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Monitoring of Dioxins

Concepts and solutions for continuous sampling techniques for emissions

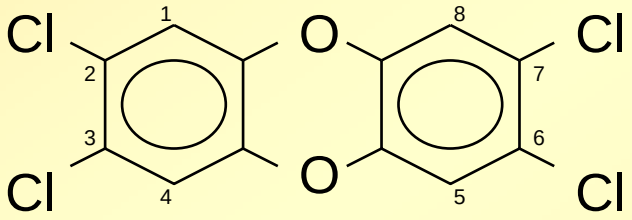
Formation and measurement basics

About the
mathematical and physical reason
for the advantage
of continuous sampling techniques...

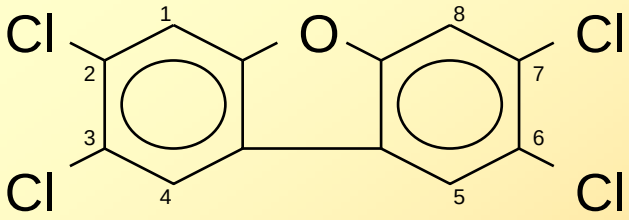
Formation and measurement basics

Dioxin basic chemistry

- Polychlorinated dioxins and furans (PCDD & PCDF) are a group of 210 single compounds (congeners) ➔ “Dioxins”
- Among these 210 congeners, 17 congeners, the „2,3,7,8”-substituted congeners are extremely toxic



2,3,7,8-substituted dioxins

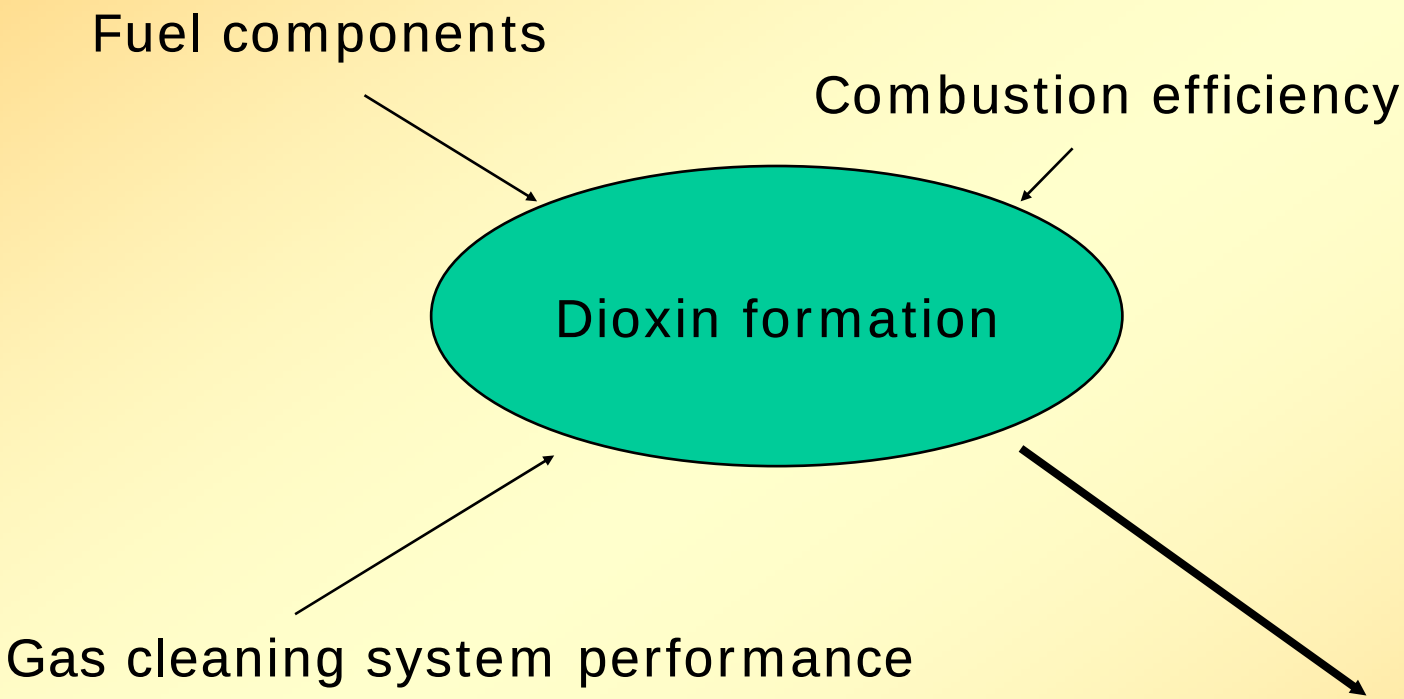


2,3,7,8-substituted furans

- The relative toxicity of these 17 compounds is in the range of a factor of 1000
- To gain comparable data a total toxicity number is calculated, the toxic equivalent (TEQ)

