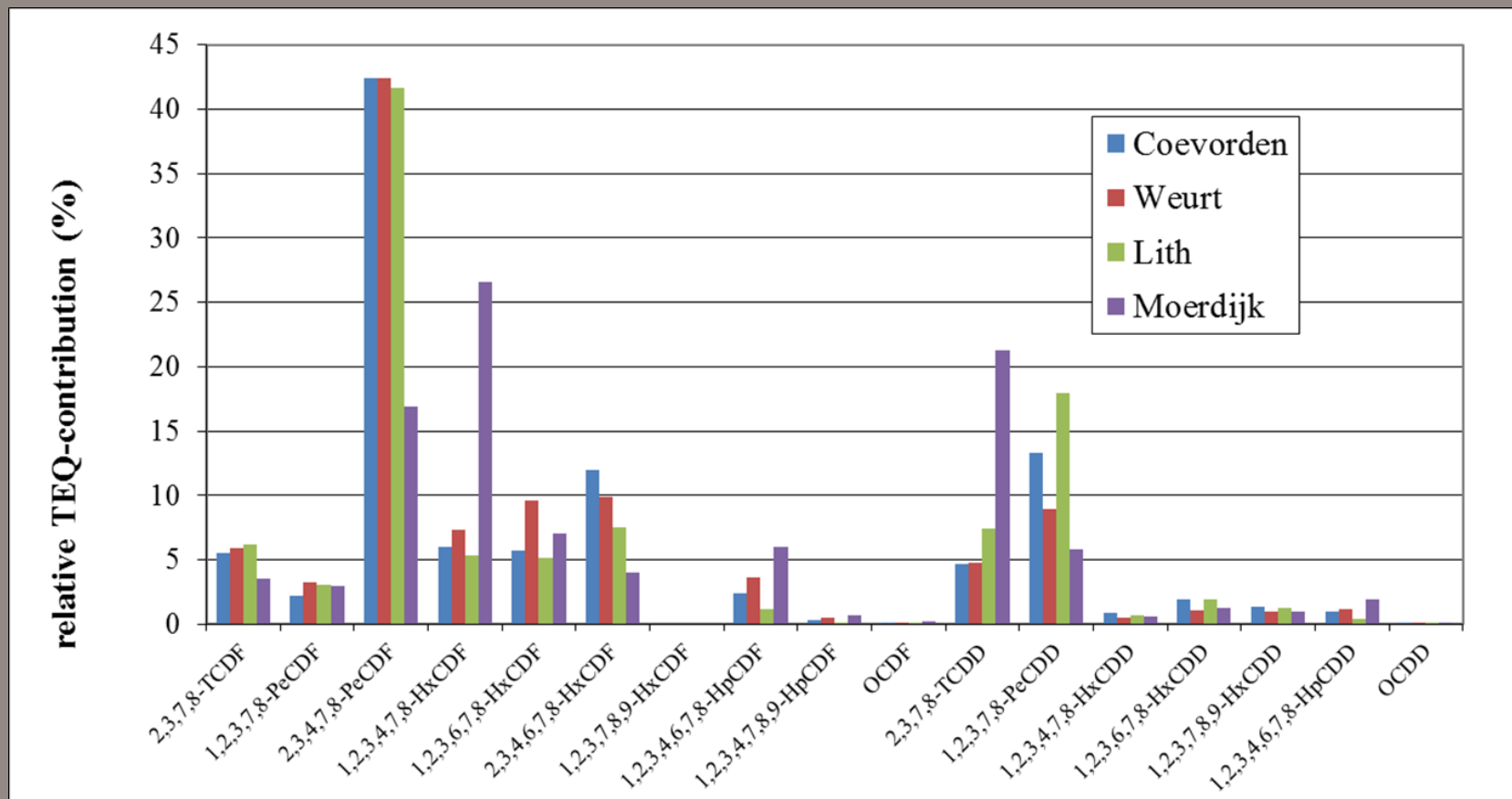
Accidental fires





- High levels, especially near fire
- Effect area several kms

