



## Comparability of analytical data as a basis of possible evaluation of European deposition, soil and foliage data

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## 0. Introduction

1. Quality assurance in the participating laboratories
2. Interlaboratory quality assurance
3. Development of ring test results during the last 15 years
4. Standard comparison in different labs over time
5. Combined standard comparison and ring test program within the 2nd German Soil Survey (BZE II)
6. Conclusions



## 0. Introduction

Many laboratories from almost **30 different European countries** are producing **hundreds of thousands** analytical results each year!

Kind of laboratories (2009-2011)	Number of Labs
Labs for water analysis (deposition, soil solution)	41
Labs for plant analysis (foliage, litterfall, vegetation)	36
Labs for soil analysis (soil, humus layer)	38
Labs for soil physics analysis	25
<b>Total number of Labs</b>	<b>63</b>

To guarantee the **comparability** of the produced results a quality assurance program **within each laboratory and between all laboratories** is necessary.



## 1. Quality assurance in the participating laboratories

On basis of the manual each participating laboratory has developed its own quality control system.

Basics are:

- the use of harmonized, well-defined and documented analytical methods (reference methods in the ICP Forests program)
- different quality checks like:
  - ion balance
  - Nitrogen-balance
  - comparison of measured and calculated cond.
  - plausible range checks
- repeated measurement of standard material

**mandatory within the ICP Forests monitoring program!**  
**Results have to be submitted with analytical data!**





## 2. Interlaboratory quality assurance

The following topics are part of interlaboratory quality assurance program of ICP Forests:

- continuous analytical information exchange by meetings of the heads of the labs
- participation in interlaboratory ring tests
- definition of tolerable limits for these ring tests

Additional quality assurance program part in BioSoil program:

- repeated measuring of the same standard material during a survey in all participating laboratories





### Tolerable limits for foliar ring tests

**Table 3.4.1.2.3:** Inter-laboratory tolerable limits for high and low concentrations of mandatory and optional foliage and litterfall parameters.

### Tolerable limits for ring tests:

basis for ring test  
evaluation

and criteria for lab  
qualification

Parameter	Conc. Range	Conc. Level	Inter-Laboratory Tolerable limit (% of mean)
N mg g <sup>-1</sup>	Low	≤ 5.0	± 15
	High	> 5.0	± 10
S mg g <sup>-1</sup>	Low	≤ 0.50	± 20
	High	> 0.50	± 15
P mg g <sup>-1</sup>	Low	≤ 0.50	± 15
	High	> 0.50	± 10
Ca mg g <sup>-1</sup>	Low	≤ 3.0	± 15
	High	> 3.0	± 10
Mg mg g <sup>-1</sup>	Low	≤ 0.50	± 15
	High	> 0.50	± 10
K mg g <sup>-1</sup>	Low	≤ 1.0	±15
	High	> 1.0	±10
Zn µg g <sup>-1</sup>	Low	≤ 20	± 20
	High	> 20	± 15
Mn µg g <sup>-1</sup>	Low	≤ 20	± 20
	High	> 20	± 15
Fe µg g <sup>-1</sup>	Low	≤ 20	±30
	High	> 20	±20



## 3. Development of ring test results in ICP Forests monitoring program during the last 15 years

The most important step to force quality assurance and control was the introduction of **mandatory ring tests** for water (each 2 year), soil (each 3 year) and plant (each year) samples.

In the meantime **6 soil, 7 water and 17 foliar ring tests** have been organized within the ICP Forests program and FutMon project.

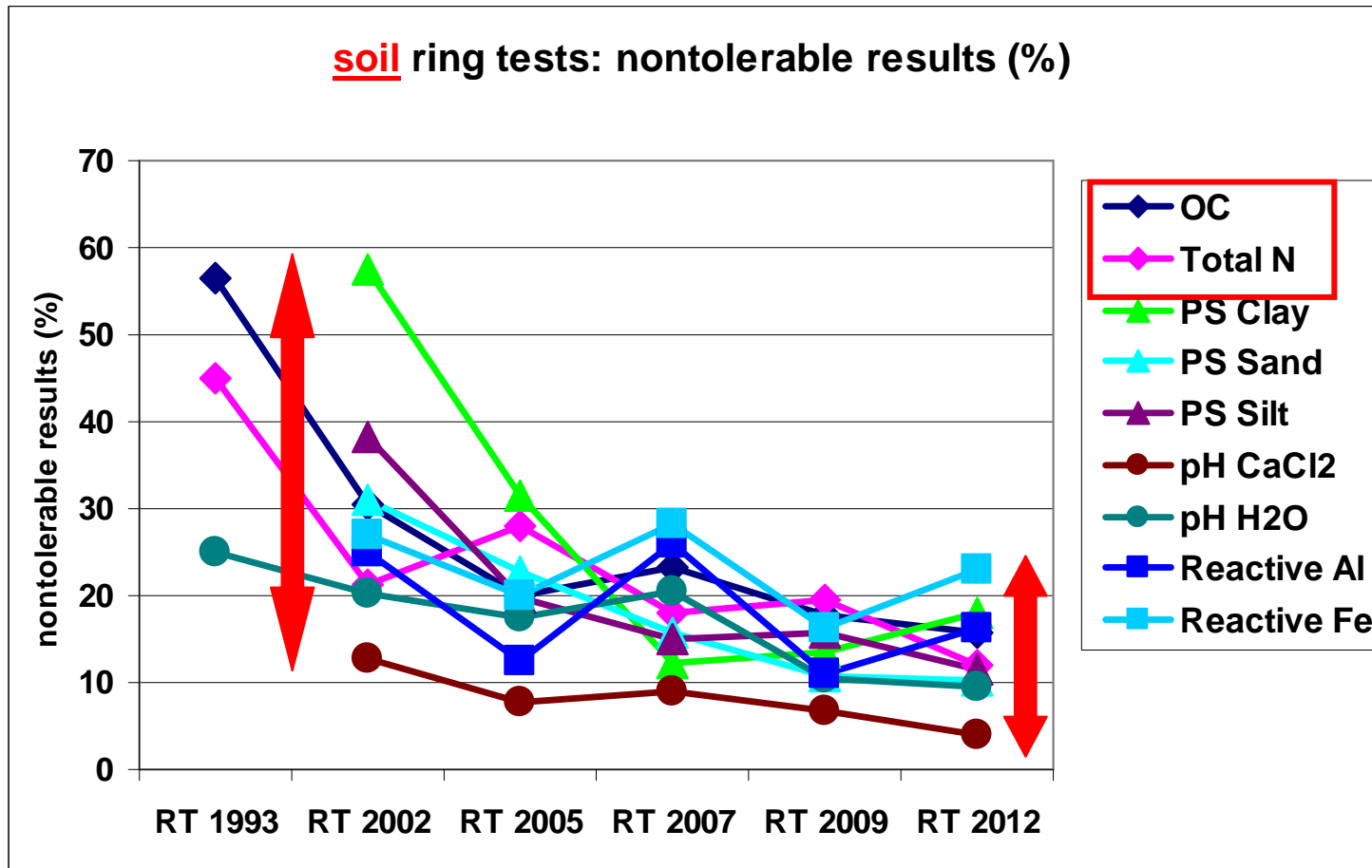
All ring tests has been evaluated again on the basis of the **actual tolerable limits**.

From the results of these ring tests the **development of quality** in the labs can be seen.





