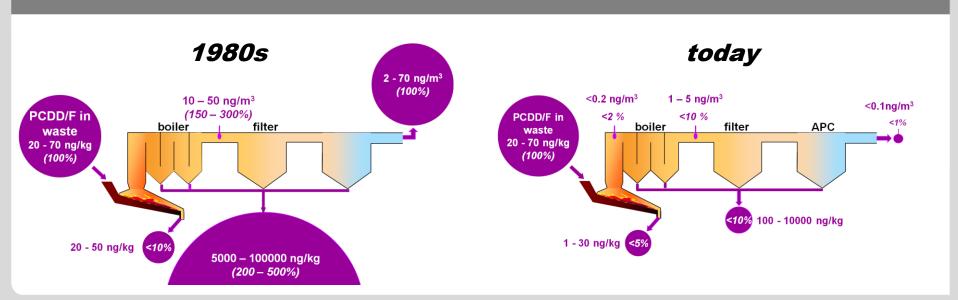


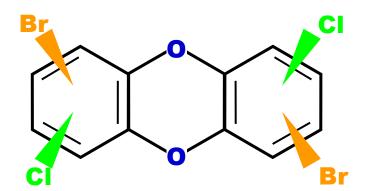
# Reduction of Dioxin Emissions from Thermal Treatment Plants

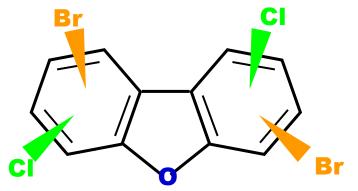
J. Vehlow

#### INSTITUTE FOR TECHNICAL CHEMISTRY









## congeners:

chlorinated brominated	210 210

polyhalogenated dibenzo-p-dioxins und -furans



'since this compound caused heavy chloracne it did not invite to further investigations' (Stockmann/Sandermann)