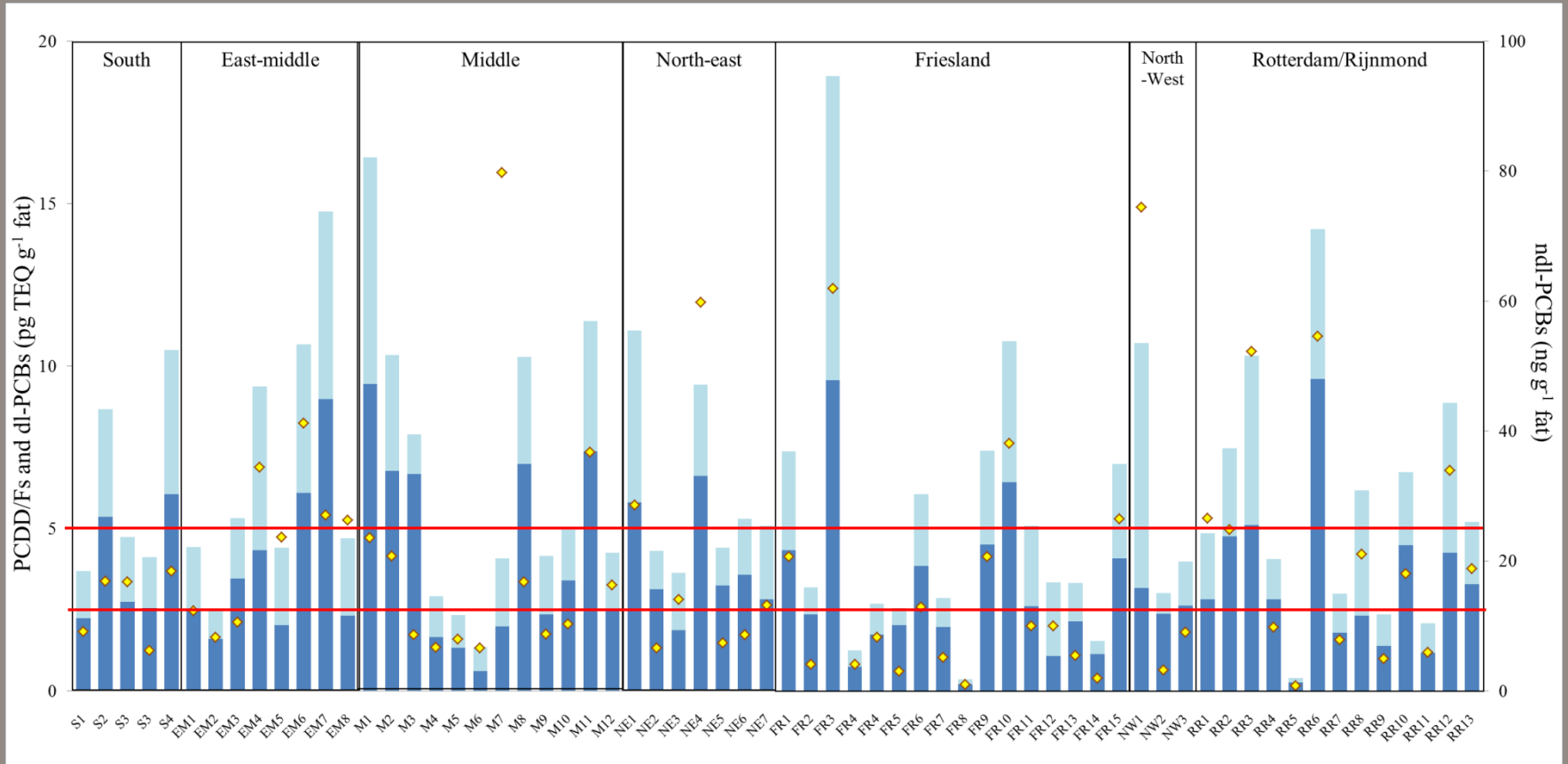
Accidental fires (grass)



Eggs from private owners (not for sale)

