ASSESSMENT OF CHANGES IN THE PHOSPHORUS STATUS OF FOREST ECOSYSTEMS IN GERMANY – LITERATURE REVIEW AND ANALYSIS OF EXISTING DATA

A report to the German Federal Ministry of Food, Agriculture and Consumer Protection

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Forstliche
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CONTENTS

RECOMMENDATIONS

1. The results of this study suggest that P nutrition appears to be a substantial problem in German forests, and the problem is becoming more severe in the main coniferous species, *Picea abies* and *Pinus sylvestris*.

2. Foliar P values depend upon a number of site and stand factors and one time sampling of stands during national forest soil surveys (BZE) may provide general trends at the population level, but otherwise has limited site specific information.

3. Repeated sampling at individual sites, when carried out over for a long time (data available for 10 years period on 27 monitoring sites of Lower Saxony), provided trends in foliar P levels, showing that P concentrations declined in pine and spruce, but were stable in beech. However, the data base was too small, of regional nature and covered only a restricted number of site and soil characteristics to extrapolate the results to a national level for predictions in foliar P status of forest stands.

4. To assess, whether a decline in P nutrition is a widespread phenomenon, or restricted to certain regions or site types, there is a need to carry out further evaluation of temporal dynamics in foliar P concentrations for other Level II sites in additional German States. These analysis should also include litter fall data from Level II sites across different German States.

5. There is a need to monitor changes in the amount of soil P available to trees in the medium- to long-term.

6. Presently available pedo-transfer functions in the literature to predict labile soil P fractions from total soil P values were developed on restricted soil types and cannot be used at an extensive scale of nationwide forest soil inventories. Moreover, P fractions representing different chemical (organic and inorganic) forms of P would not indicate small scale changes in labile P. We therefore recommend that this area of investigation should not be pursued further.

7. Methods employed to determine available soil P in agriculture were developed for specific purposes to make recommendation regarding fertilizer application rates. Their usefulness to assess medium- to long-term changes in the P status of forest soils is highly questionable, as has been demonstrated in many long-term monitoring experiments. They can however be employed to show comparative and short term changes in soil P status after silvicultural treatments (fertilization, fire, slash management). We do not recommend their use for soil samples from the nationwide forest soil inventory (BZE).

8. We recommend to develop suitable and robust techniques to assess the amount of soil P which would become available to trees through desorption processes in the medium to long term. For this purpose, P desorption isotherms (sequential extraction procedures) using anion based extractants on a representative set of samples (from the BZE collective) are suggested. This part of method development would require intensive research efforts.

9. In order to apply the above method to all the BZE samples, two alternatives are available: (a) To develop suitable pedo-transfer functions to assess P desorption parameters. This may require additional analysis of the soil samples causing additional cost and the need for substantial financial resources. (b) To use near infrared spectroscopy methods to develop suitable predictive models for determining parameters of P desorption isotherms. We recommend the latter because of its simplicity, low cost, and versatility, which makes it an appropriate and usefulness technique for a very large sample collective (grid samples from nationwide forest soil inventory study).

EXECUTIVE SUMMARY

1. The first nationwide forest soil survey, BZE1, included an assessment of tree nutrition on 1014 sites. For the assessment, concentrations of nutrients in the foliage and total amounts in the litter layer and soil samples were determined. In the report by BMELF (1997), it was noted that a significant number of forest sites had low to very low P levels in the foliage. The percent of sites for the different tree species which had low to very low P concentrations in the foliage were (in brackets are the critical limits used) : Norway spruce (*Picea abies*) – 59 % (<1.2 mg P/g), Scots pine (*Pinus sylvestris*) – 58 % (<1.2 mg P/g), European beech (*Fagus sylvatica*) – 58 % (<1.3 mg P/g). These foliar P concentrations indicated that there might be a problem in P nutrition across many sites, though none of the bedrock types or any other site parameter could be identified as specifically related to foliar P concentrations in the different species. Before this suggested wide spread P limitation can be accepted, it was important to examine whether the critical values used to delineate the different categories of P nutrition in the different species were appropriate, or whether these values might have been too high, thus resulting in a great proportion of trees with deficient P nutrition. The validity of the critical values used was thus tested by evaluating the information from the literature.

