6 RING TESTS AS MAIN PARTS OF THE QUALITY ASSURANCE AND CONTROL PROGRAMME FOR THE COMPARABILITY OF ANALYTICAL DATA WITHIN THE ICP FORESTS MONITORING PROGRAMME

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Many laboratories from almost 30 different European countries are producing hundreds of thousands of analytical results each year within the ICP Forests monitoring programme. They are analysing water, soil and foliage samples from Level I and Level II plots all over Europe (Table 6-1).

Table 6-1: Number of laboratories within ICP Forests during the FutMon programme 2009–2011

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 physical analysis	25
Total number of labs (some labs are analysing two or more sample types)	63

To guarantee the comparability of the analytical results between different laboratories in several countries and over time, a quality assurance (QA) programme is necessary with participation of all laboratories. The ICP Forests QA programme is based on three pillars:

- the use of harmonized, well-defined and documented analytical methods
- an internal quality control (QC) procedure within each lab
- an external QC programme coordinated by the monitoring programme organisers

To assure comparable results, first of all harmonized, well-defined and documented analytical methods are needed and have to be used by all laboratories. Therefore the expert panels and working groups of ICP Forests have compiled the “ICP Forests Manual on methods and criteria for harmonized sampling assessment, monitoring and analysis of the effect of air pollution on forests”, where all analytical reference methods have been described and published.

On the basis of this ICP Forests manual each participating laboratory has developed its own quality control system. Basics are:

- the use of the reference methods in the ICP Forests programme
- different quality checks like ion balance checks (for water samples), nitrogen balance checks (for water samples), comparison of measured and calculated conductivity (for water samples), sum checks (for soil samples) or plausible range checks (for all types of samples)
- repeated measurement of standard material
- the use of control charts for continuous controlling of analytical repeatability and instrument stability

Control charts are mandatory within the ICP Forests monitoring programme; the results have to be submitted to the ICP Forests database together with analytical data.

The main part of the external QC programme is the implementation of interlaboratory comparisons (ring tests) between all labs. At present the participation is mandatory; ring tests for water (every 2 years), soil (every 3 years) and plant (annualy) samples are organised regularly. So far 8 soil, 7 water and 18 foliar ring tests have been organised within the ICP Forests programme and the FutMon-project. For each parameter the different expert panels have determined tolerable limits (in percentage of the mean) to assess the ring tests. The percentage of non-tolerable results in ring tests can be seen as a degree of quality and comparability of results from participating labs.

When the ring test programmes have been started, the tolerable limits were higher than today. For comparing the ring tests over time all ring tests have been evaluated again on the basis of the latest tolerable limits.

The results of all water, soil and foliage ring tests within the last 20 years are shown in the following graphs. The development of the quality of the labs, but also the limitations due to different analytical methods can be seen from these results.