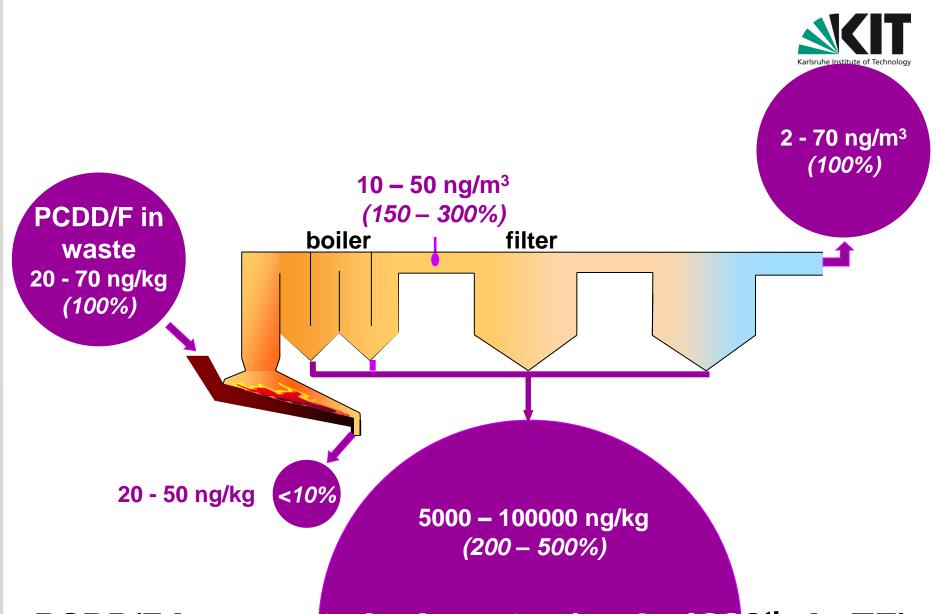
## 1957: birth of halogenated dioxins



## birth of a problem

1976 Seveso accident (10. July)

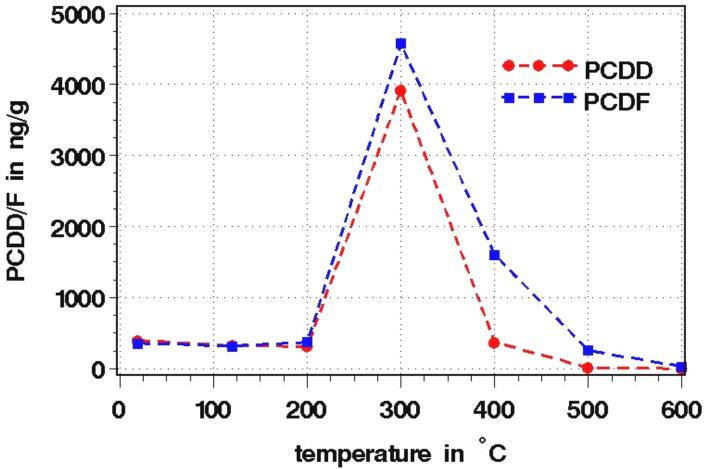
1977 detection of dioxins in fly ashes from Dutch waste incinerators



PCDD/F in a waste incinerator (early 1980th, in TE)

J. Vehlow (2011)





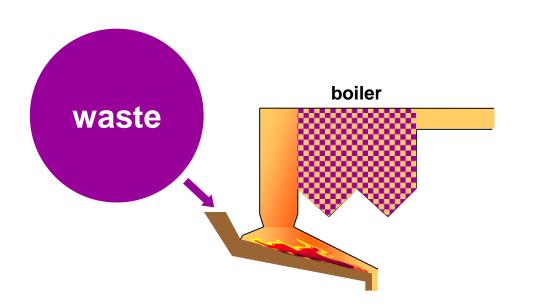
source: Vogg/Stieglitz 1984

## formation of PCDD and PCDF in fly ashes



## de-novo synthesis

(Vogg / Stieglitz 1985, Hagenmaier 1986)



## ingredients:

- PICs (e.g. soot)
- halogenides (Cl<sup>-</sup>)
- catalysts (Cu)

#### conditions:

- oxidising atmosphere
- T > 200 °C (300-350 °C)

#### main PCDD/F formation mechanism



## options for reducing dioxin emissions

suppression of generation

(head-end techniques)

and (/ or)

efficient abatement technologies

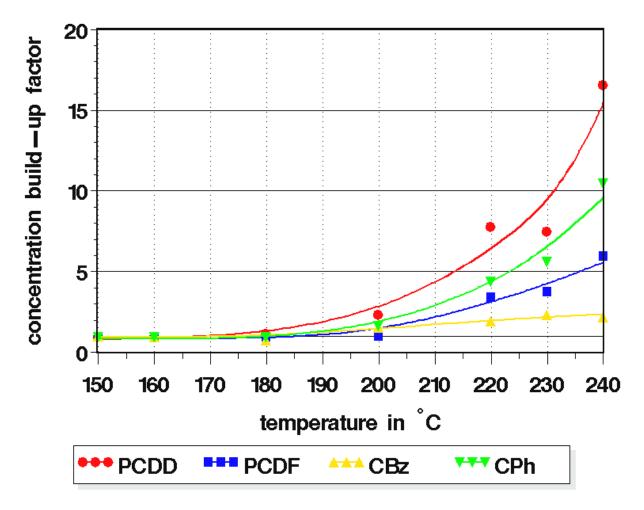
(secondary measures)