2. For this purpose the critical P ranges used were compared with a very large data set which was obtained by considering the relationship between tree growth responses and foliar nutrient concentrations. This data set was originally assembled by van den Burg (1985, 1990) based on a literature review, and it was subsequently digitised. Data for the four main tree species, Norway spruce, Scots pine, European beech and oak were included in our analysis. Five different nutrition classes describing P status in the tree were defined. Classes were: a) obvious deficiency symptoms, b) deficiency with positive effect to fertilisation, c) normal nutrition, growth average to good, no or only small response to fertilisation, d) optimal nutrition, e) luxury consumption, higher than normal, but not toxic. The grouping of foliar P concentrations of the different species according to these nutrition ranges showed considerable overlap in foliar P values between the different nutrition categories. However, the comparison of the critical P-values used to define deficiency ranges in the nationwide forest soil survey with the ranges provided by van den Burg showed that the upper limits of the classes indicating low and very low P concentrations were not set too high for the three tree species, Norway spruce, Scots pine, and European beech. The comparison revealed further that the ranges for foliar P were most fitting for Scots pine. The ranges may have been set even at too low concentrations for young spruce stands.

From this it can be concluded that the serious situation in relation to P nutrition of German forests is described adequately.

3. Due to many plant and site factors outlined in the review, one time foliage sampling is not considered adequate to assess the P status of individual sites. Therefore a data set from the intensive monitoring sites from Lower Saxony, where repeated foliage samples were taken, was included in the analysis. Temporal dynamics in P concentrations in the current year needles and mature foliage of 27 long-term monitoring plots in Lower Saxony (Level II sites), for which annual or biannual P-concentration values existed, were analysed for a ten year period using mixed linear models. Foliar P concentrations at these sites revealed a decline in P concentrations across all sites for spruce and pine over a ten-year period from the mid 90s to 2004 or 2005. The decline over a ten-year period equated to a reduction in P concentrations in the youngest needles of 0.06 mg g^{-1} in spruce and 0.15 mg g^{-1} in pine. In both species, the decline was more pronounced in older needles. For beech, no decline in P concentrations could be observed. Similar results of a decrease in P foliage levels of periodically collected samples during the last 20 years have been reported in the literature from different parts of Europe and North America as described in detail in the review.

4. In order to assess the general validity of the results reported above for Lower Saxony, there is a need to carry out further evaluations for additional Level II sites covering a wider range of site conditions. It is therefore recommended that additional analysis be carried out to evaluate data from Level II sites across different German States.

5. A number of reasons have been provided in the reviewed literature for this decreasing trend in foliar P values. In most cases, this decreasing trend has been related to high inputs of N and acidity to forest stands. These changes in N inputs and soil acidity can affect the P status of forest ecosystems in a number of ways: (a) High N inputs have resulted in higher growth rates, thereby causing additional demand for P uptake and causing increased levels of P retention in the woody components. This would decrease the fraction of P turnover. (b) High N inputs may decrease the rate of litter decomposition and thereby the associated organic P mineralisation. This would further decrease the amount of P turnover present in the recycled organic matter. (c) P uptake may be impaired due to high soil acidity and associated reduction in fine-root and mycorrhizal activity. (d) Under high acidity conditions, the amount of easily desorbed P may decrease due to an increase in P fixation by soils. (e) High N inputs usually causes high nitrate levels in soils which may compete with the uptake of phosphate (anion competition). (f)

High N inputs and uptake by plants may cause an imbalance of N to P ratios, affecting plant vitality. The review provides examples for the different possible processes described here. To what extent the different mechanisms captured by these hypotheses are responsible for the current situation for different sites and tree species remains unknown.

6. To analyse whether the variation in foliar P concentrations, soil P content, or forest floor P content may be explained by the large set of independent parameters determined in the nationwide forest soil survey, a regression tree approach was used. This data mining approach is often used to generate hypotheses from large data sets with a multitude of independent variables. The explorative analysis of the nationwide inventory (BZE1) data set did not provide an explanation for the variation in foliar P levels. The absence of any pattern in relation to soil P was assigned to the lack of sensitive methods to determine long term changes in plant-available P content of forest soils.

7. The exploratory analysis of the data set indicated that P content in forest floors was more closely related to their N content than to the C content, which suggests that P accumulation in the forest floor may not be a simple function of organic matter accumulation, but may be related to the accumulation of organic matter with lower C/N ratios, such as in OH layers.