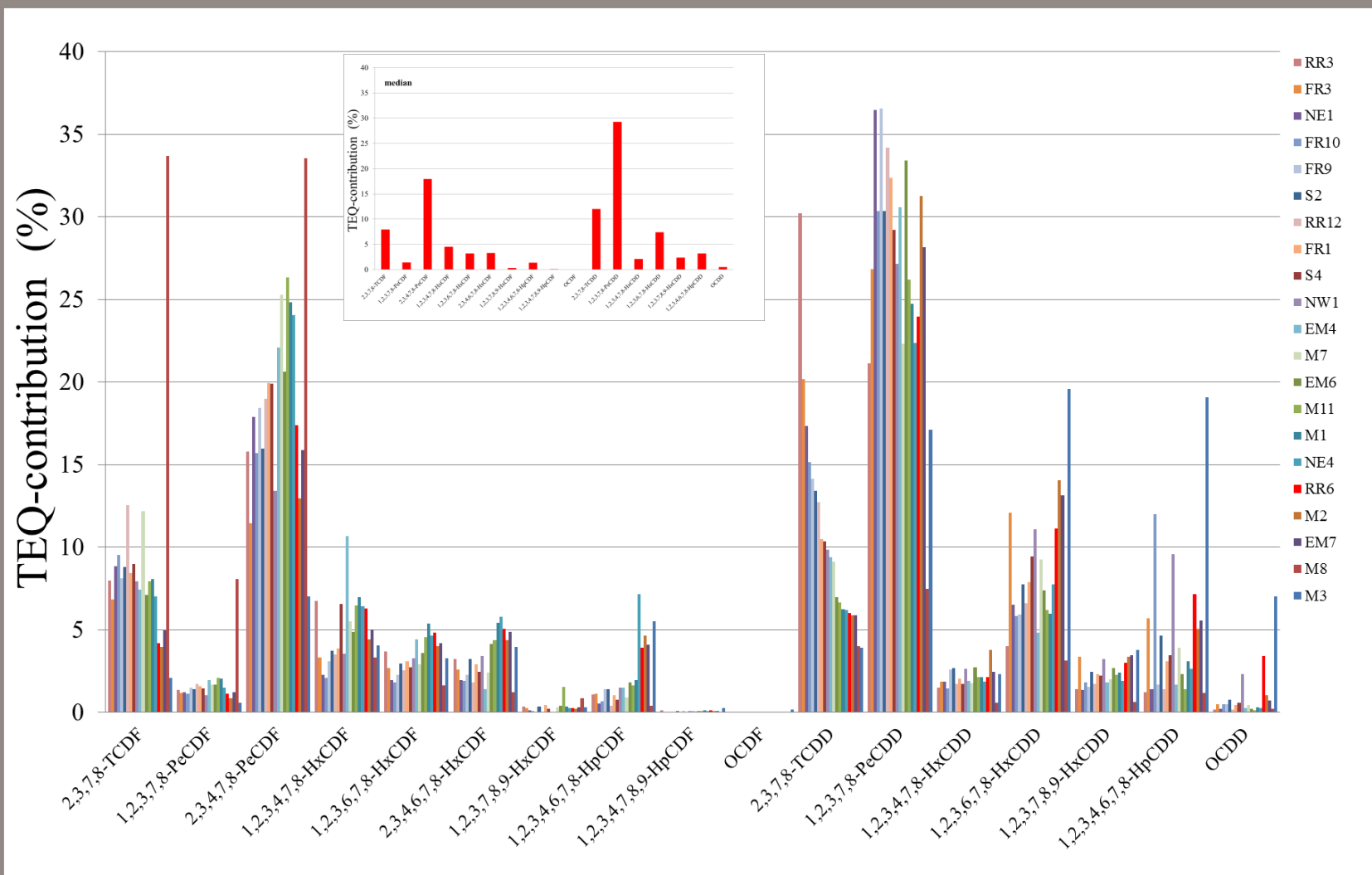


Levels in eggs (GC/HRMS)