## head-end techniques

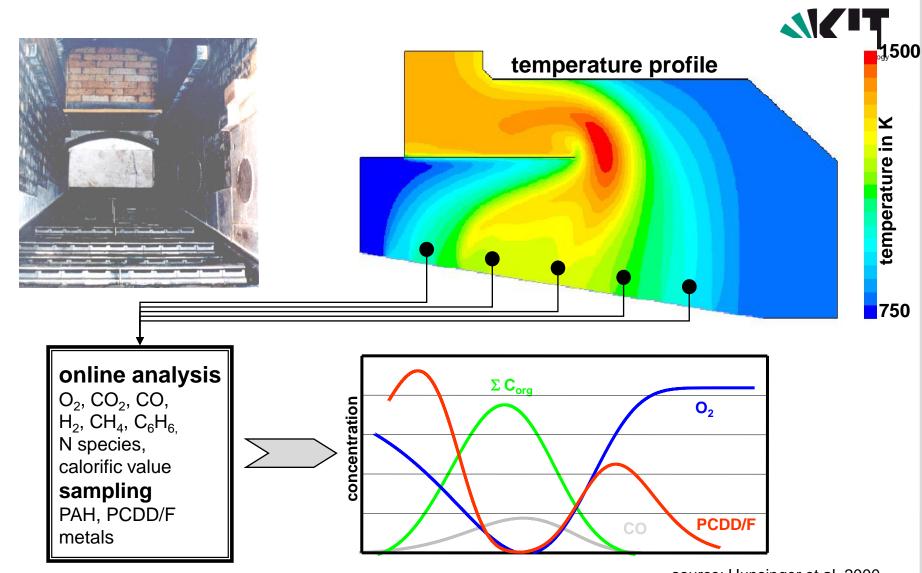
- complete burnout
- limited dust release
- low oxygen surplus in the flue gas
- reduced CI/S ratio
- stationary combustion
- clean boiler
  - limited dust deposits
  - limited residence time of dust deposits
- filter temperature < 200 °C</li>





source: Hunsinger 1994

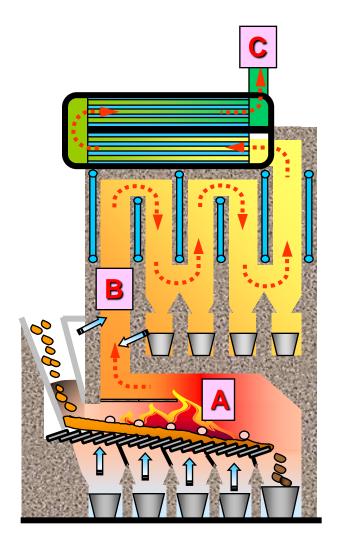
## build-up of organic micropollutants with temperature

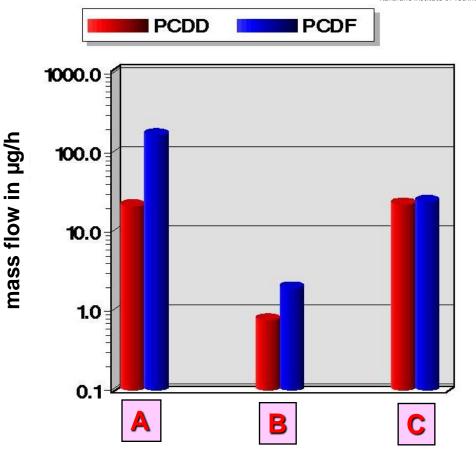


source: Hunsinger et al. 2000

#### formation of PCDD/F inside the furnace



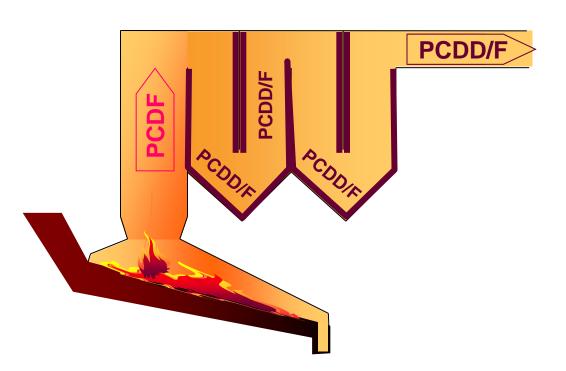




source: Hunsinger et al. 2000

## PCDD/F mass flow in TAMARA furnace





#### fast reaction:

- 1. PCDF, PIC in raw gas
- 2. PIC deposition

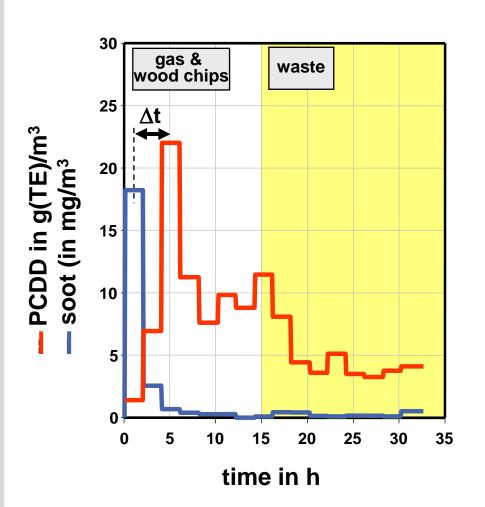
slow reaction / memory effect:

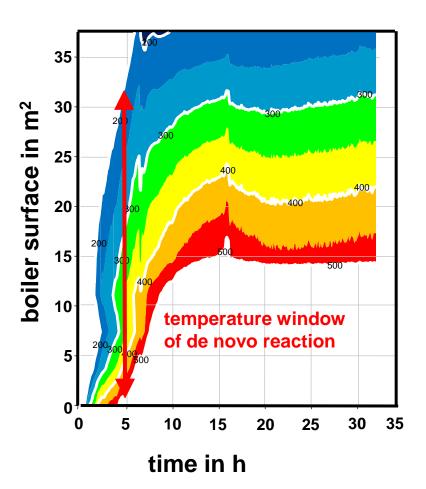
de novo synthesis

source: Hunsinger et al. 2002

## stationary combustion

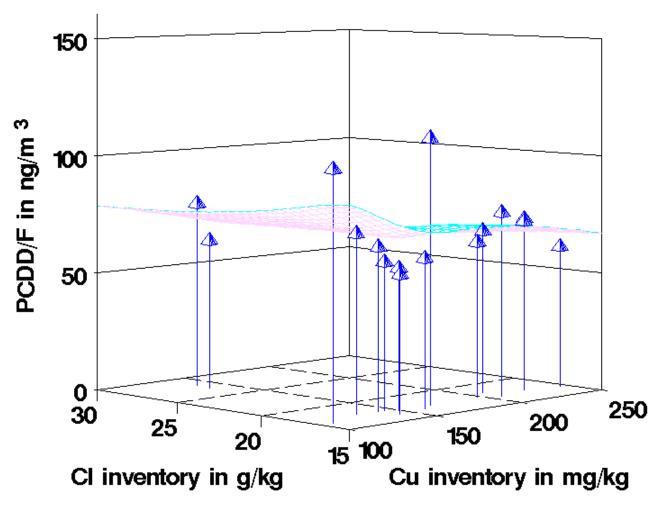






## transient conditions - start-up





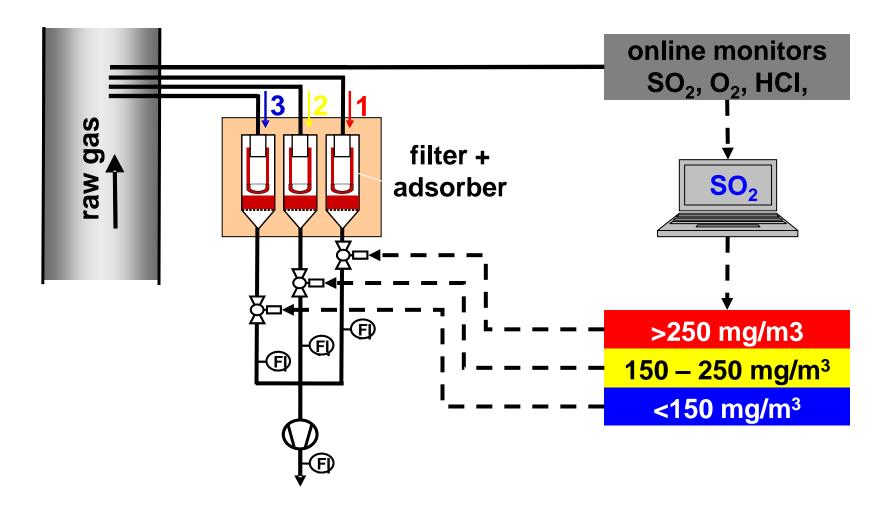
source: Vehlow et al. 1996