Formation and measurement basics

Formation process influences



mathematical chaotic system

Formation and measurement basics

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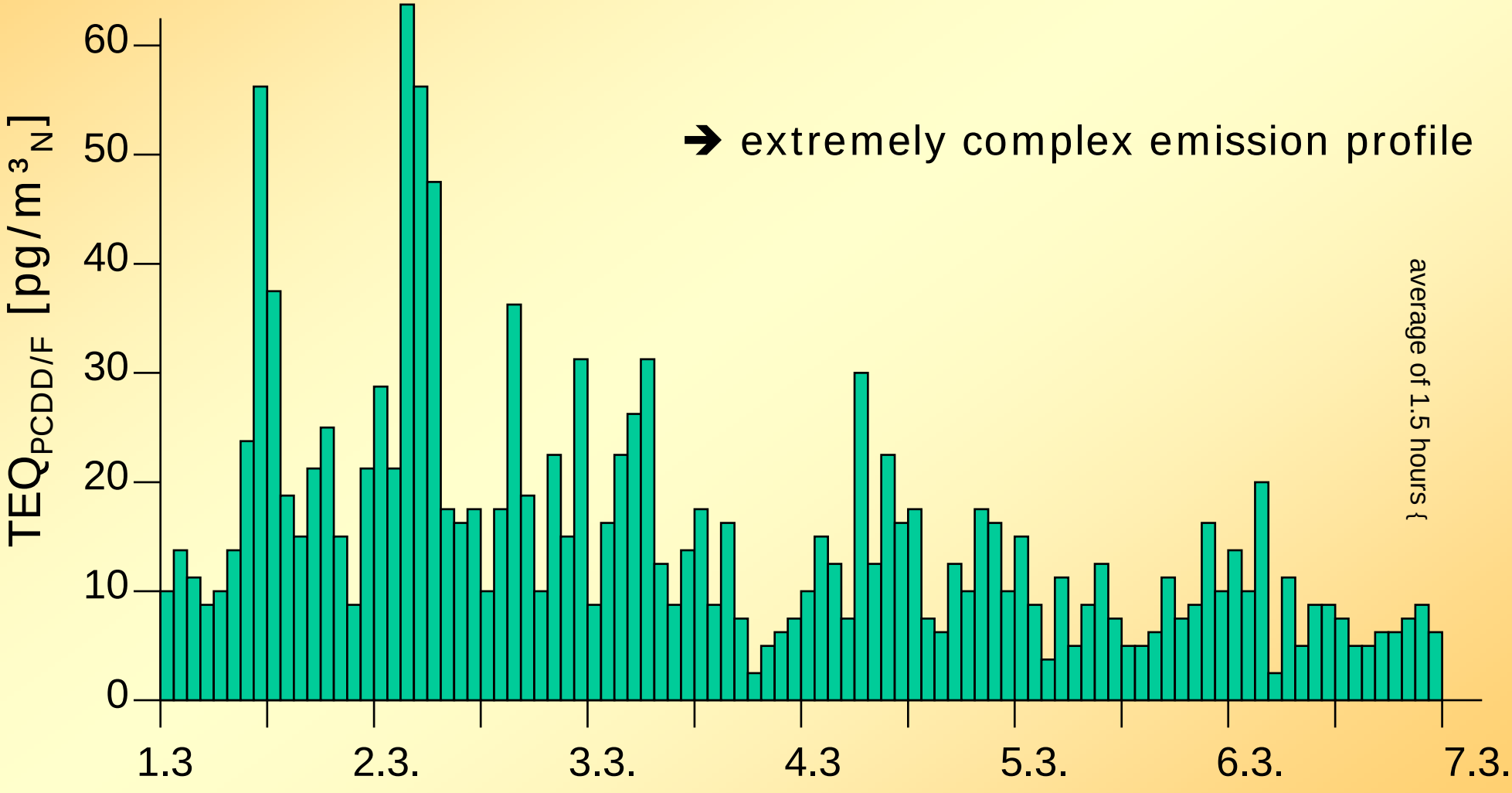
Formation process: mathematical chaotic system



➔ extremely complex emission profile

Formation and measurement basics

Measurement series 1: classical spot measurements

4 samplings on different days

each sampling 7 ½ hours

Formation and measurement basics

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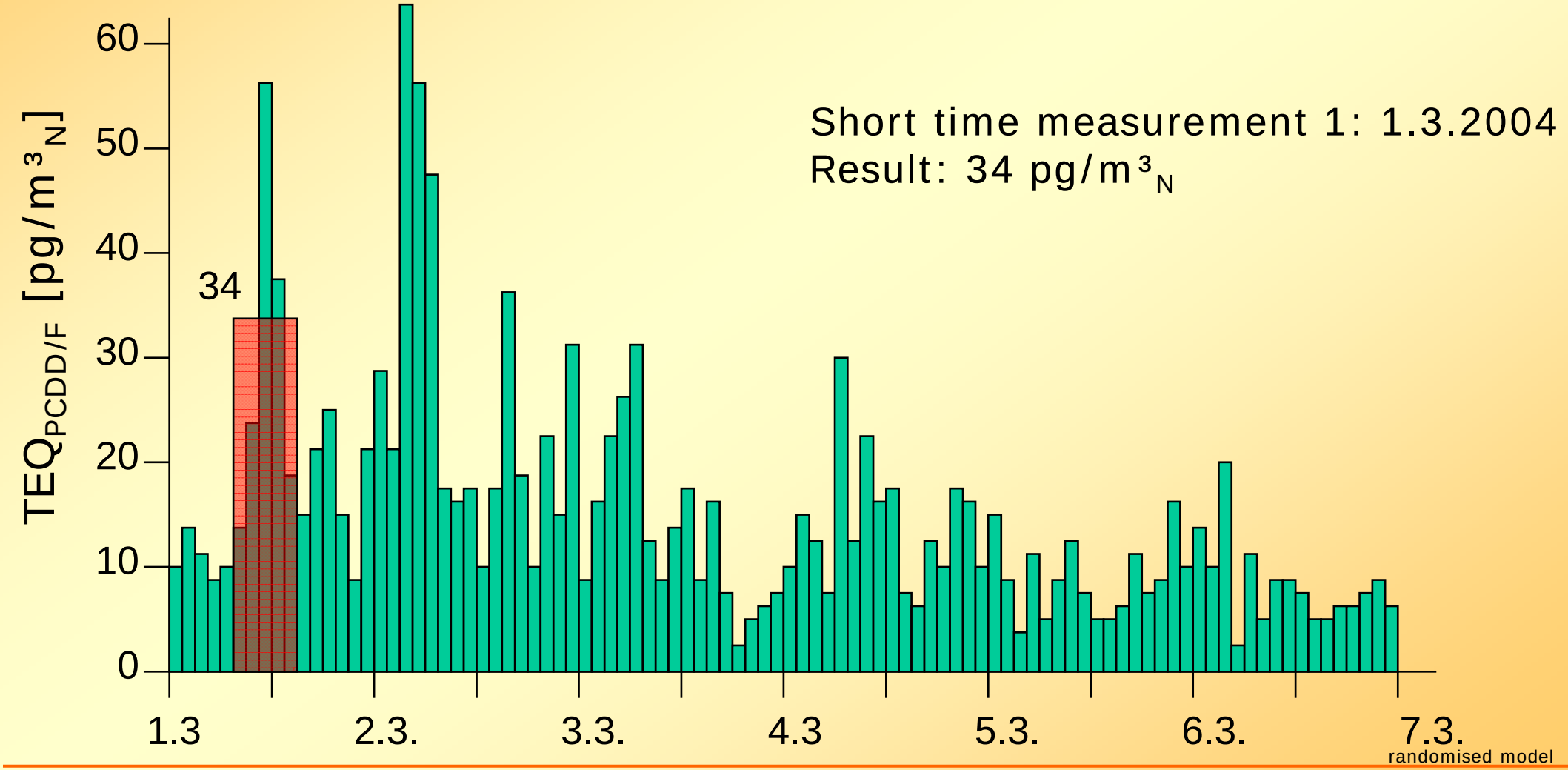
Spot measurements in the mathematical chaotic system