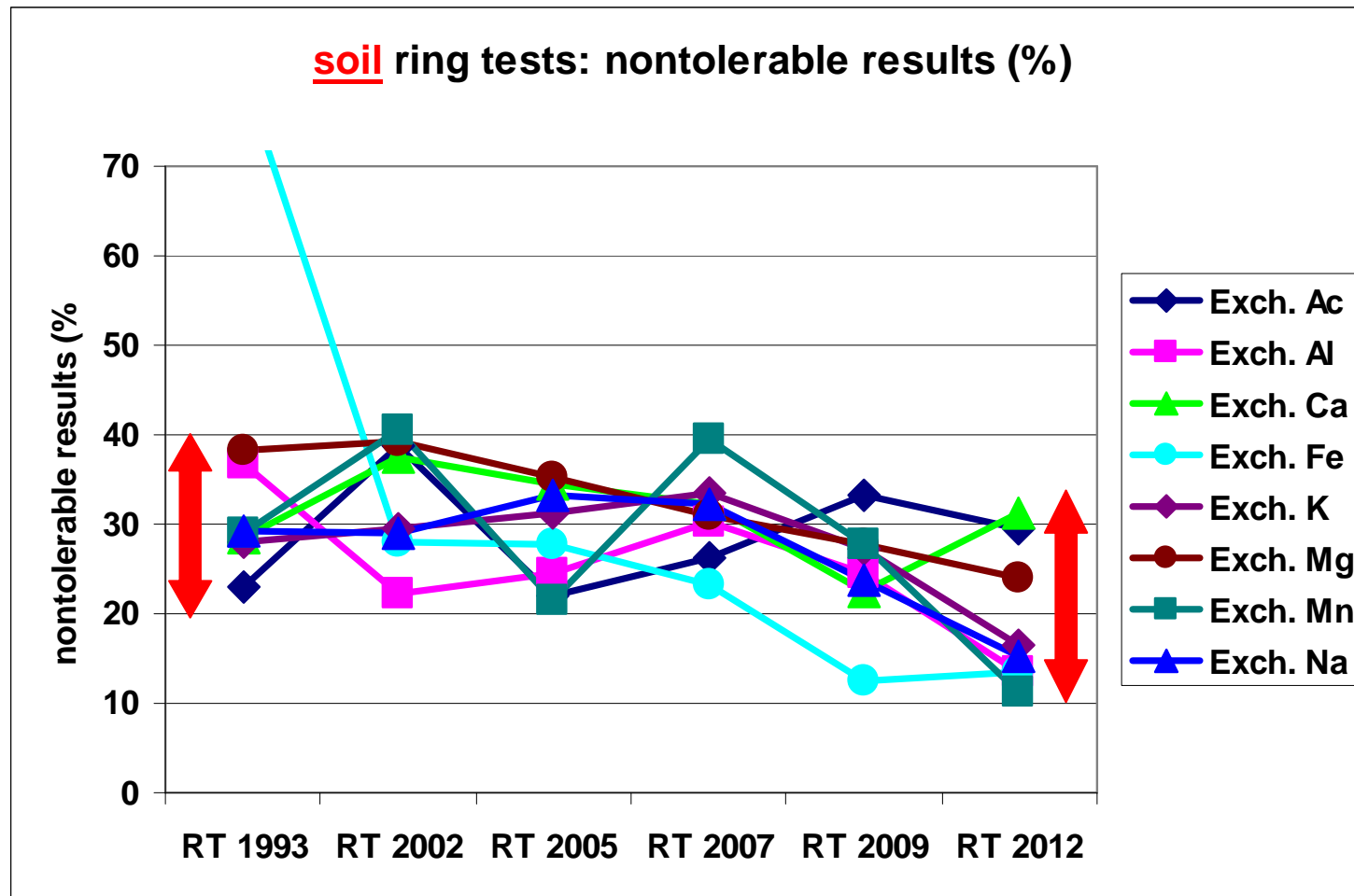
### Ring tests soil: Particle Size, TN, OC, pH, reactive Fe + Al