## influence of PVC on PCDD/F raw gas level in TAMARA

#### **Griffin hypothesis:**

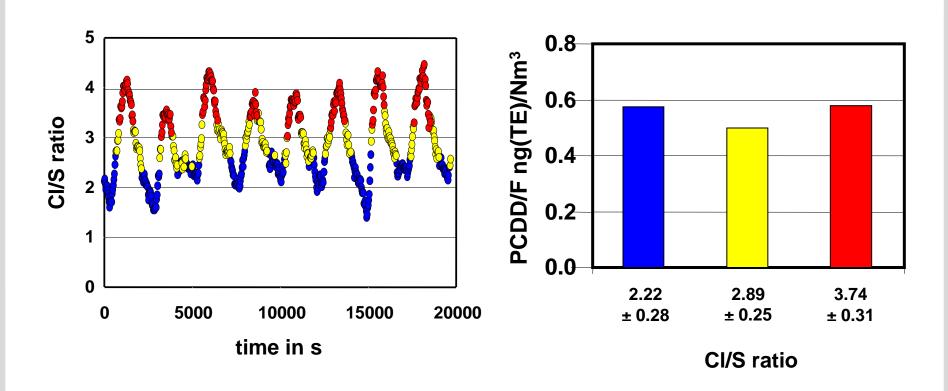
## $Cl_2 + SO_2 + H_2O \Rightarrow SO_3 + 2 HCI$





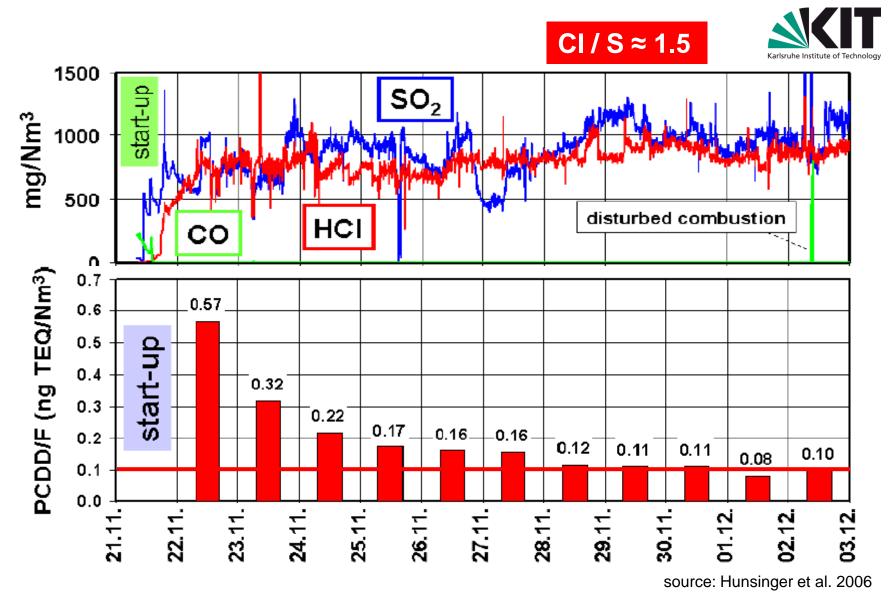
SO<sub>2</sub> specific raw gas sampling (full scale)