Short time measurement 1: 1.3.2004
Result: 34 pg/m³N

Formation and measurement basics

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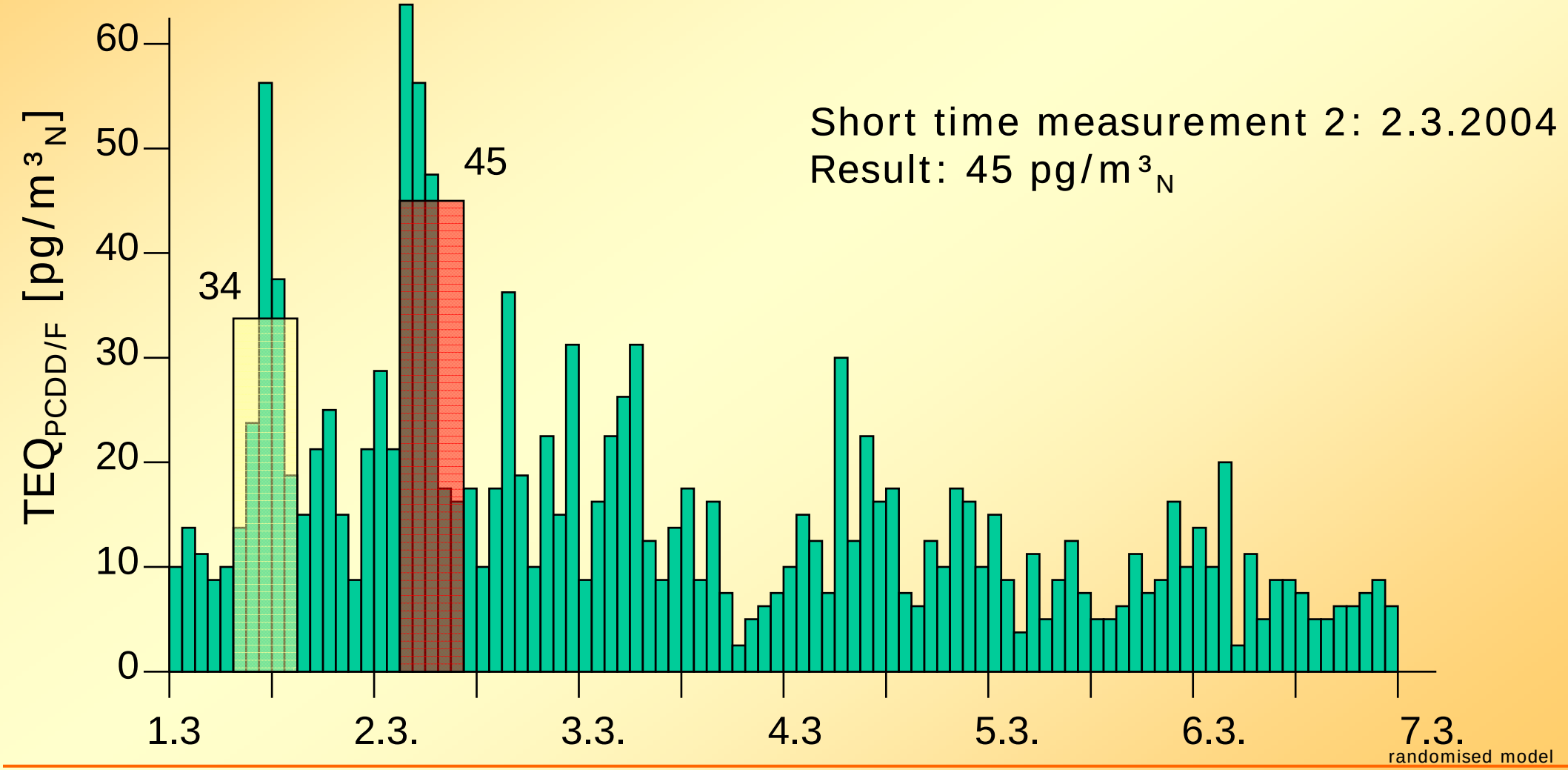
Spot measurements in the mathematical chaotic system