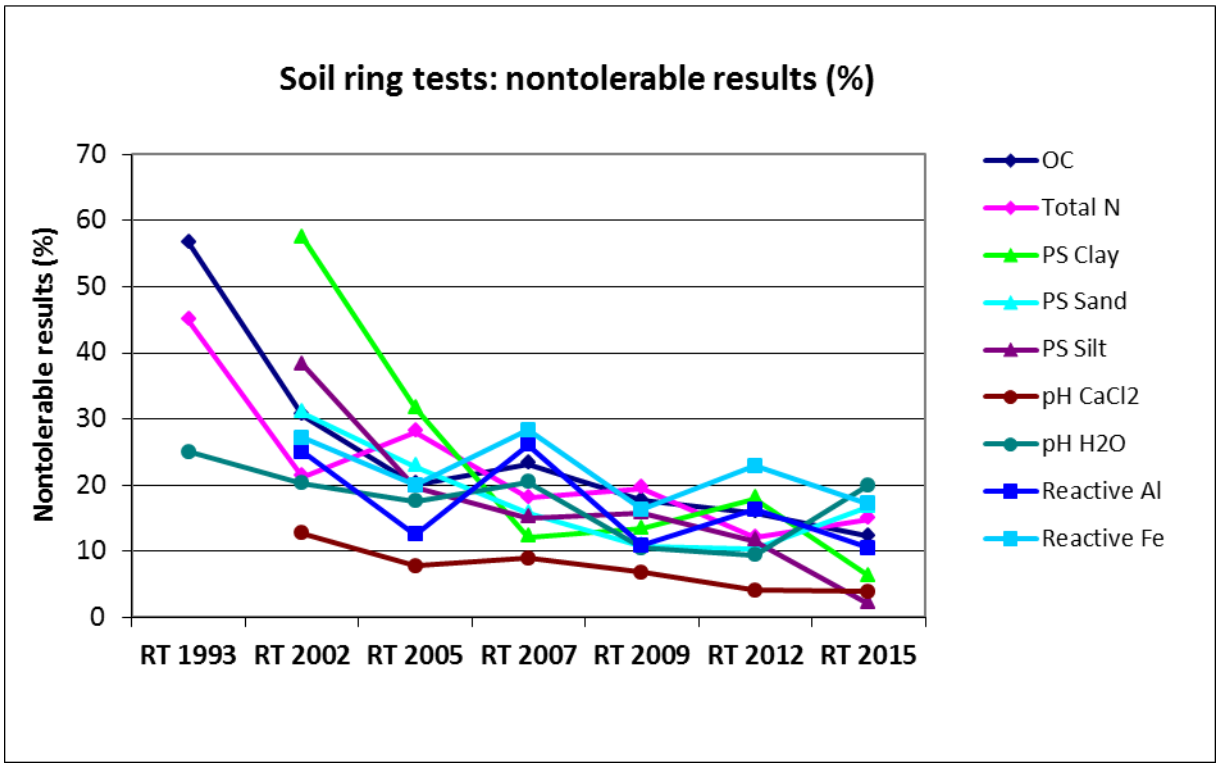

Figure 6-1a: Percentage of non-tolerable results in soil ring tests from 1993 to 2015 (parameters: OC = Organic Carbon, Total N = total nitrogen, PS Clay = particle size distribution clay, PS Sand = particle size distribution sand, PS Silt = particle size distribution silt, pH $CaCl_2$ = soil pH in 0.01 M $CaCl_2$, pH H_2O = soil pH in water, Reactive Fe = acid oxalate extractable iron, Reactive Al = acid oxalate extractable aluminium)