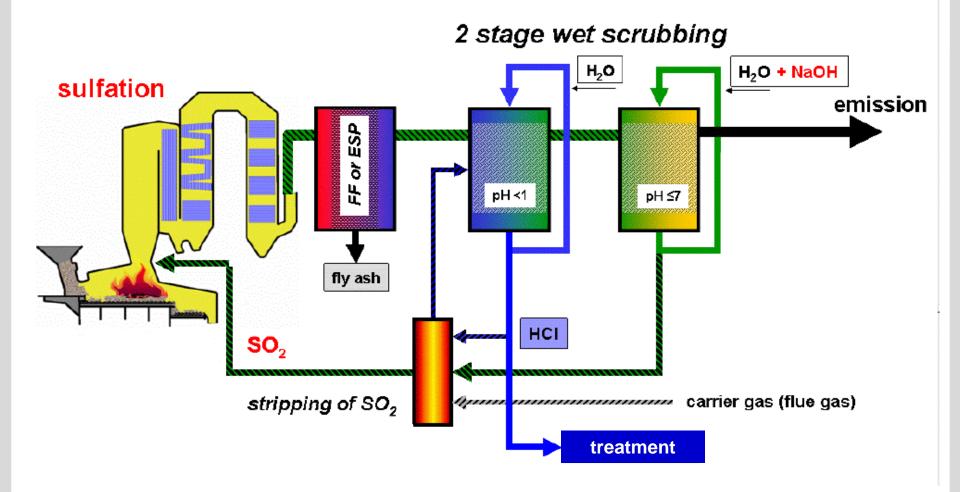
source: Hunsinger et al. 2004

## influence of CI/S ratio in the flue gas (full scale)



PCDD/F raw gas concentration (TAMARA)





## scheme of a S recycle process

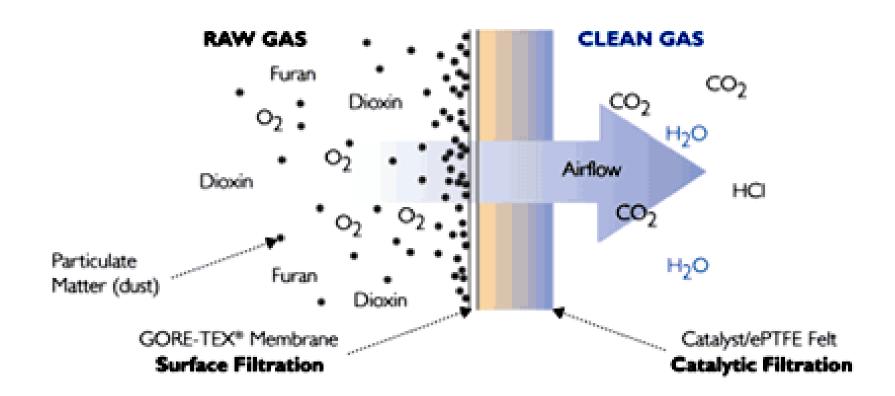


## abatement technologies - flue gas

- carbon adsorption (fixed or moving bed, scrubber)
- PAC injection + dust removal
- oxidation catalyst
- chemical oxidation in the flue gas
- combined filtration and catalytic destruction
- absorption by polymers



# Combining the Principles of Surface Filtration and Catalysis

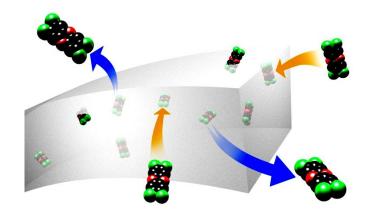


#### **Gore REMEDIA Process**



#### PCDD/F in pure plastic

#### PCDD/F in ADIOX®

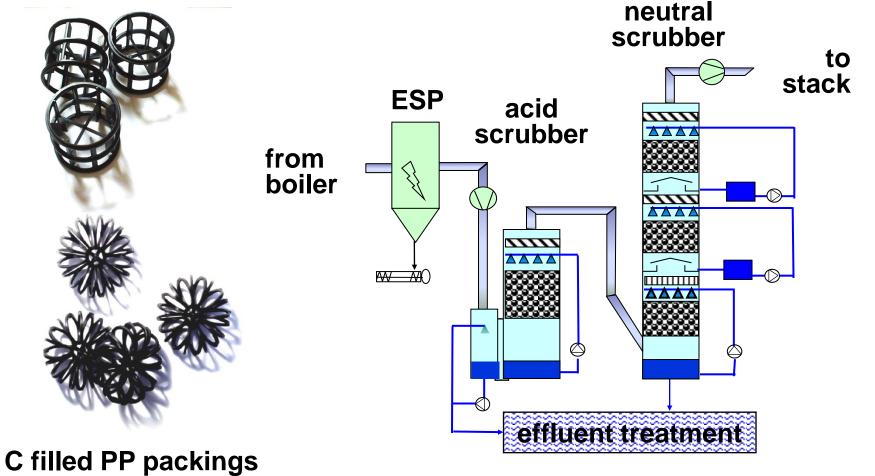


adsorption-desorption equilibrium: "memory effect"

absorption in plastic and adsorption at carbon particles: "dioxin is fixed"