Short time measurement 2: 2.3.2004
Result: 45 pg/m³N

Formation and measurement basics

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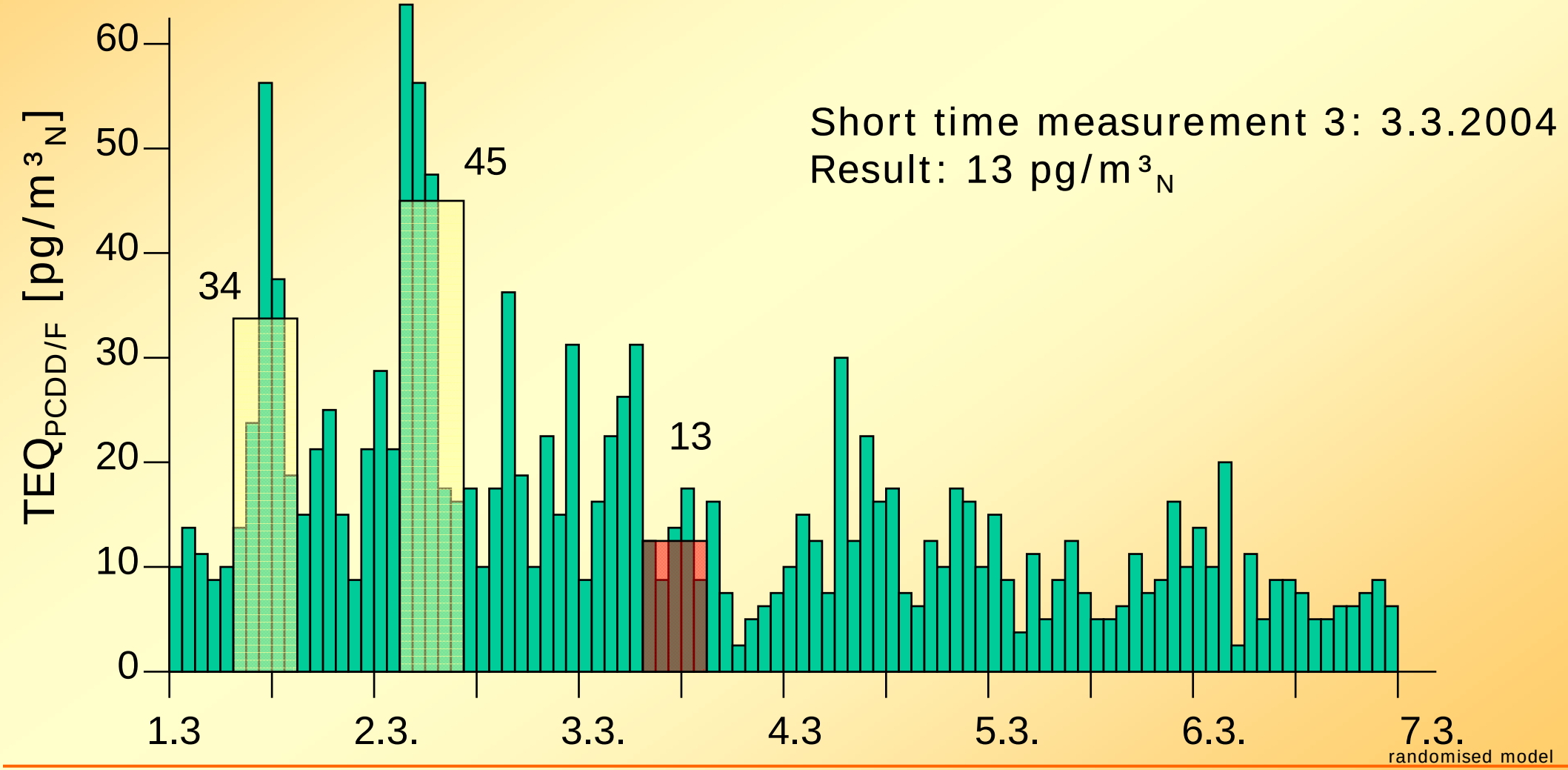
Spot measurements in the mathematical chaotic system



Short time measurement 3: 3.3.2004
Result: 13 pg/m³N

Formation and measurement basics

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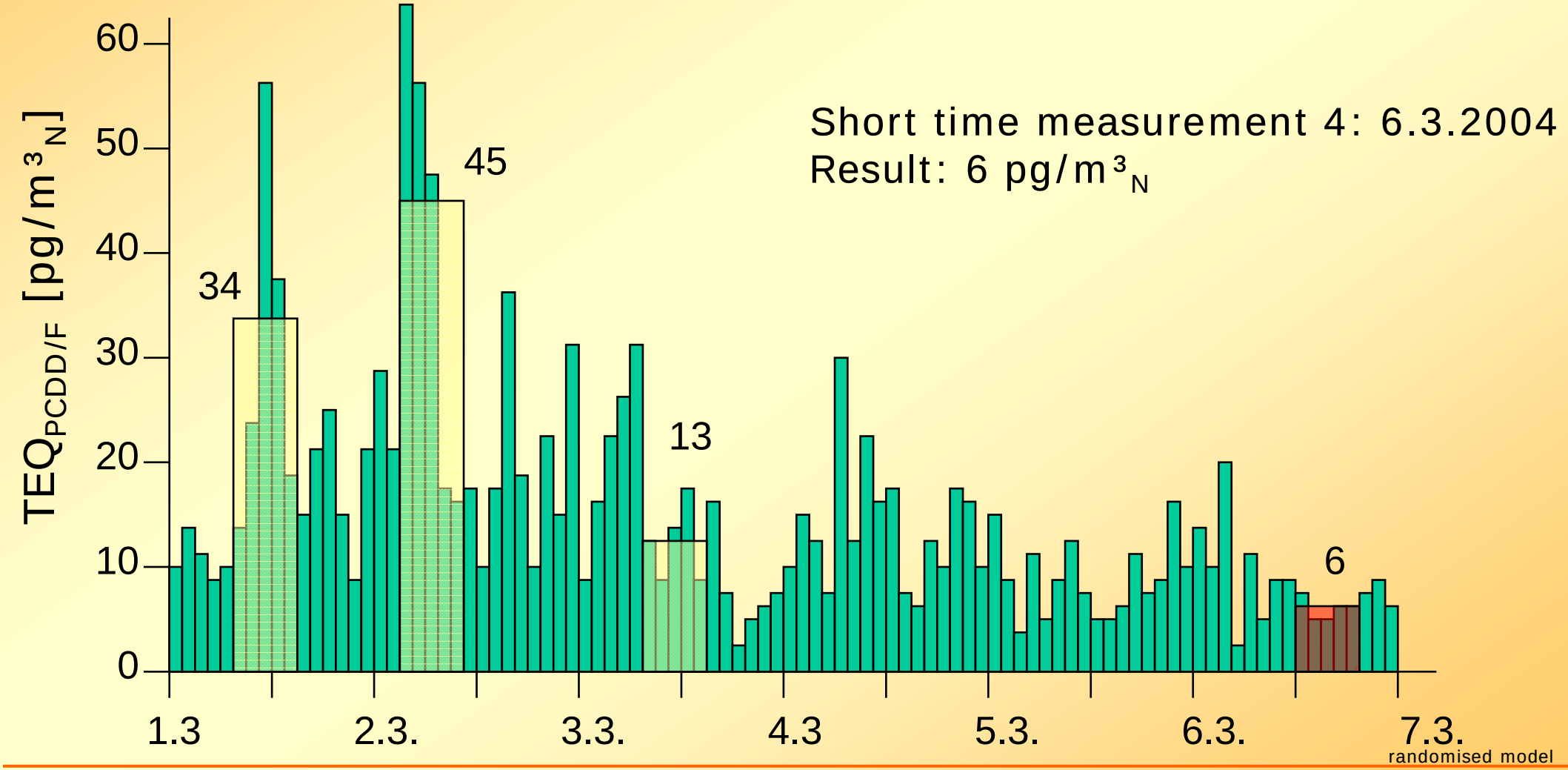
Spot measurements in the mathematical chaotic system