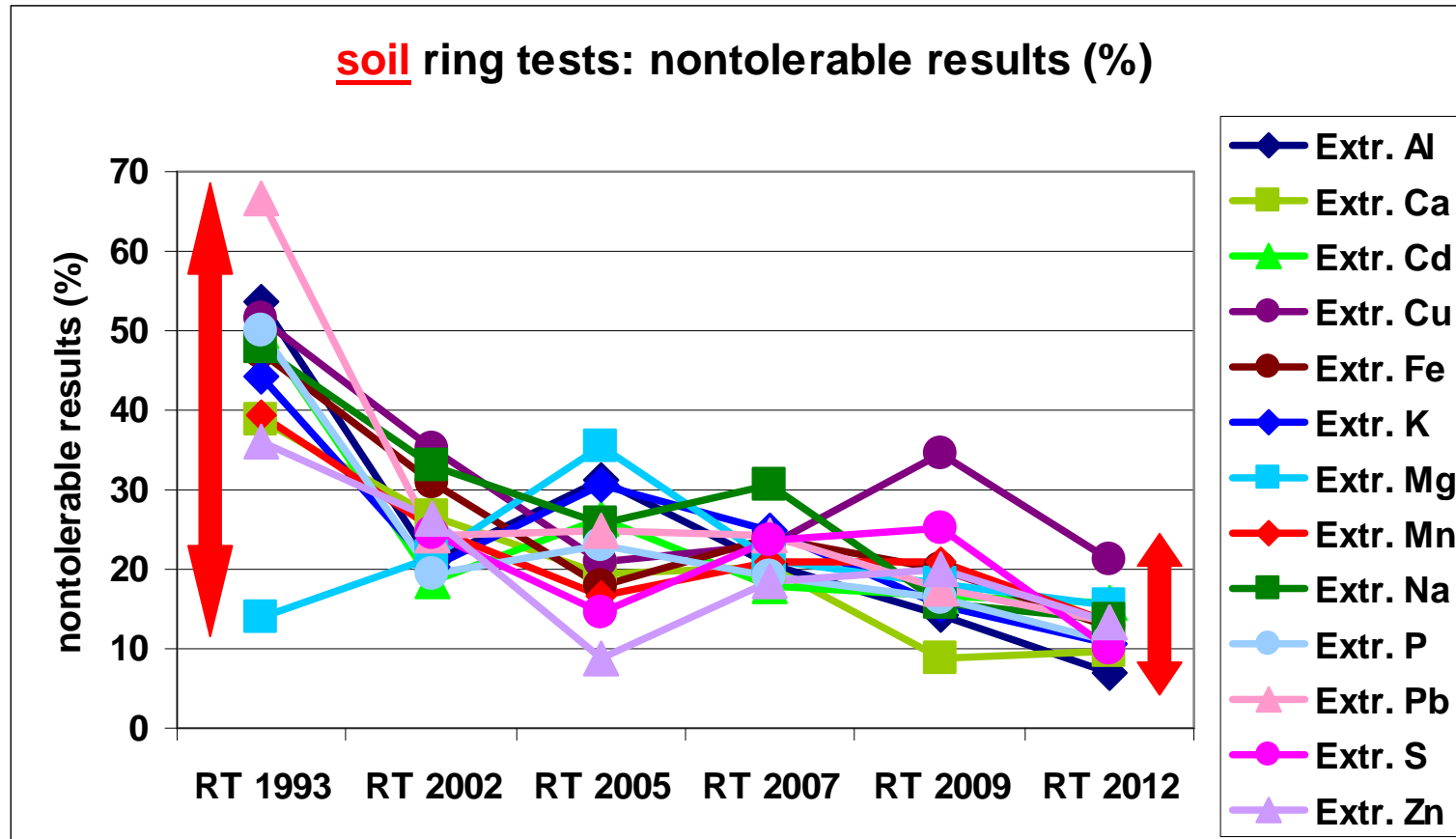


### Ring tests soil: exchangeable cations



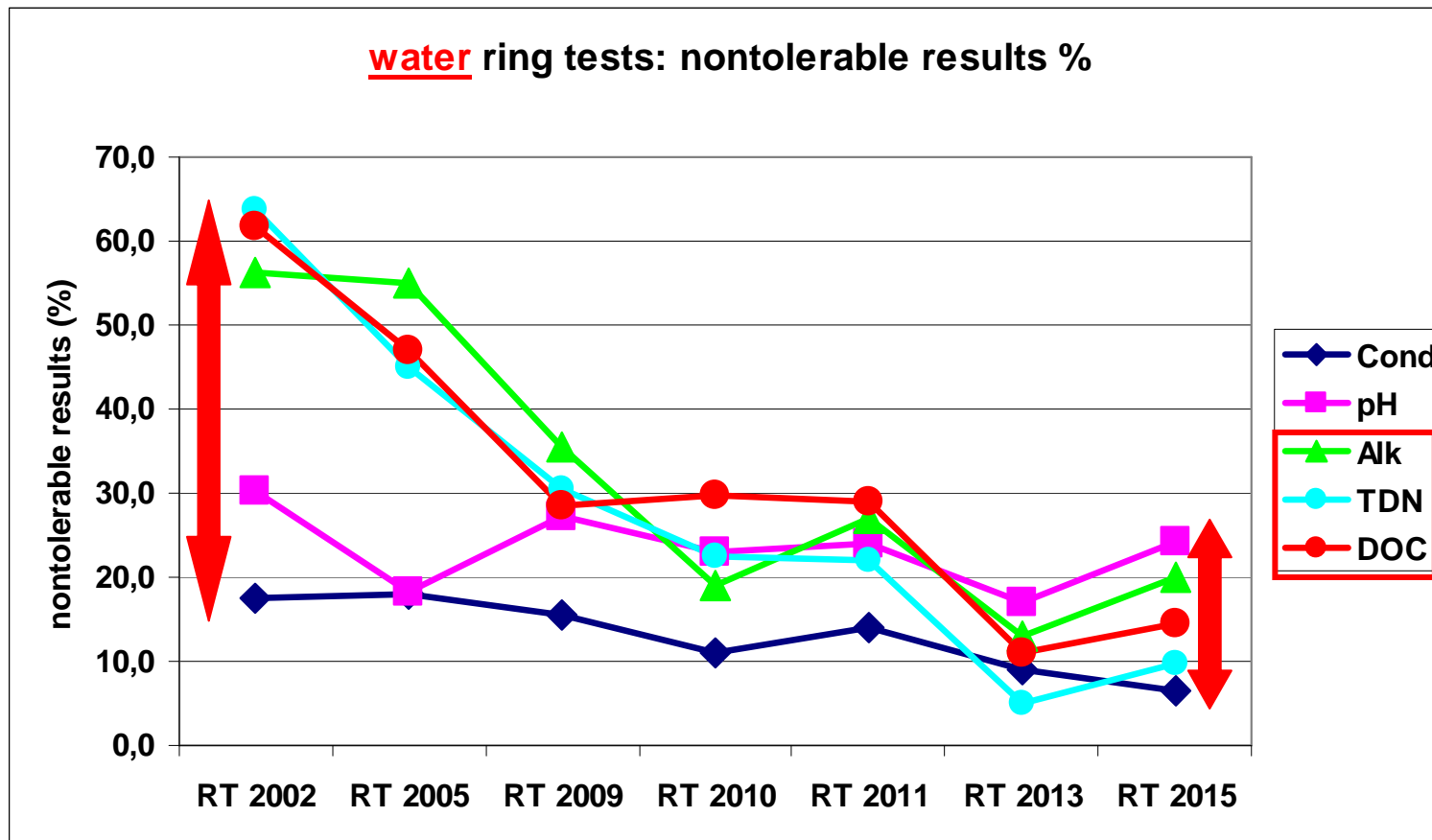


### Ring tests soil: aqua regia extractable

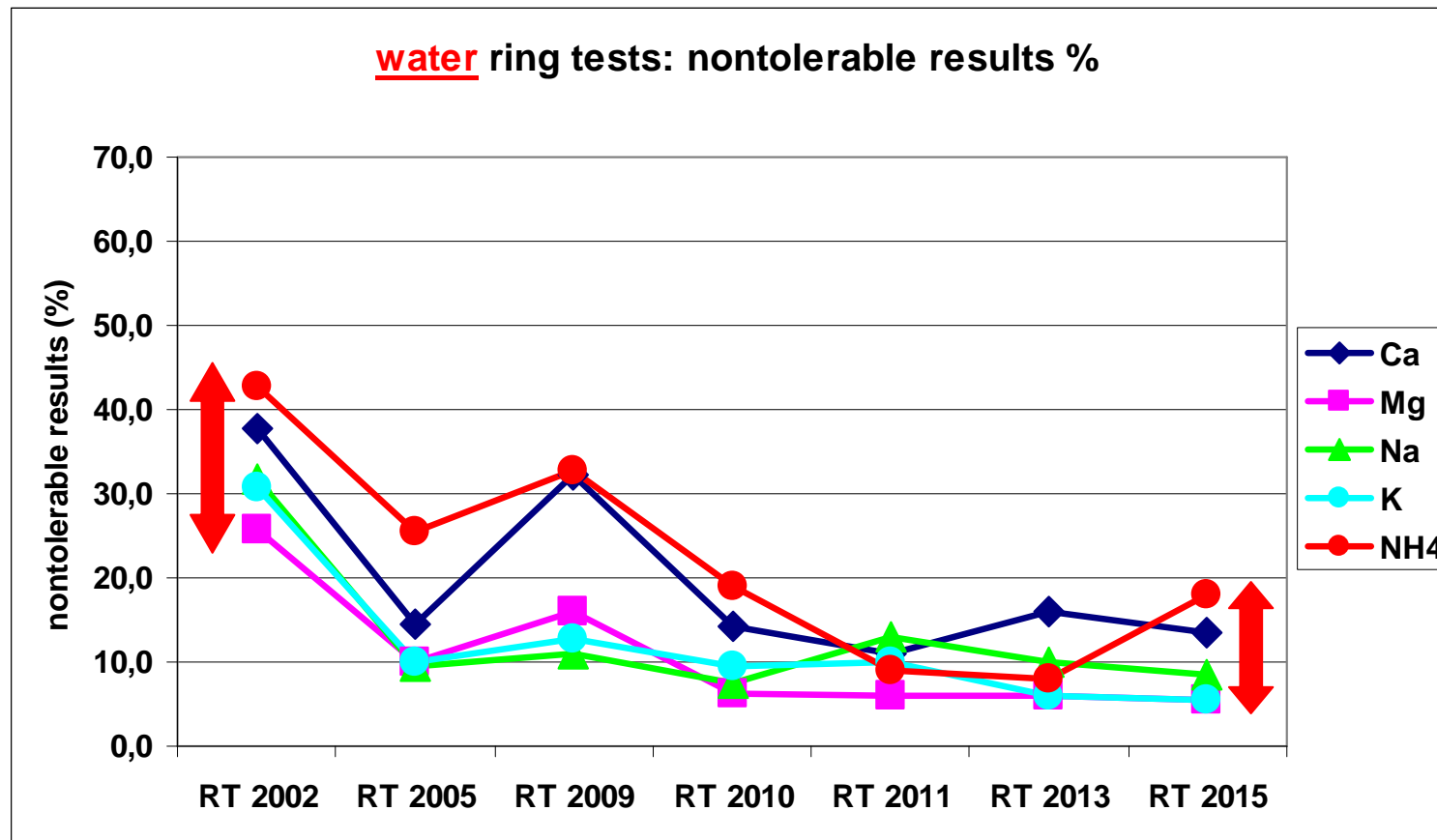




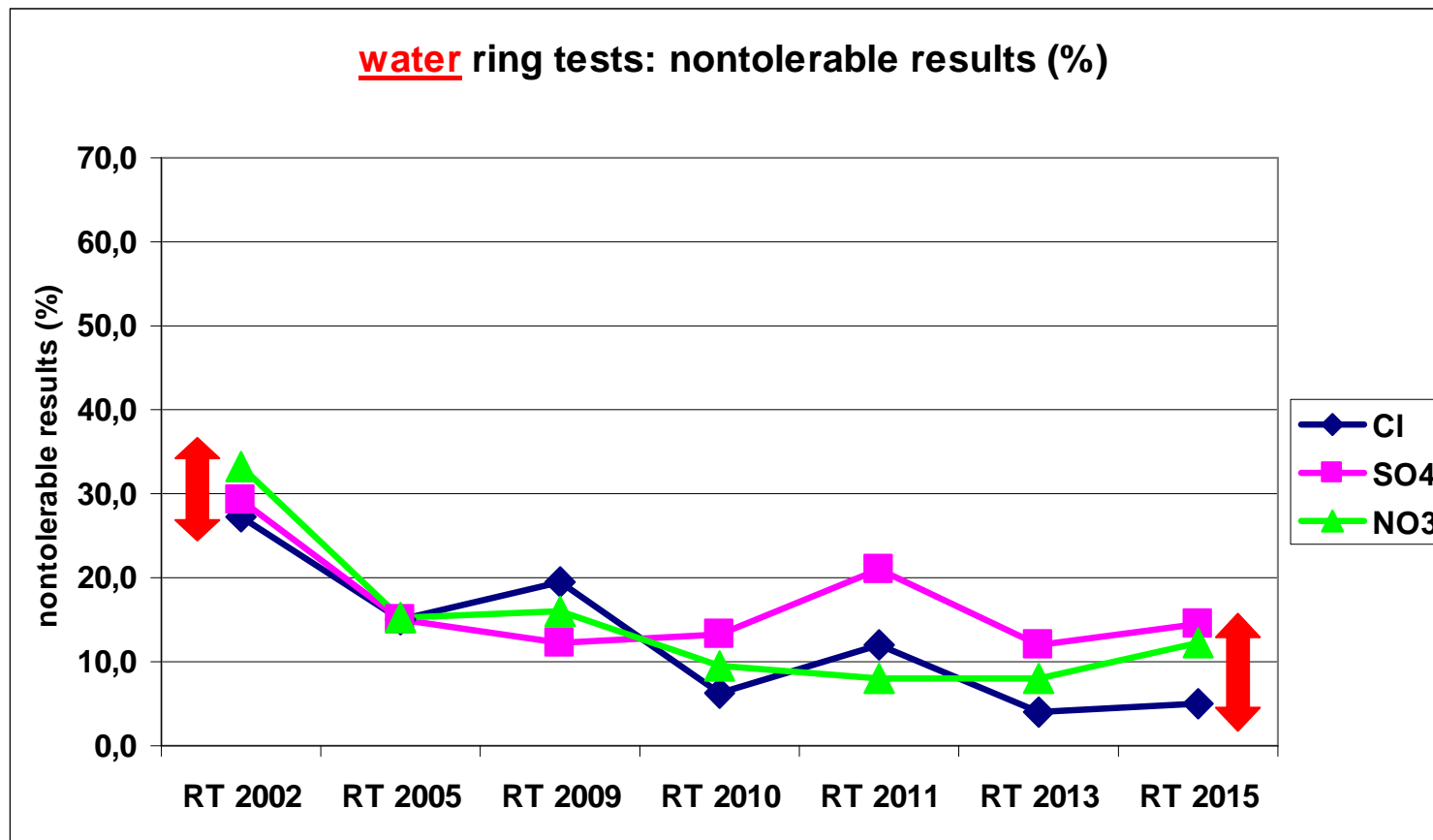
### Ring tests water: DOC, TDN, pH, Alk, Cond