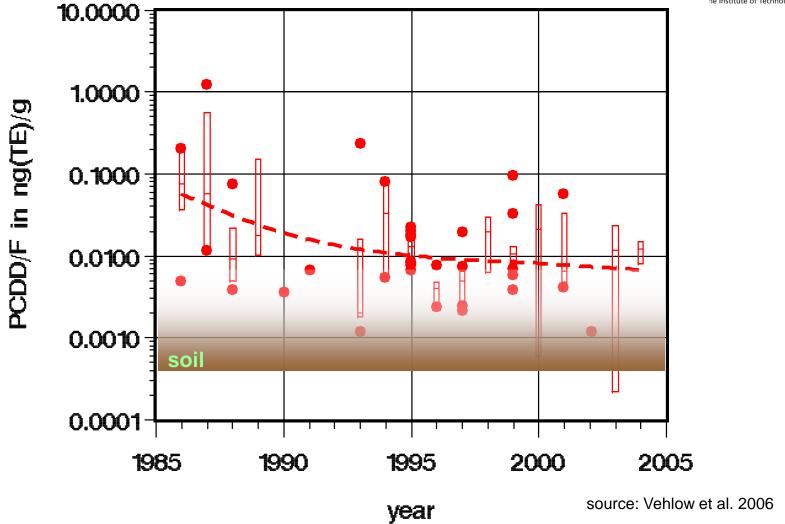
## **ADIOX® PCDD/F abatement system**





## **ADIOX®** application





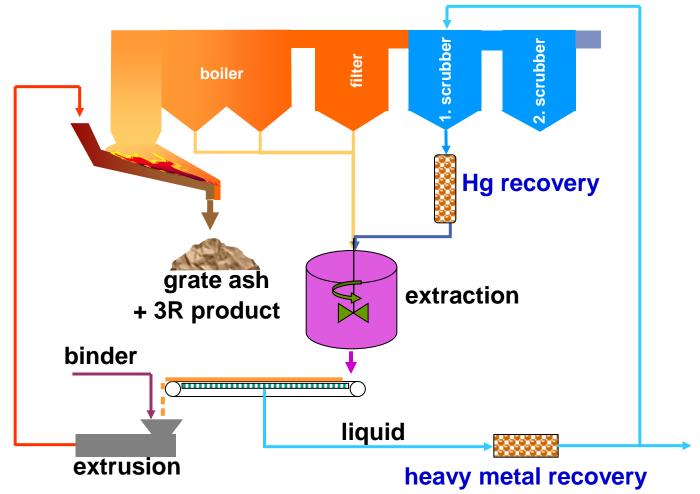
PCDD/F in bottom ash between 1985 and 2005