Short time measurement 4: 6.3.2004
Result: 6 pg/m³N

Formation and measurement basics

Statistical evaluation of short term measurements

Date	Measurement	Result pg/m³N
1.3.	1	34
2.3.	2	45
3.3.	3	13
6.3.	4	6

average: 24,5 ± 18 (P=63 %)

convidence interval: -33 to +82 ng/m³N

($P=95\%$, $t_{0,95;f=3}=3,18$)

➔ **statistical not useable result**

randomised model

Formation and measurement basics

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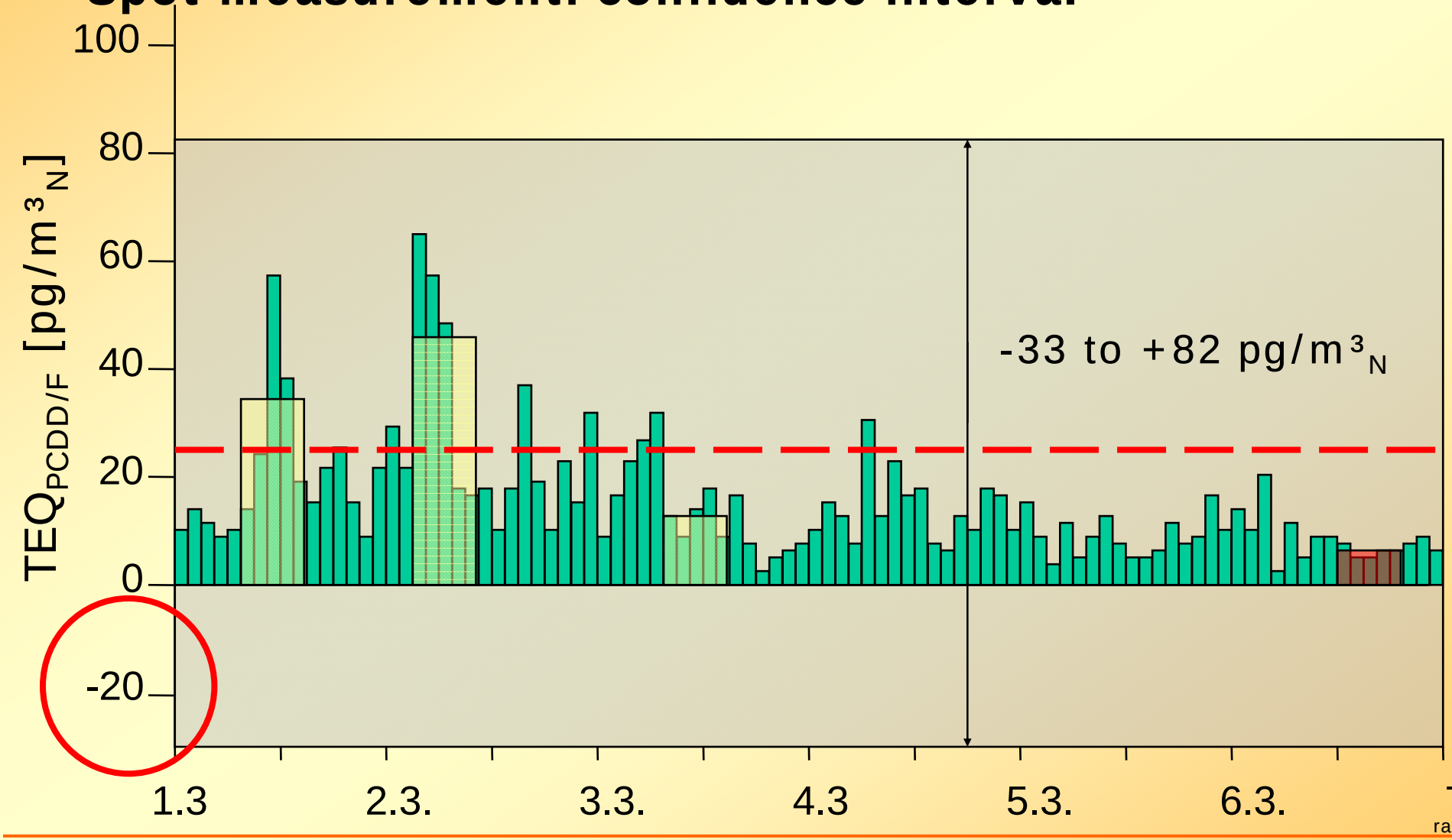
Spot measurement: confidence interval