### Ring tests water: cations



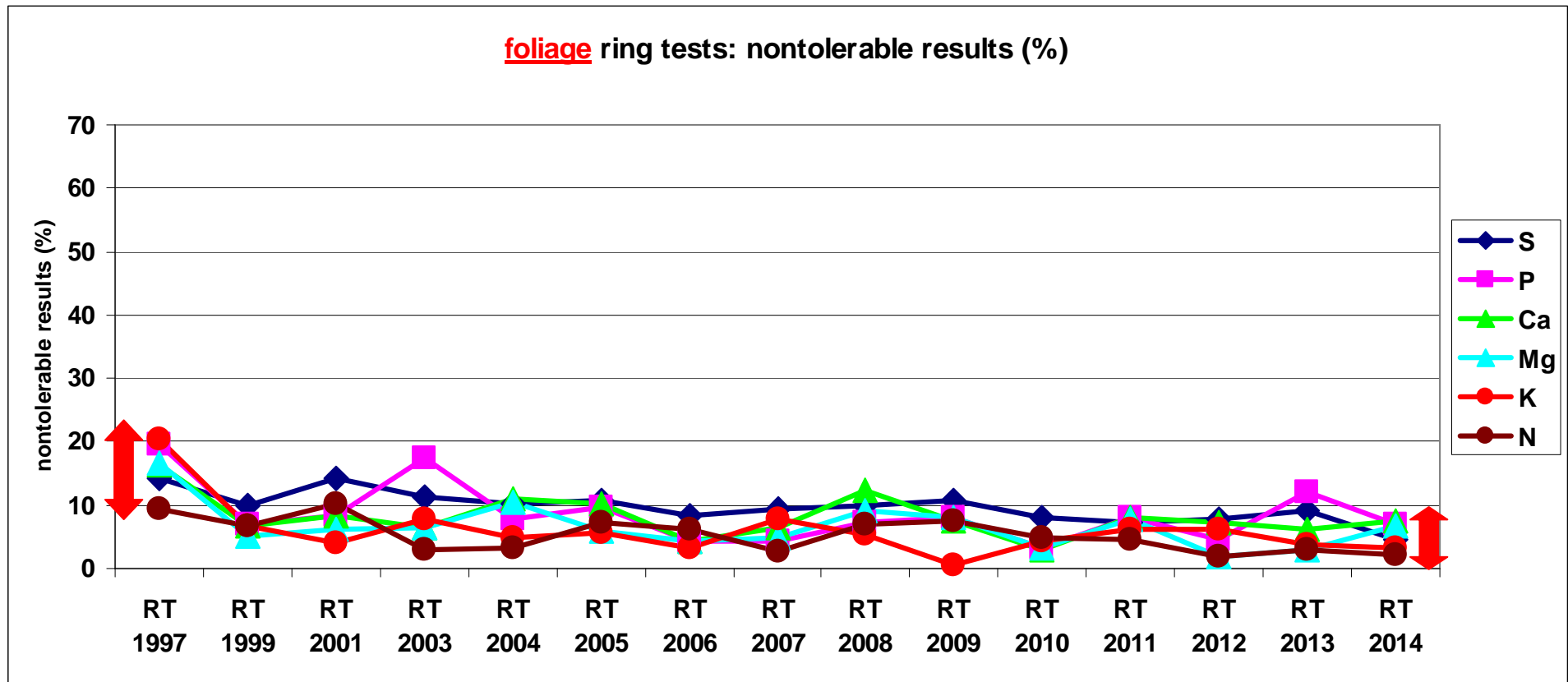
### Ring tests water: anions







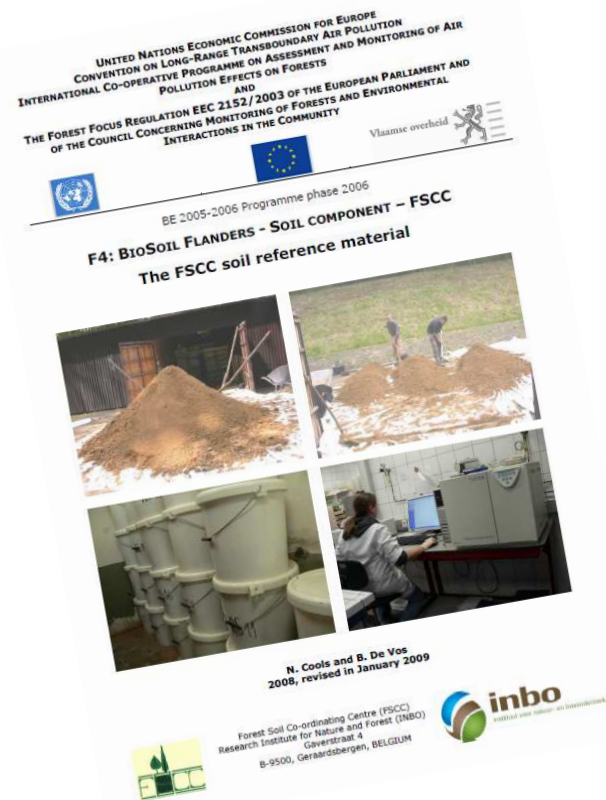
### Ring tests foliage: total contents





### 4. Standard comparison in different labs over time

Unother possibility for quality control between labs is the repeated measurement of the same standard material during a survey in all participating laboratories.