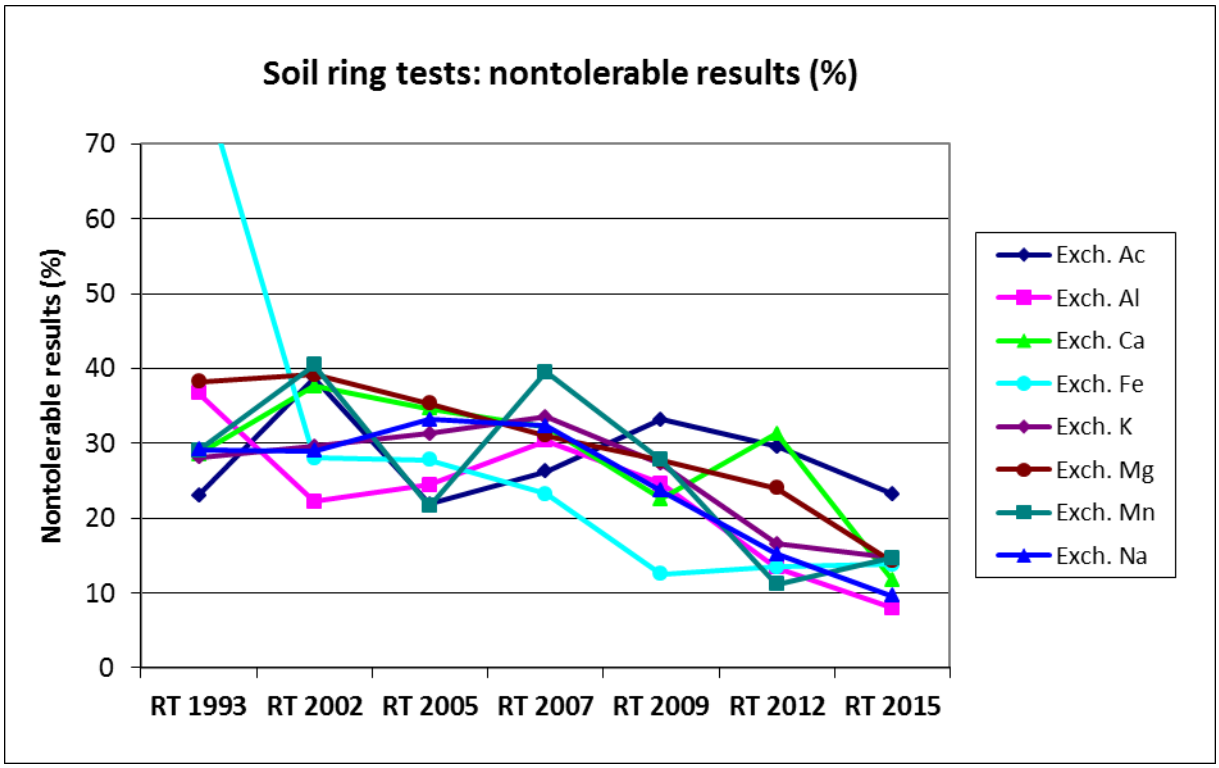

Figure 6-1b: Percentage of non-tolerable results in soil ring tests from 1993 to 2015 (parameters: Exchangeable cations and acidity; Ac = acidity, Al = aluminium, Ca = calcium, Fe = iron, K = potassium, Mg = magnesium, Mn = manganese, Na = sodium)