randomised model

Formation and measurement basics

Measurement series 2: long term measurement

1 samplings over 6 days

Total covered time 144 hours

Formation and measurement basics

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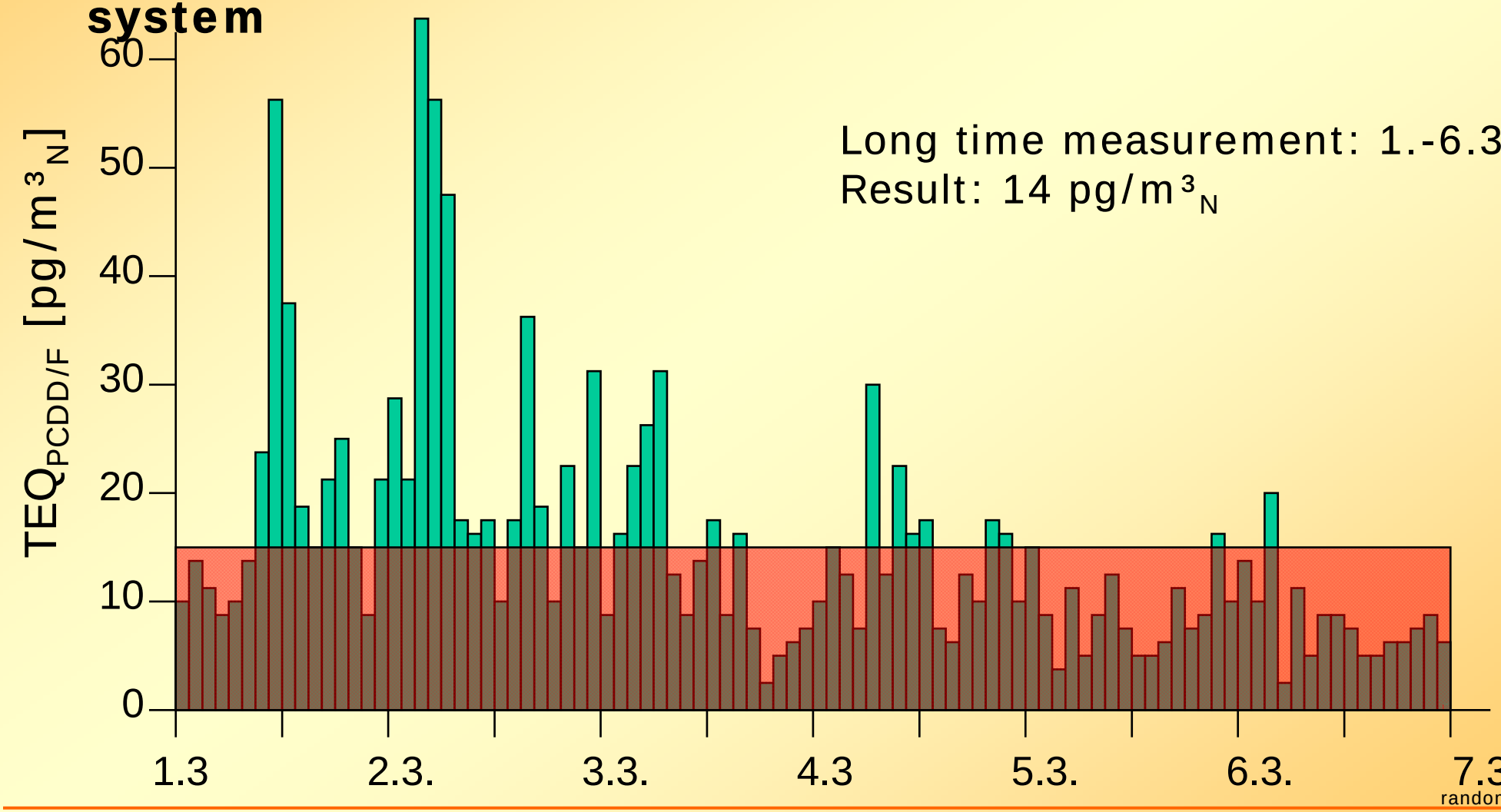
Long term measurements in the mathematical chaotic system



Long time measurement: 1.-6.3.2004
Result: 14 pg/m³N

Formation and measurement basics

Statistical evaluation of long term measurements

Date	Measurement	Result pg/m³N
1.-6.3.	A	14

average built by long term technique

convidence interval 10 to 18 ng/m³N
(±30%, P=95%)