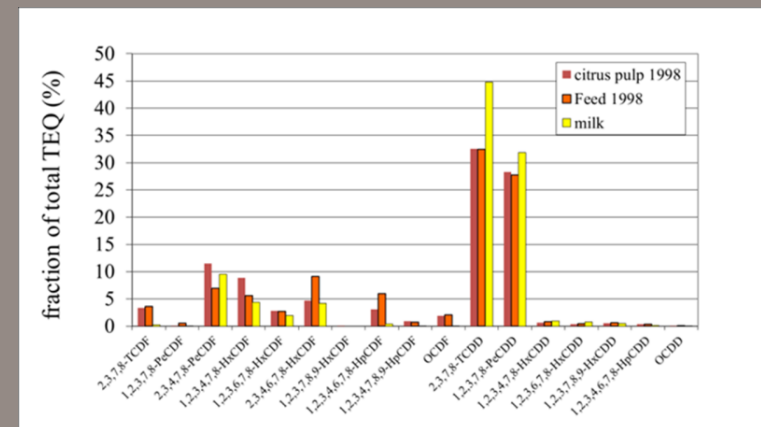
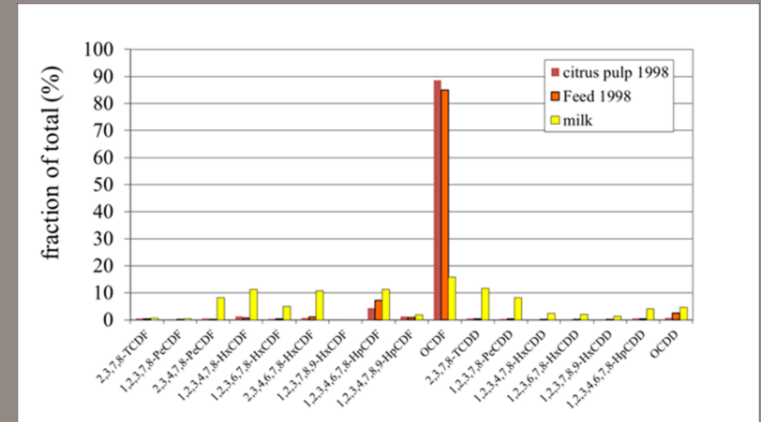
Median 4.6, mean 6.1, range 0.4-18.9 pg TEQ/g fat. 30% > ML sum-TEQ

Patterns of the most contaminated eggs



Actual source in citrus pulp?

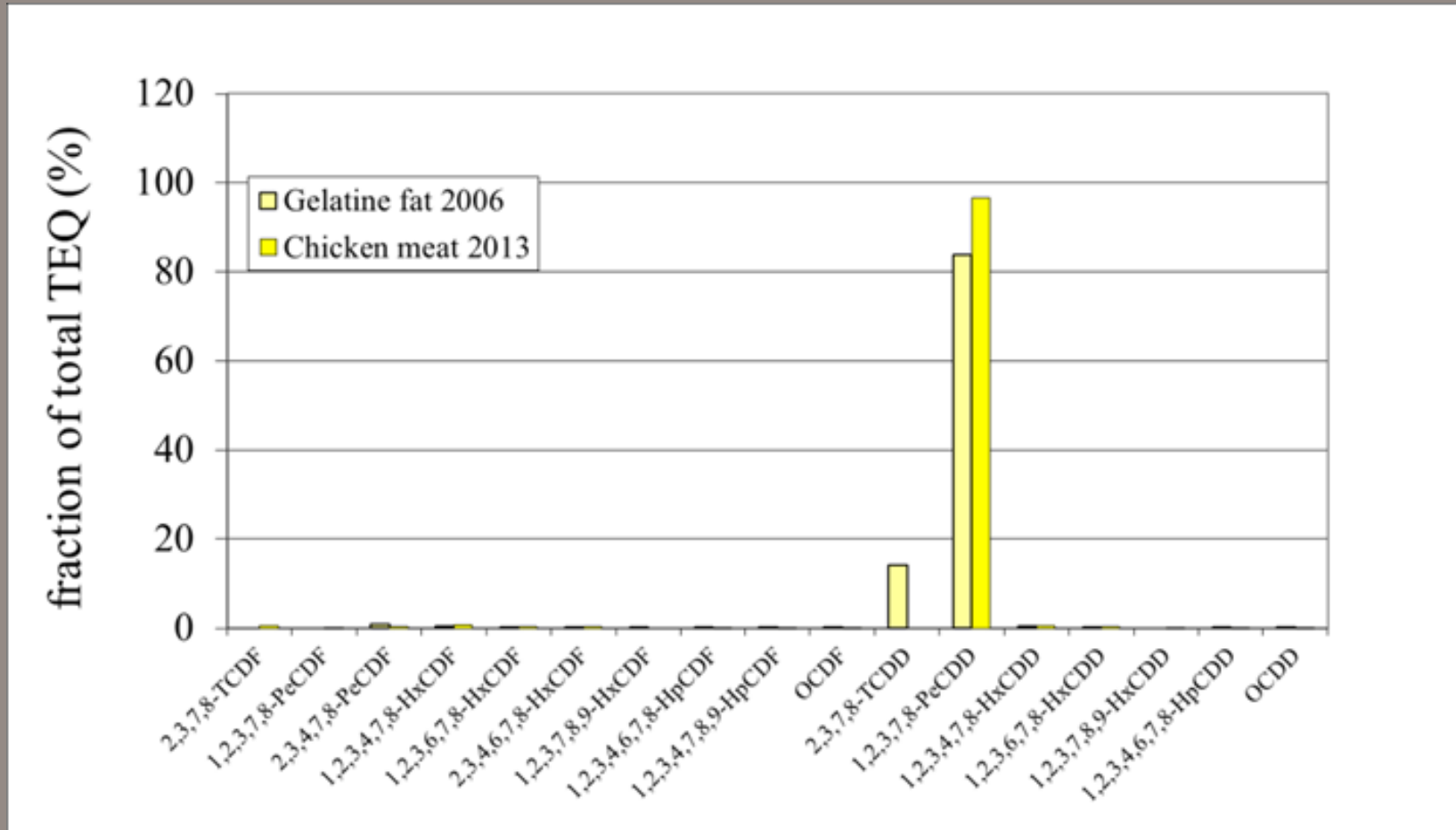
- Paper Torres et al. 2013
- Absolute congener pattern primarily OCDF
 - points to ethylene dichloride (EDC) used in production PVC
- But most relevant congeners in pulp and milk not connected to EDC
- Source of these congeners?