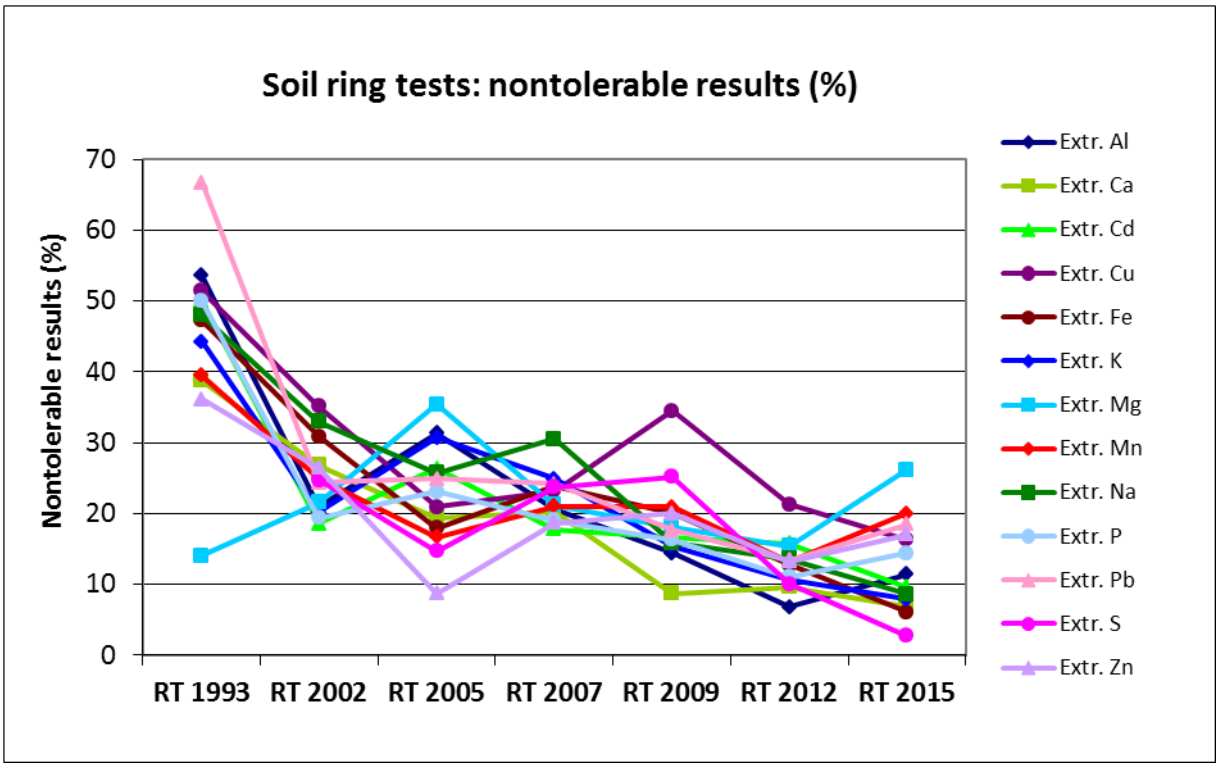

Figure 6-1c: Percentage of non-tolerable results in soil ring tests from 1993 to 2015 (parameters: aqua regia extractable elements; Al = aluminium, Ca = calcium, Cd = cadmium, Cu = copper, Fe = iron, K = potassium, Mg = magnesium, Mn = manganese, Na = sodium, P = phosphorus, Pb = lead, S = sulphur, Zn = zinc)