➔ **statistical well useable result**

Formation and measurement basics

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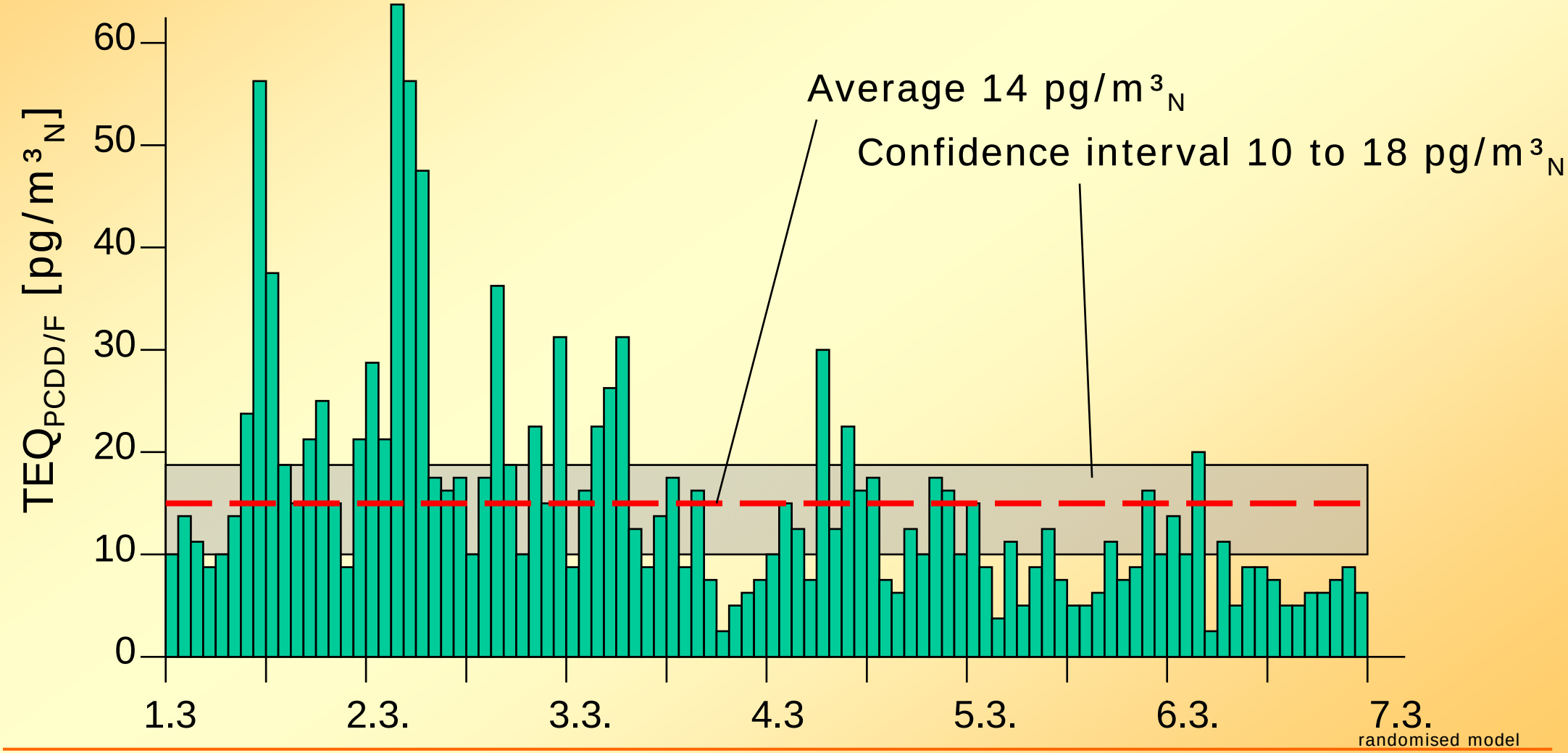
Long term measurement: confidence interval



Legal frame in Europe

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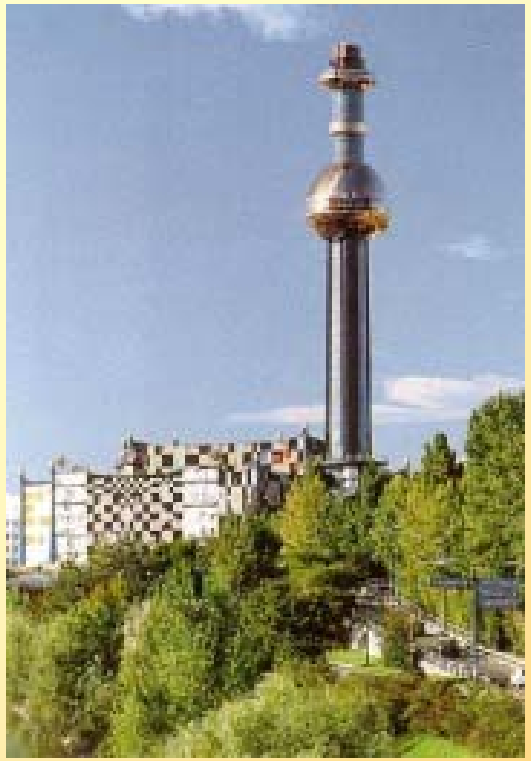
Why, how and how often measurements are to be done…

Legal frame in Europe

History of Dioxin Measurement

- Need for dioxin measurements bases on emission limit values
- First emission guarantee value late 80's in Austria
- First legal limit 0,1 ng per m^3 in Sweden
- Obligation of continuous sampling in Belgium since 2000/2001
- Acceptance of long term sampling **replacing** short time sampling in the United States
- Obligation of continuous sampling in France since mid 2014
- Today limit of 0,1 ng/m^3 in many countries



Municipal waste incinerator Vienna
designed by Friedensreich Hundertwasser

Legal frame in Europe

67/1994/EC
General rules for measurement techniques

76/2000/EC (WID – Waste Incineration Directive)
Limitation of emissions for different plant types

EN1948
Standard for measurement of Dioxins

2010/75/EU (IED - Industrial Emissions Directive) requesting BREF / BAT
Obliges authorities to prescribe “Best Available Techniques Reference” for plant permissions

National laws
providing the EC directives to the countries including local specifics

Legal frame in Europe

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76/2000/EC (WID – Waste Incineration Directive)

- Incineration and co-incineration plants
- Limitation to 0,1 ng/m³
- Measurement according CEN-Standards (in case of Dioxins: EN 1948)
- New directive in preparation, will include continuous sampling

Legal frame in Europe

EN1948: Standard for measurement of Dioxins

Five main parts

1948-1: Sampling

1948-2: Extraction and clean up

1948-3: Analysis and statistics

1948-4: Measurement of PCBs

1948-5: Continuous sampling (TS: in preparation)

Legal frame in Europe

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EN: European Standard

- regulating and reference document

TS: Technical specification

- guidance document
- non binding
- valid for 3 years
- after 3 years changed to EN or cancelled
- for change to EN: validation to be processed

Legal frame in Europe

EN1948-1: Sampling of Dioxins from stack emissions
TS1948-5: Continuous sampling

Tree principal methods

- Filter-cooler method
- Dilution method
- Cooled probe method

Legal frame in Europe

EN1948-1 and TS1948-5: Sampling of Dioxins from stack emissions

For each method several “minimum requirements”

e.g. for cooled probe method:

> “The condensate is caught in a condensate flask.
> The filter is incorporated before the last ab/adsorption stage.”

e.g. for dilution method:

> “A solid adsorber stage is downstream from the filter.”