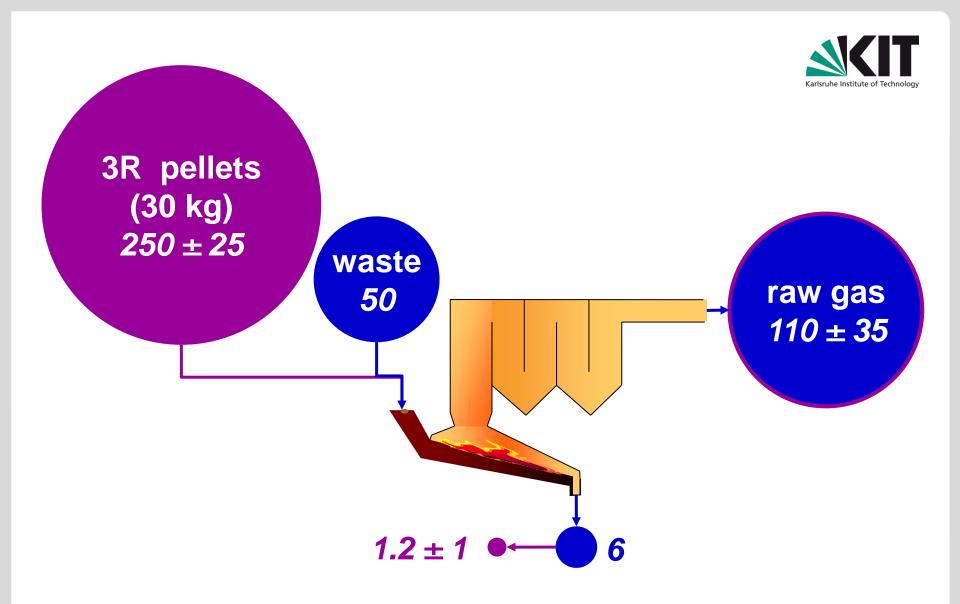
## abatement technologies - residues

- vitrification
- Hagenmaier drum
- 3R Process



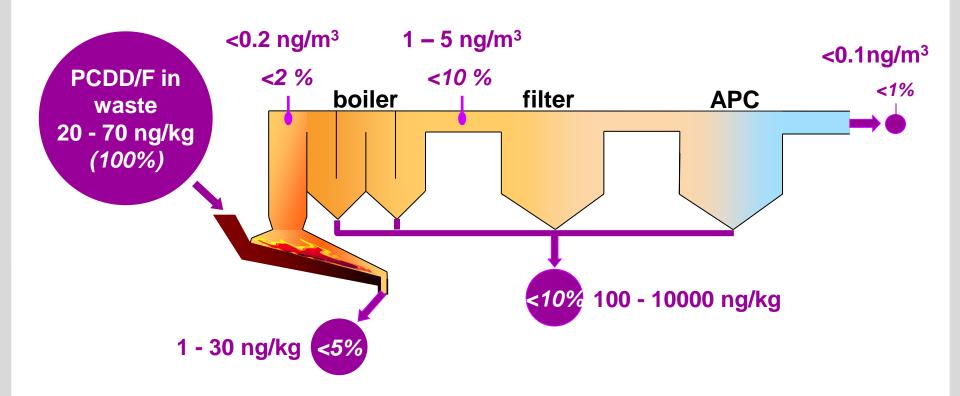


### scheme of the 3R Process



PCDD/F flow during 3R pellet recycling (1 Mg MSW)





#### PCDD/F in a state-of-the-art waste incinerator

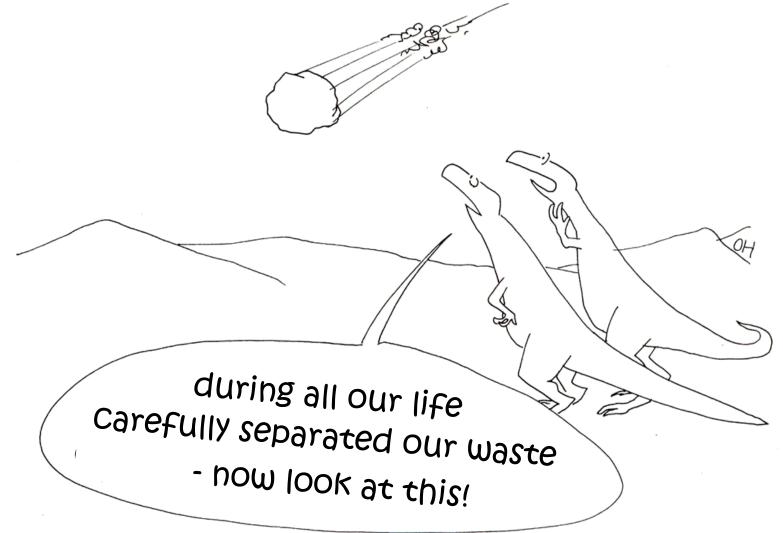


#### conclusions

- the formation of PCDD/F can be minimized by optimized combustion control
- the boiler cleaning should be improved
- the temperature in the dedusting unit should be kept below 200 °C
- efficient secondary abatement measures have been developed
- the method of choice is depending on the gas cleaning strategy and the economics

# 65 million years ago





source: Spektrum der Wissenschaft 7/2002