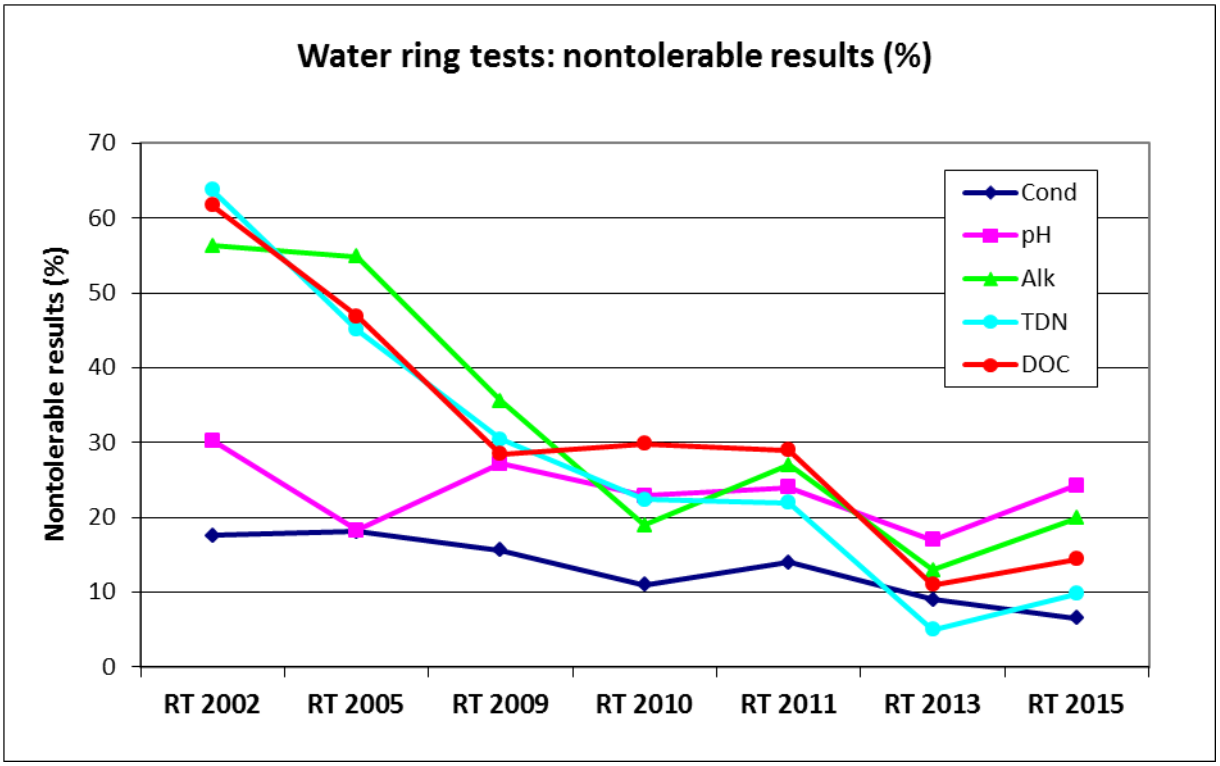

Figure 6-2a: Percentage of non-tolerable results in water ring tests from 2002 to 2015 (parameters: Cond = conductivity, pH, Alk = alkalinity, TDN = total dissolved nitrogen, DOC = dissolved organic carbon)

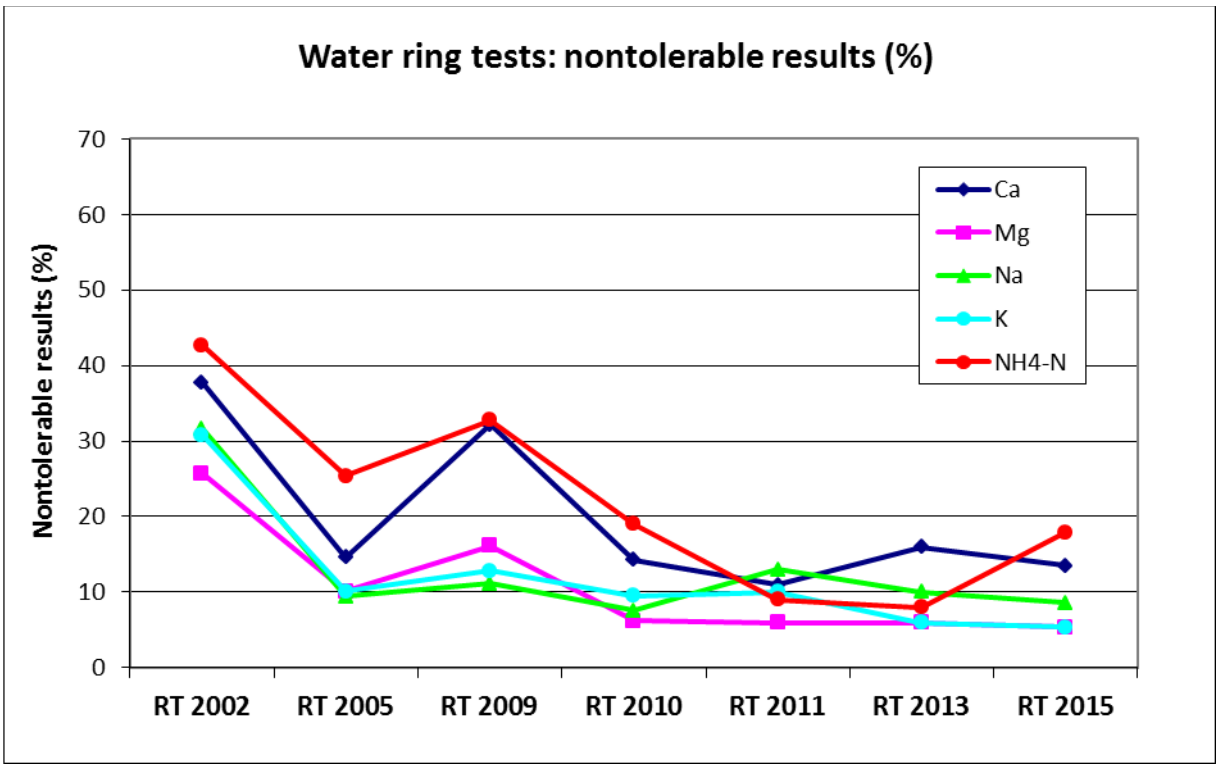

Figure 6-2b: Percentage of non-tolerable results in water ring tests from 2002 to 2015 (parameters: cations; Ca = calcium, Mg = magnesium, Na = sodium, K = potassium, NH4-N = ammonium-N)