Legal frame in Europe

Long time monitoring basing on EN 1948-1

- EN 1948-1 includes one of three methods for selection
- Two of the methods work with condensation of the gas humidity (cooled probe method, filter-cooler method), the complete liquid phases and the filters have to be analysed in the laboratory.

  For long term sampling the liquid amount is about 50 liters ---> these methods are not applicable correctly for long term sampling
- One of the methods works with dry precipitation (dilution method)
  The solid filters are analysed in the laboratory

→ Dilution method only possible and allowed method

Legal frame in Europe

Long time monitoring basing on EN 1948-5

- Standard in preparation
- Available earliest 2021
- Will allow some adaptations of sampling compared to EN1948-1 to enable long term sampling similar to all three methods
- Evaluation of adapted methods open, results of evaluation will be the base for the decision if all three methods can be used for long term sampling
- EN1948-5 will be the base (measurement standard) for the mandatory continuous measurement (sampling)

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Examples for the use of devices for continuous dioxin sampling...

Solutions for measurements

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Long term sampling of stack emissions

DioxinMonitoringSystem®

(long term AND short term sampling applicable)

Compounds:

PCDD/F, PCB, other POPs

with ParTrace® add on: PM10, PM2.5, PM1 additionally

Applications:

emission limitation, legal limits
mass balance, inventory
process optimisation

Availability since 1993

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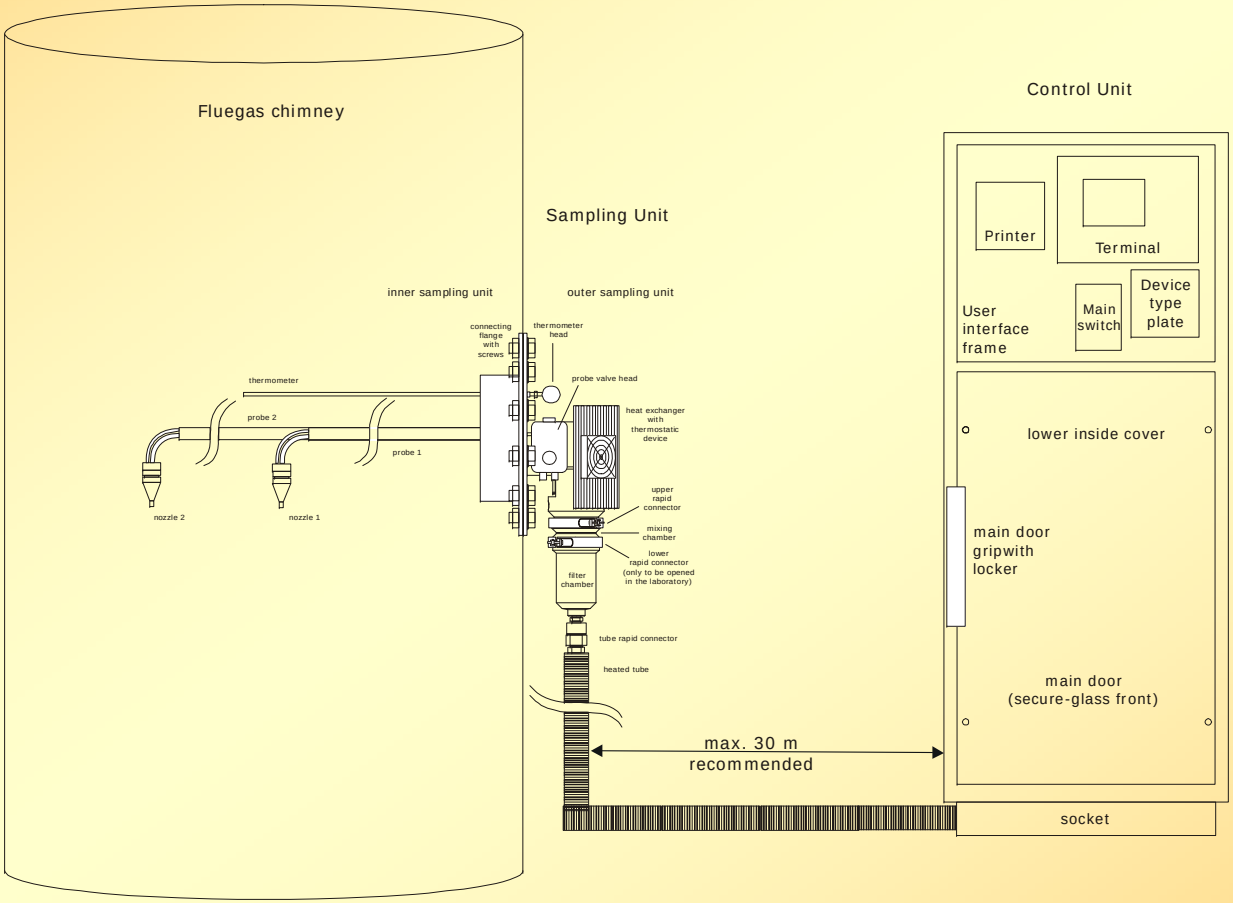
Method: EN1948-1:2006 dilution method, EN1948-5 prepared



Picture 1: DioxinMonitoringSystem® schema

DioxinMonitoringSystem®

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References:

~80 international installations

Applications:

Incineration plants (municipal, hazardous, industrial,...)

Cement production industry

Brick production industry

Petrochemical industry

Metallurgic industry

Solutions for measurements

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Long term sampling of ambient air

AmbientAirMonitoringSystem®

Compounds:

PCDD/F, PCB, other POPs

with ParTrace® add on: PM10, PM2.5, PM1 additionally

Applications:

general environmental measurements

SolUtions® for measurements

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Sampling of fine dust fractions

Analytical targets:

PM, PM10, PM2.5, PM1

Applications:

Add on for DioxinMonitoringSystem®
Add on for AmbientAirMonitoringSystem

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