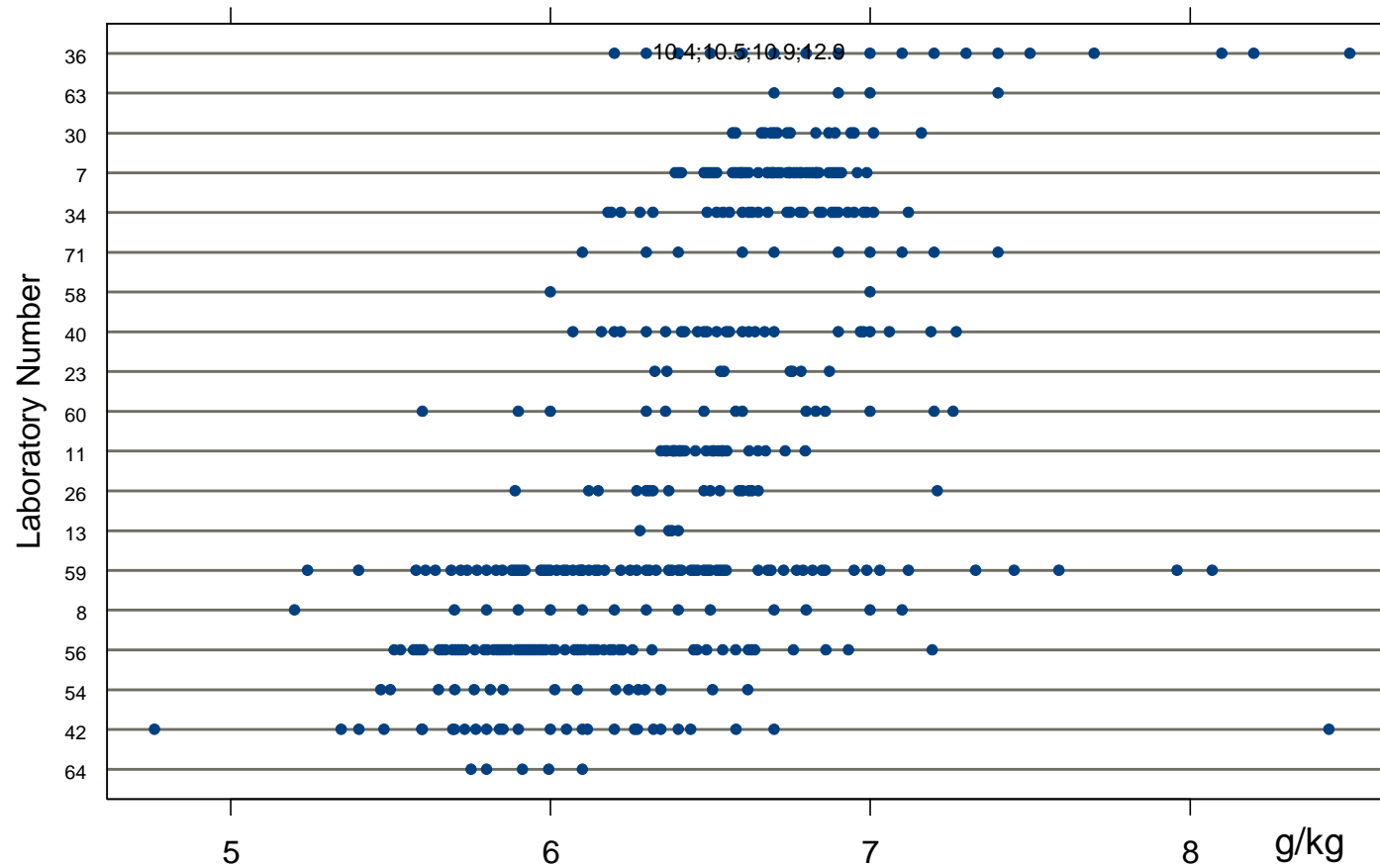


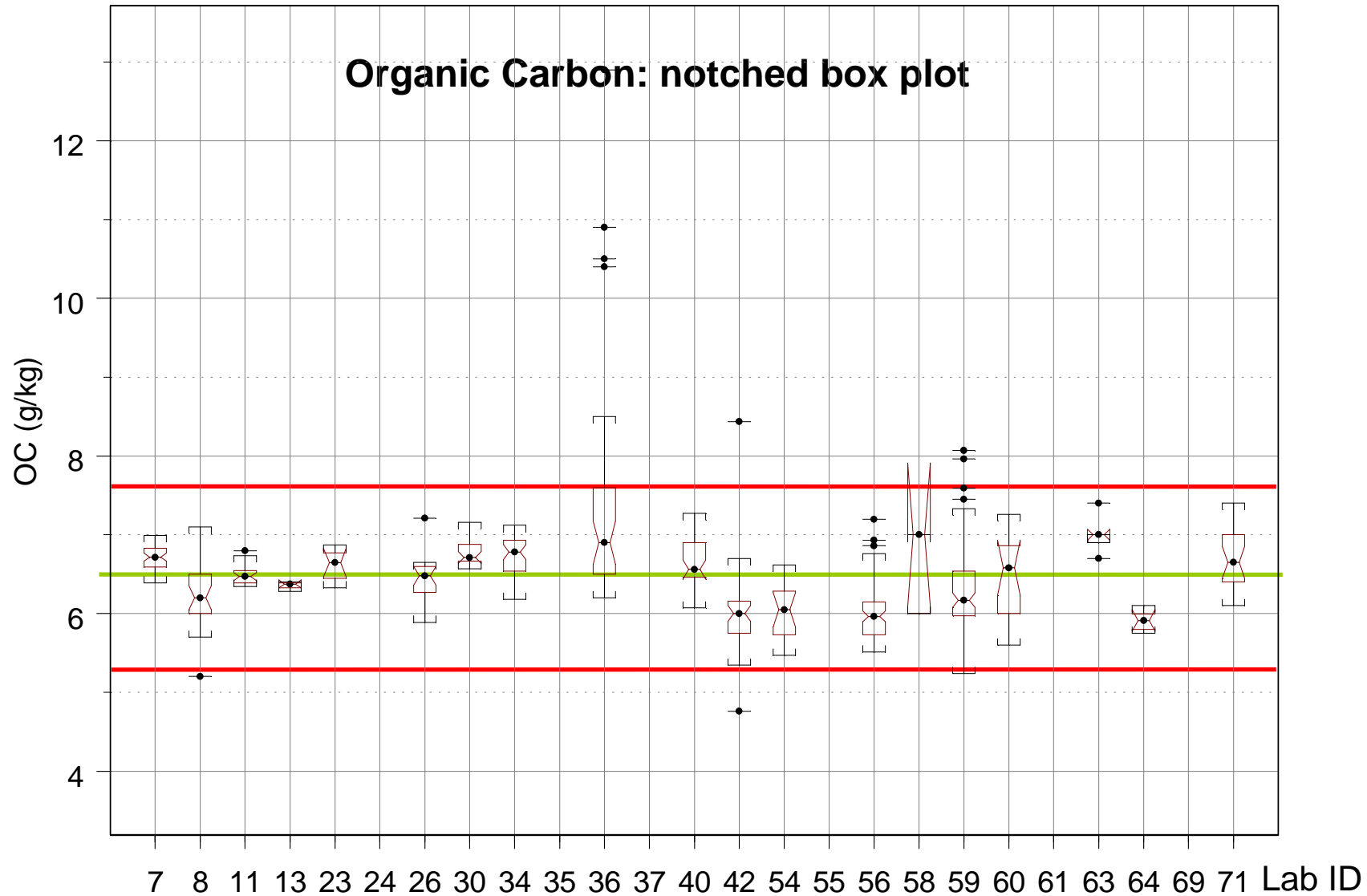
This has been done within the BioSoil Projekt, organized by the FSCC (Forest Soil Coordinating Center of ICP Forests)





### Organic Carbon: dot plot per laboratory







## 5. Combined standard comparison and ring test program within the second German Soil Survey (BZE II)

In Germany the experience of the work of the **expert commission for Forestry Analysis** during the last years together with the **Working Group QA/QC in Labs** within ICP Forests led to **a specific quality control program** for the 2nd German soil survey (BZE II), which has been running from 2006-2009.







## Quality control program of the 2nd German Soil Survey (BZE II)

- the use of harmonized, **well-defined and documented analytical methods** for each parameter, published in the German Handbook of Forestry Analysis (**reference methods**)
- a **ring test program** with annual ring tests (3 soil and 2 humus) before and during the survey; the participation and the requalifying after each ring test was mandatory
- **mandatory measurement** of specially produced **standard material** for each parameter during the survey; measurement of the control standards all 20 samples; mandatory recording of the results in control charts



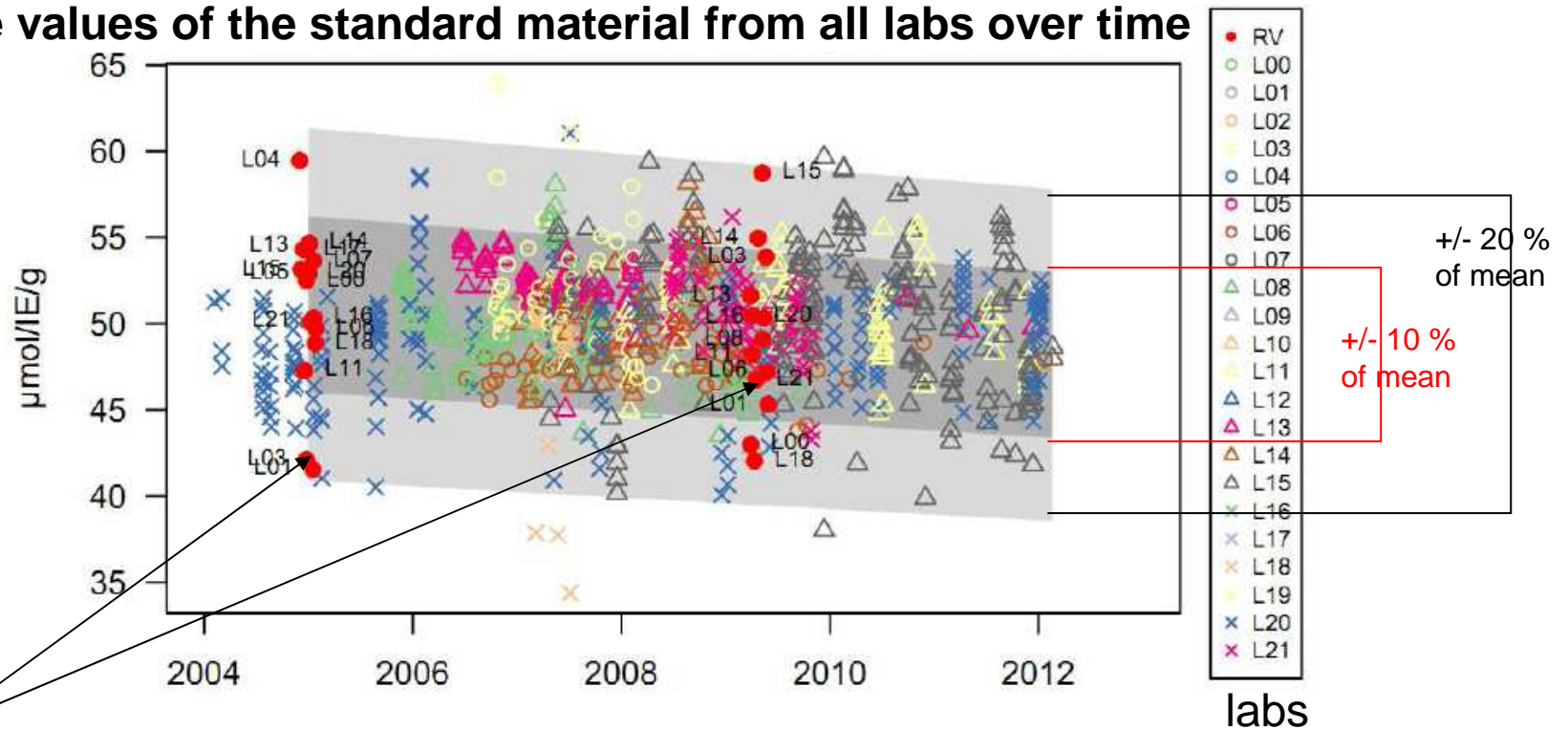
## Evaluation of the standard material measurements and the ring test result of all labs

for each parameter 3 graphs are shown:

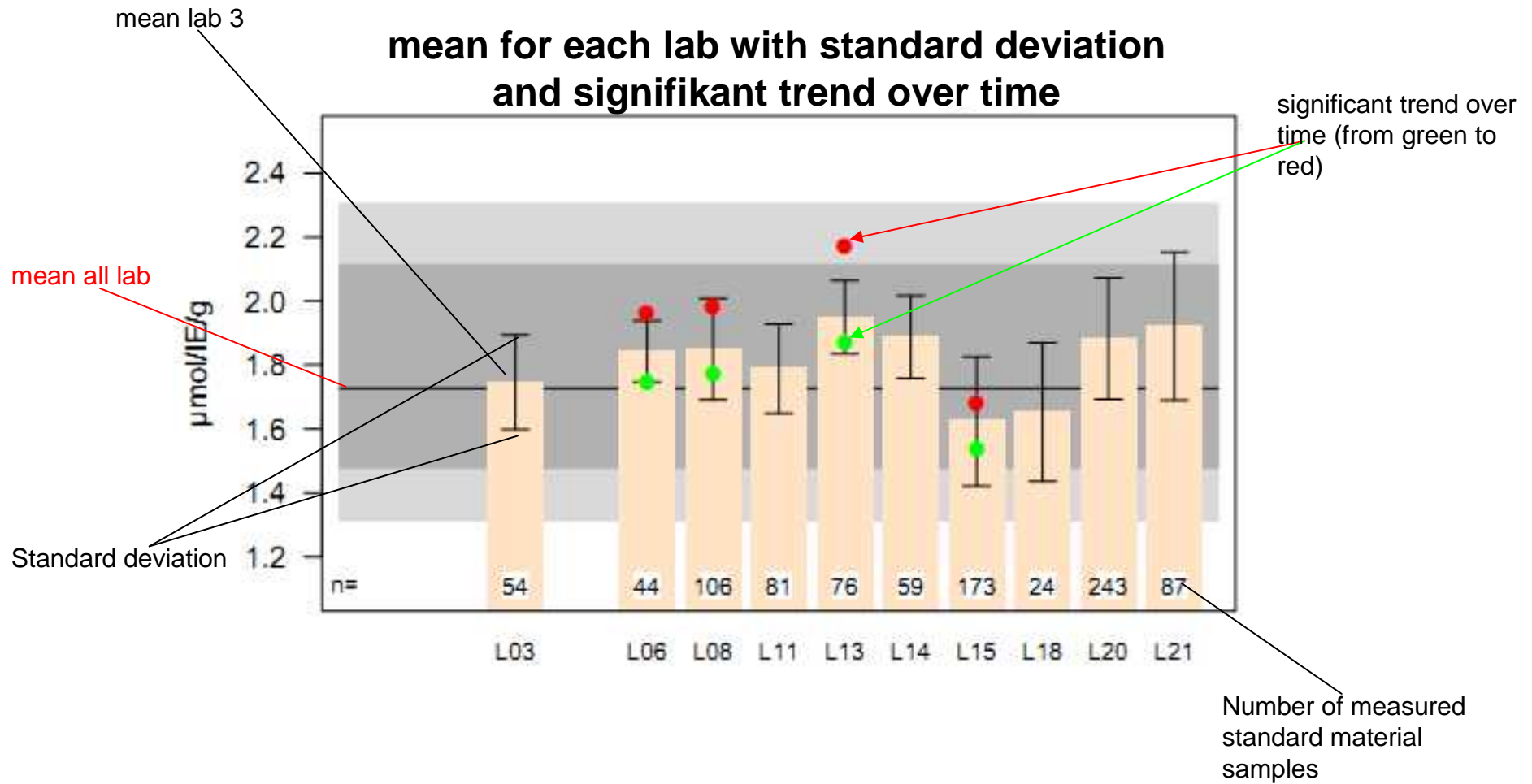
1. all single values of the standard material from all labs over time
2. mean for each lab with standard deviation and significant trend over time
3. mean of the z-score of all ring test samples results for each lab



all single values of the standard material from all labs over time



Red dots: results of the ring tests of the labs



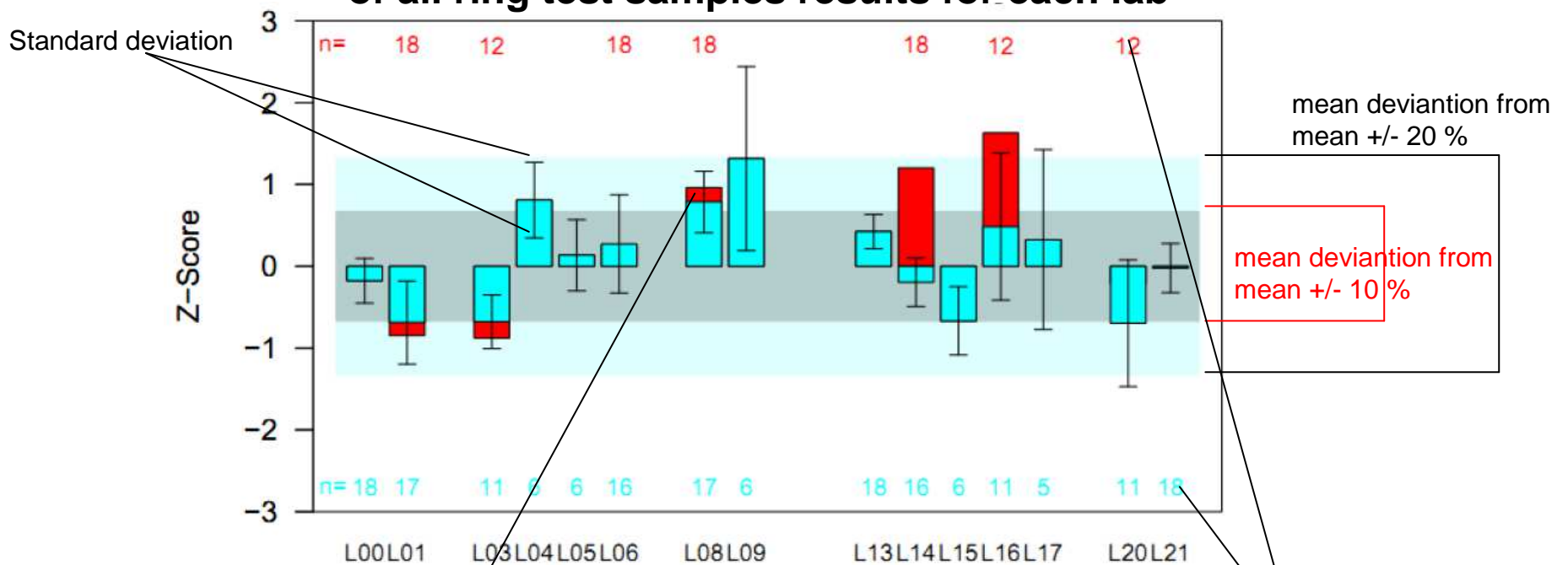




$$Z\text{-score} = (\text{mean}_{\text{lab}} - \text{mean}_{\text{tot}}) / SD_{\text{tot}}$$

(the Z-score shows the dimension of the deviation of the mean of a lab from the mean of all labs as a function of the variation among the labs)