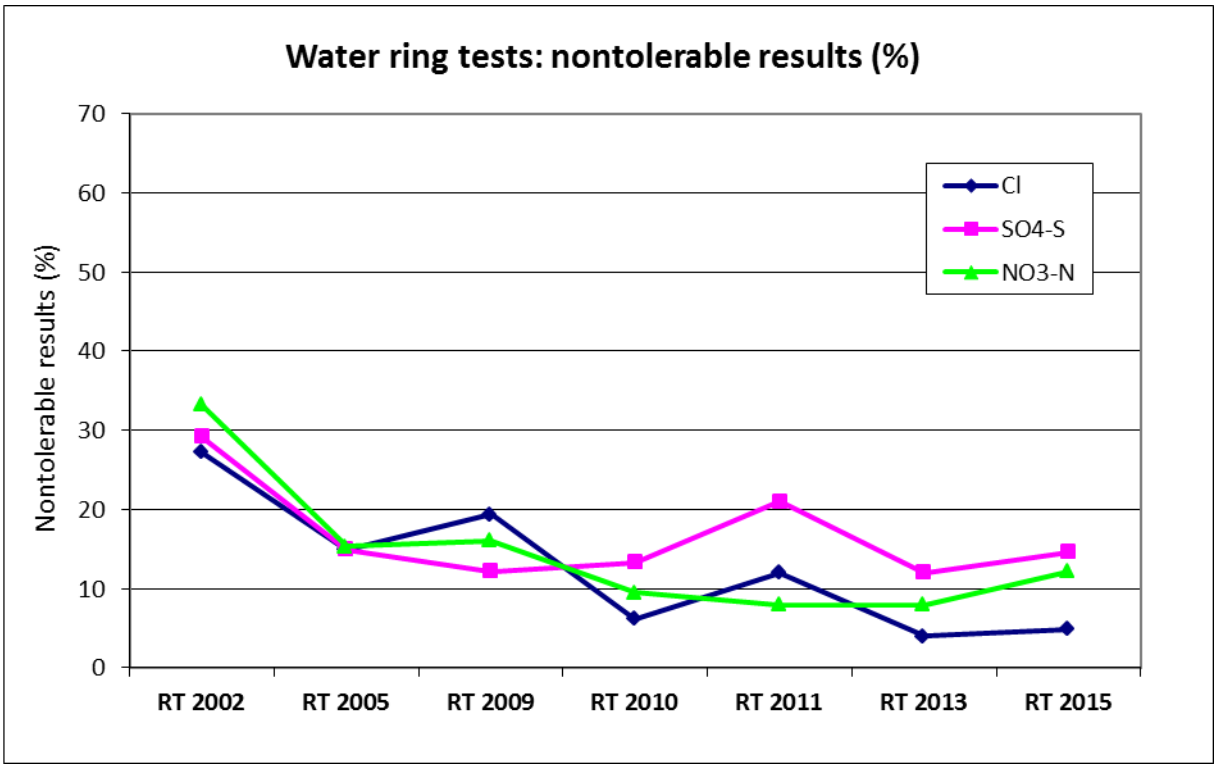

Figure 6-2c: Percentage of non-tolerable results in water ring tests from 2002 to 2015 (parameters: anions; Cl = chloride, SO4-S = sulphate-S, NO3-N = nitrate-N)