Food and feed incidents (unknowns?)

Gelatin fat/Hydrochloric acid 2006

Unknown sources (by-product chemicals?)



Patterns and sources

- Number of different patterns
 - PCBs (different chlorination)
 - Chlorophenols (different chlorination)
 - Clays
 - Minerals
 - Burning
 - Unknowns
 - ??????????

Primarily PCDFs

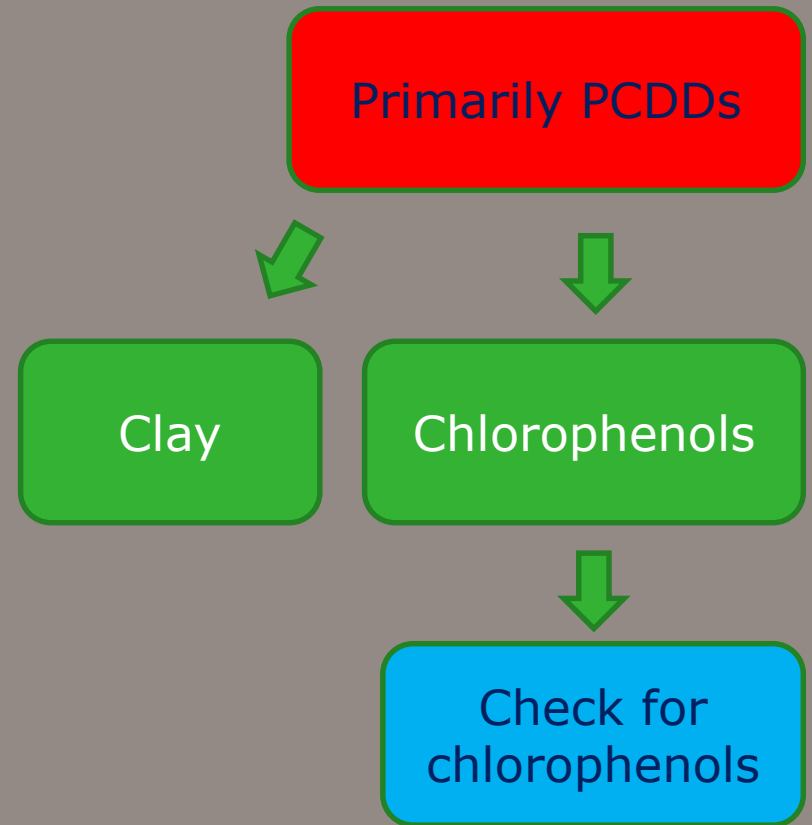


PCBs
including burning



Check for PCBs





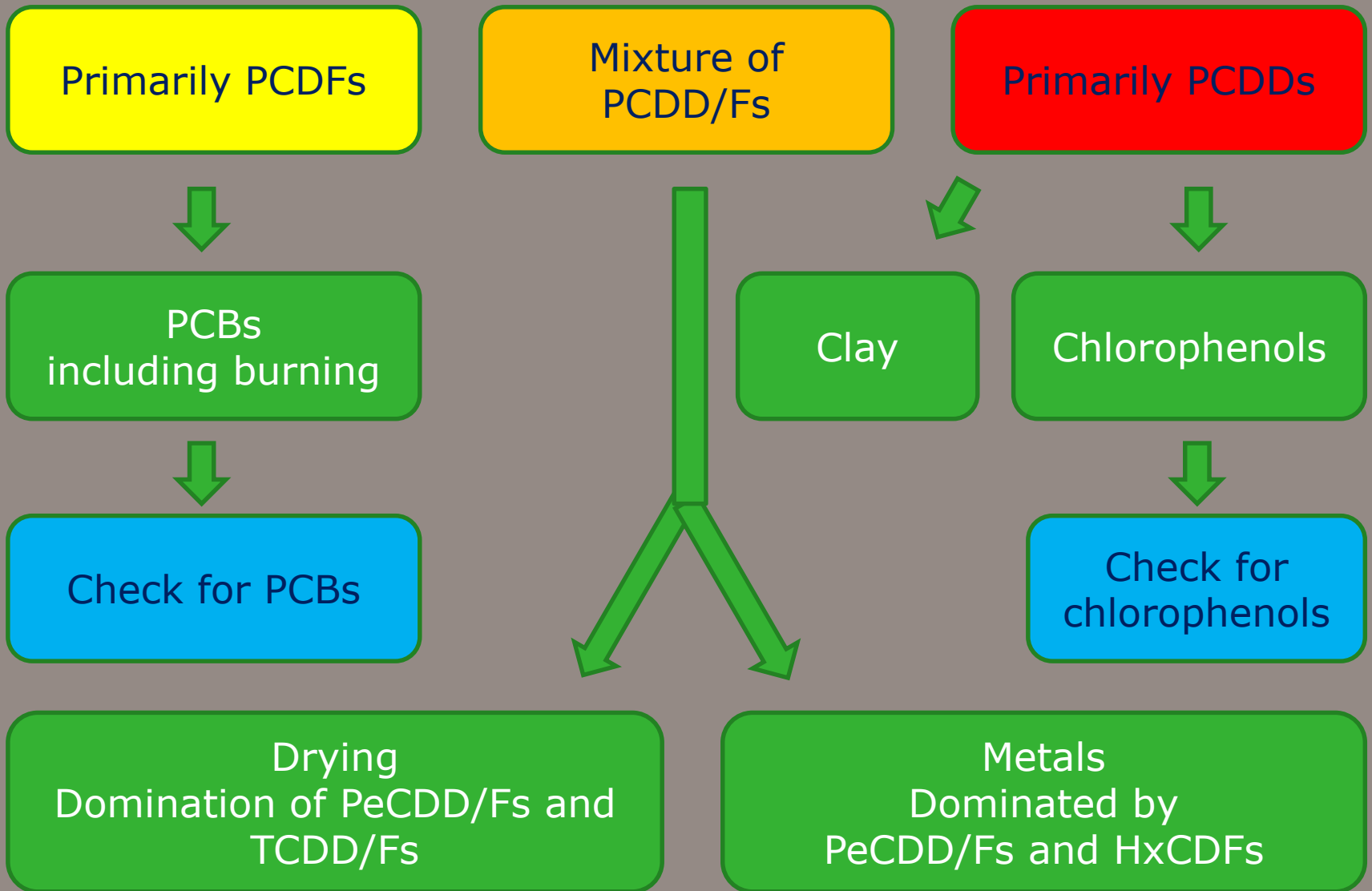
Mixture of
PCDD/Fs

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graph TD; A[Mixture of PCDD/Fs] --> B[Drying Dominated by PeCDD/Fs and TCDD/Fs]; A --> C[Metals Dominated by PeCDD/Fs and HxCDFs];
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Drying
Dominated by
PeCDD/Fs and TCDD/Fs

Metals
Dominated by
PeCDD/Fs and HxCDFs





Dissemination

- Scientific paper (2017)
- Excel file
 - Supplementary files, and/or
 - Via website (preference, if accepted by journal)
- Other tools (decision support system)

Inclusion of transfer factors

- Transfer factors for eggs and milk
 - Carry-over rates (CORs)
- Transfer factors meat from pigs, chicken, cows, sheep
 - Bioconcentration factors (BCFs)
- Apply to various primary profiles (and reverse)

Questions?

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