### mean of the z-scores of all ring test samples results for each lab

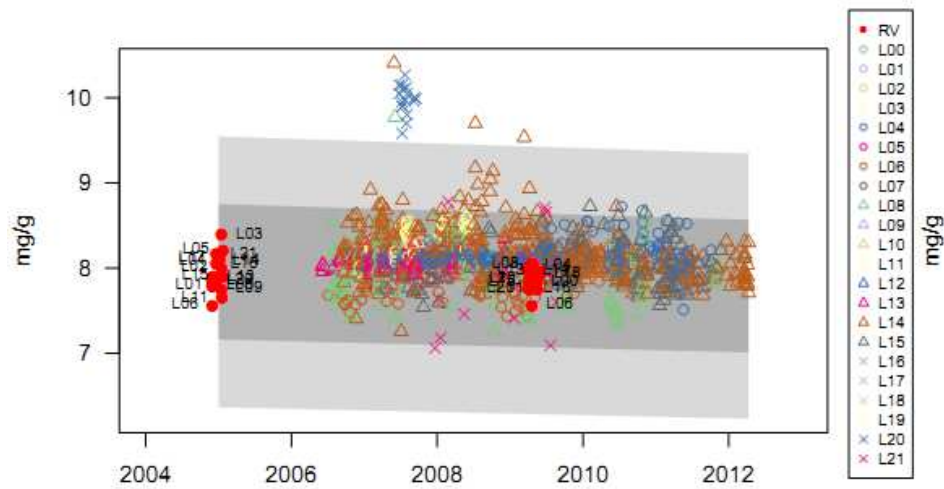


mean of the Z-scores of lab 08 **without** (blue) and **with** (red) outliers

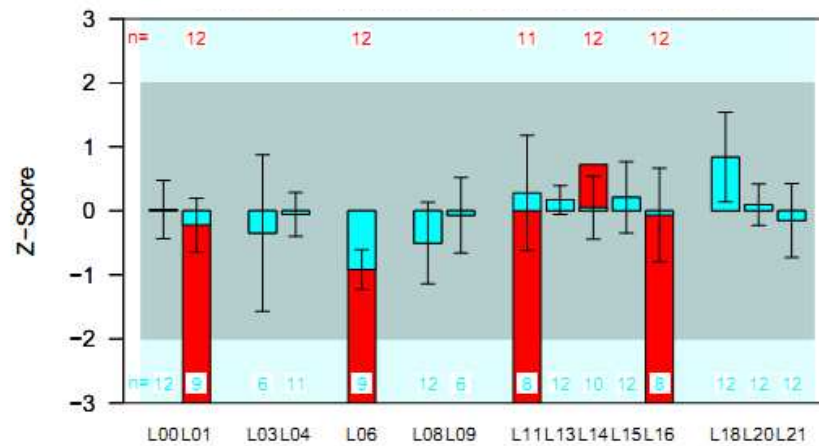
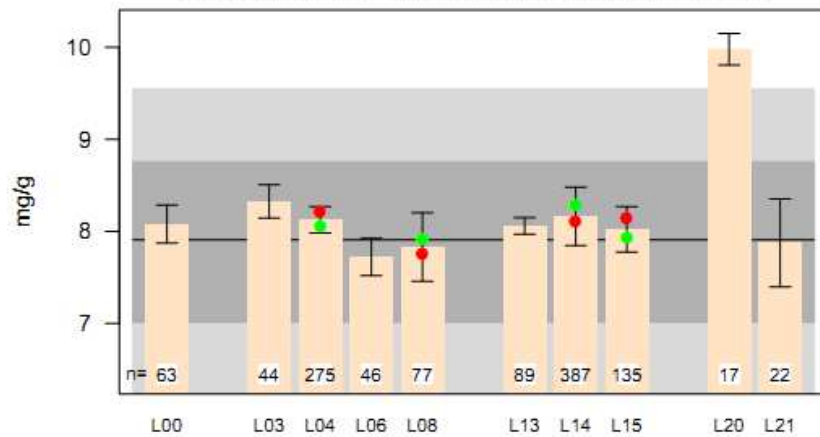
Number of measured ring test samples of lab 11 **without** (blue) and **with** (red) outliers

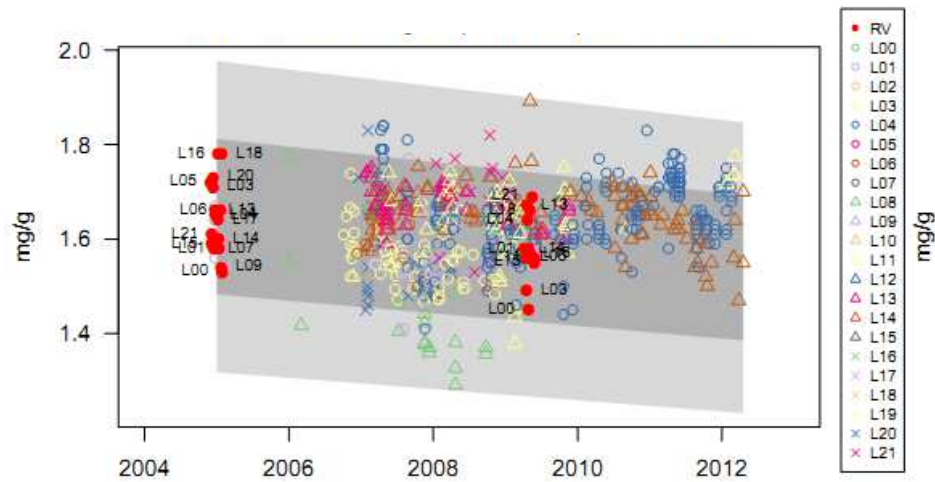






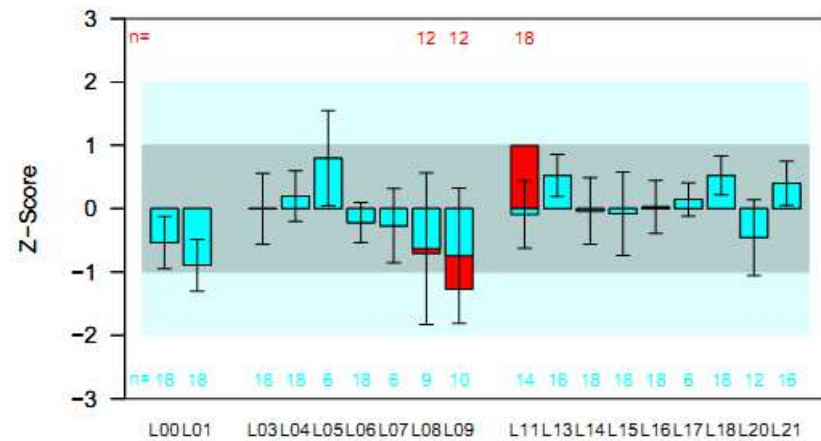
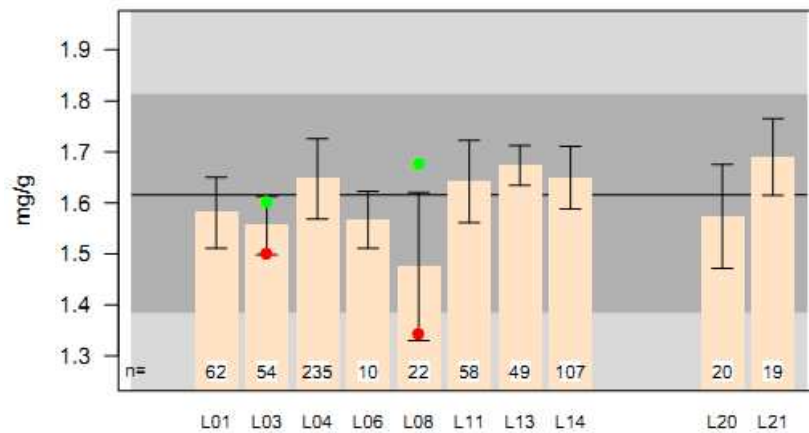
**example 1:  
C (total carbon)**

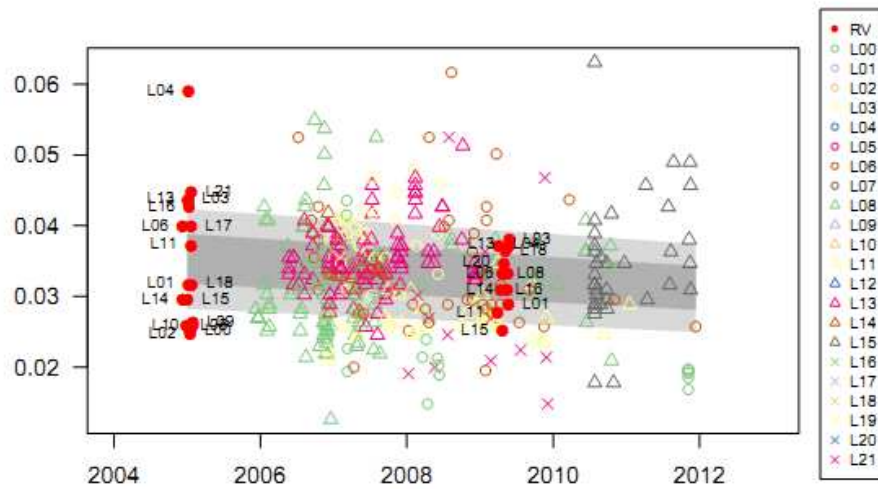




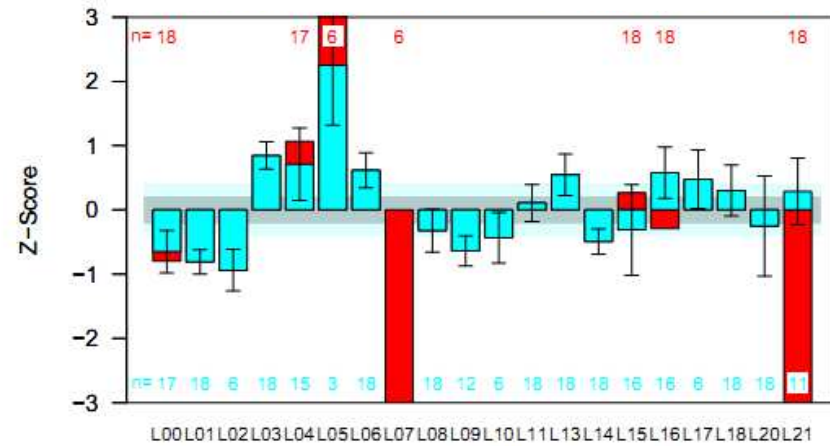
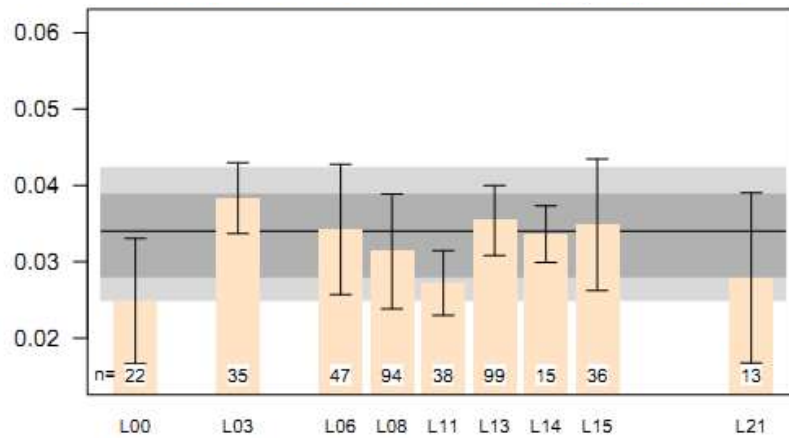
example 2:

Ca (aqua regia extractable)





example 4:  
pH (H<sub>2</sub>O)

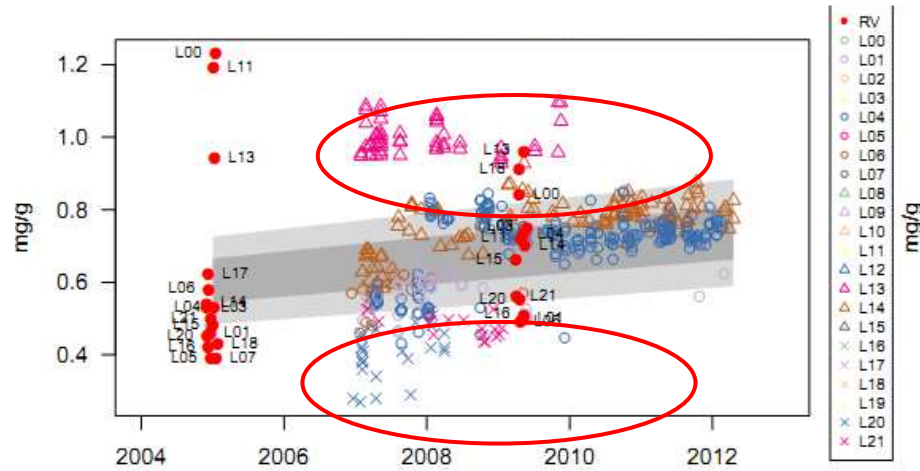




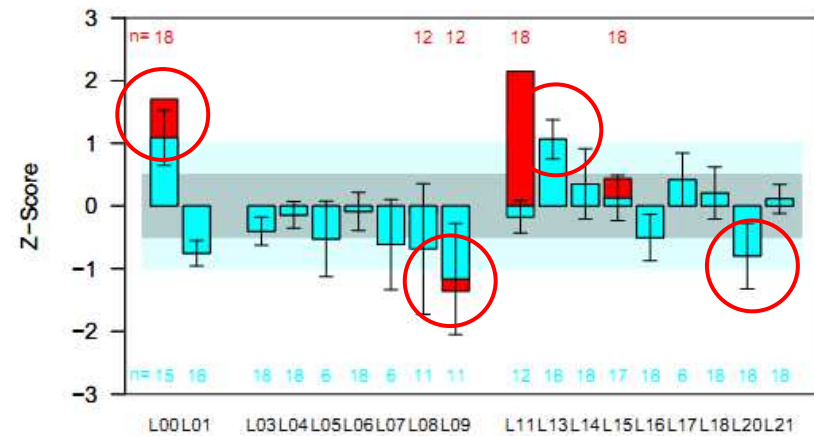
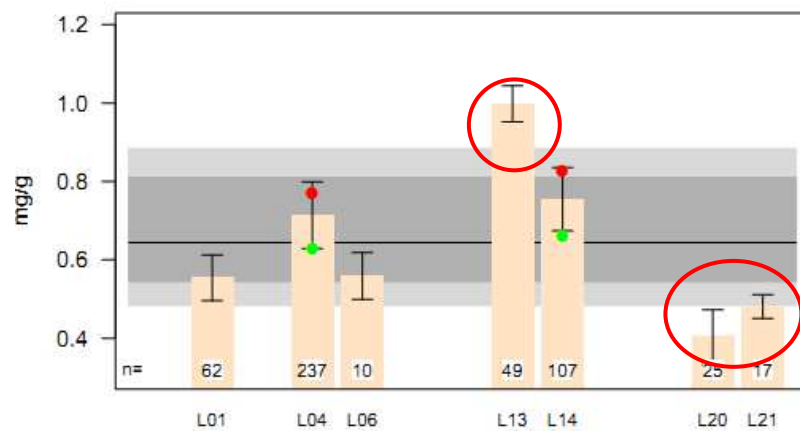


# ICP Forests

4. Scientific Conference of ICP Forests  
Ljubljana, Slovenia, Mai 2015



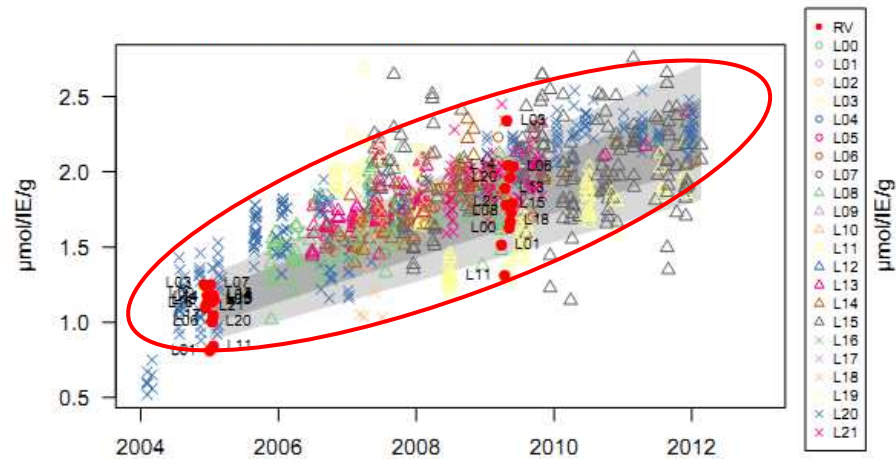
example 4:  
K (aqua regia extractable)



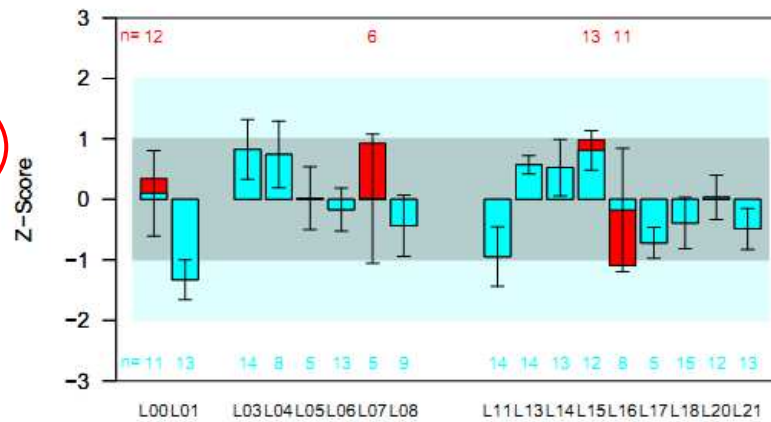
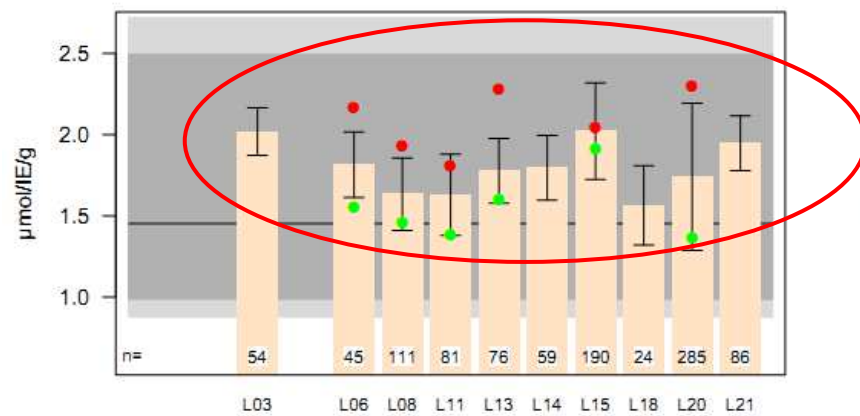
**NW-FVA**  
Northwest German Forest  
Research Station

Comparability of analytical data as a basis of possible evaluation  
of European deposition, soil and foliage data (N. König et. al.)





**example 4:  
Mn (exchangeable)**







### Comparability of the analytical results of the 2nd German Soil Survey between labs and over time

parameter group	mean variation of the means (standard m.)	mean variation of the deviation of the mean (ring tests)	parameters not comparable
total C, N	+/- 10 %	+/- 5 %	
pH (H <sup>+</sup> )	+/- 20 %	+/- 40-50 %	
exchangable	+/- 10 %	+/- 15 %	Na
aqua regia extractable	+/- 10-15 %	+/- 15 %	K, Na
total	+/- 10-20 %	+/- 15 %	
reactive Fe, Al	+/- 10 %	+/- 15 %	





## 6. Conclusions:

### Basic needs for comparable analytical data in long term monitoring programs:

- **Reference method descriptions** and a list of **usable determination methods** for all parameters in the manuals
- **Comprehensive QA/QC guide** for laboratory work with different **quality checks**, help files etc.
- **Mandatory ring test program** with water, plant, soil and soil physics ring tests and defined tolerable limits for all parameters
- **Laboratory qualification system** by ring tests with a requalification procedure for labs with unacceptable ring test results and final qualification reports
- **Mandatory use of control charts** for all parameters