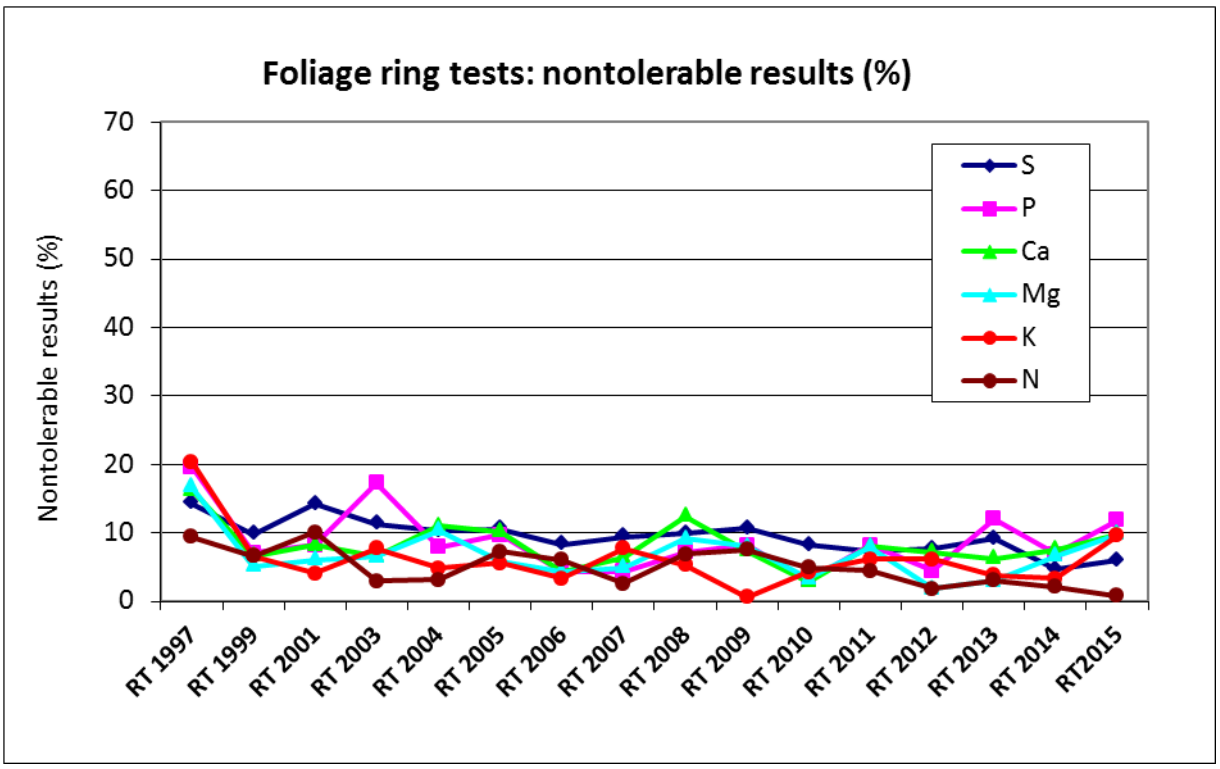

Figure 6-3: Percentage of non-tolerable results in foliage ring tests from 1997 to 2015 (parameters: S = sulphur, P = phosphorus, Ca = calcium, Mg =magnesium, K = potassium, N = nitrogen)

The best results have been achieved for the foliage ring tests. Since 2004 only 5 to 10% of the results for the main parameters have been non-tolerable. In soil ring tests the ratio of non-tolerable results started with 20 to 60% in 1993 and decreased to 10 to 20% for most of the parameters in 2015. For water samples the percentage of non-tolerable results decreased from 20 to 60% in 2002 to 5 to 15% in 2015.

The explanation could be found in the growing (or increasing) experience of the laboratories over time, especially for foliar analyses. Also the use of better equipment in many laboratories has led to better results.

One reason for the higher number of non-tolerable results for soil compared to the other matrices is the inhomogeneity of sieved soil samples which have to be used for some of the extracts. A second reason could be found in the two steps analysis (extraction/digestion and measurement), which can bring a higher variation than one step analysis used for water samples.

The participation in the regularly organised meetings of the heads of the labs, where many analytical problems have been discussed, has improved the laboratory quality and has led to better results in the ring tests during the last 10 years.