8. Analysis of total P in soils (as was done in the samples from the BZE I) does not relate to the amount of plant available P in soils. Total P occurs in many organic and inorganic forms in forest soils. Labile and mineralisable fractions can be described using chemical extraction procedures but their availability in forest soils is not appropriately defined. Moreover, chemical extraction procedures are highly resource intensive and cannot be employed directly to national survey samples. Given appropriate pedo-transfer functions which may involve analysis of forest soils for total P and other easy to measure parameters, it may be possible to assess the amount of different fractions of P in soils. However, the pedo-transfer functions developed so far are based on a limited set of samples from forest sites and they appear to be site and bedrock specific. Presently available pedo-transfer functions cannot be used to determine P fractions in a wide range of samples collected on a large grid based inventory. Due to high variation in estimating the pedo-transfer functions, the small changes expected in the estimated amount of labile P fractions may not be detectable. Therefore the use of pedo-transfer functions to determine the amount of P fractions in forest soils is unlikely to be a useful assessment technique.

9. Many chemical solutions have been proposed to extract an amount of potentially available P in soils. Soil test methods have been basically developed to assess the nutrient levels in the soil at the time of sowing a crop so that a fertiliser recommendation could be made. Details on the methods to determine available P in soils, especially for forest soils have been provided in this review. Some of these methods have been used for forest soils, mostly to describe the P status in comparative situations, or to describe the immediate effect of a fertilizer or other silvicultural treatment (fire, management of harvesting slash, windrowing, addition of thinning slash). Absolute available soil P values obtained by any of the soil test methods have not been calibrated for growth or other responses of the forest and thus cannot be used to describe the long-term P supplying status of the soils. Their use for assessing medium to long-term changes of P in forest soils cannot be recommended.

10. Most methods of soil P assessment provide static values without any consideration of kinetics involved in the desorption of soil P. In order to include this factor of kinetics, different approaches will be required. We therefore recommend that a method involving P desorption isotherms (sequential extraction procedures) using anion based extractants should be developed. For that a representative set of samples (from the BZE collective) should be selected. This technique will assess the amount of soil P which would become available to trees through desorption processes in the medium- to long-term periods This part of method development would require intensive research efforts.

11. In order to apply the above method to all the BZE samples, two alternatives are available: (a) To develop suitable pedo-transfer functions to assess P desorption parameters. This may require additional analysis of the soil samples causing additional cost and the need for research resources. (b) To use near infrared spectroscopic methods to develop suitable predictive models to determine parameters of P desorption isotherms. We recommend the second of the two approaches because of its simplicity, low cost, and versatility which makes it an appropriate and usefulness technique for a huge collective set of samples (grid samples from BZE study).

12. It is recommended that a series of sites, out of those monitored for the BZE 2, should be selected which differ in their effect of acidity and N inputs based on regional locations and representing different tree species and bedrock material. These sites should be periodically sampled for the foliar analysis in future and the soil samples should be included in the sequential extraction procedure, mentioned above.

13. In order to assess the effects of future management scenarios (e.g. removal of crown wood for bioenergy generation), expansion factors for the amount of P in different tree compartments need to be developed.

1 INTRODUCTION

The second nationwide forest soil inventory (BZE-II) provides the basis for assessing any changes in forest soil characteristics, which may have occurred for example due to atmospheric depositions on the forests, especially since the last BZE-I was carried out more than 10 years ago. Despite the importance of adequate P supply for plant growth and its possible changes, no specific efforts were made during the first survey to describe P status of the forest ecosystems. In the first BZE study, two parameters which provided some information on P status, were however included – concentration of P in the foliage samples and content of P in the acid digests (using HNO_3 or aqua regia reagents) of soil samples. However, based on these two parameters only, it is very difficult to assess the ecosystem P status. Many plant and soil factors determine P concentration in the foliage causing significant annual variation, which may limit the use of foliar P concentrations as a defined parameter of any change in P status of forest ecosystems. The amount of total P in soils as determined by acid digests, commonly gives the total amount of P minus some amount of P that is not released by the acid treatment (probably bound in silicate structures). This soil P value (total P) is commonly very high compared to the amount that undergoes transformations and is involved in the uptake processes. Such total P values are therefore only useful to describe the soil characteristics but not to characterise the availability of P to plants or to provide the basis for documenting changes in soil P.

The status of P in soils and plants may have undergone changes during recent years. We propose here three hypotheses describing any change in P levels in forest ecosystems of Germany.

- The availability of P in soils has decreased through further acidification of forest soils. At low pH, P availability is reduced in soil through its fixation by Al and Fe oxides. At low pH, activity of fine-roots and mycorrhiza may also be impaired.
- Increasing N contents in forest litter (as a result of ongoing high atmospheric N depositions) has reduced the mineralization of organic matter in the late stages of decomposition, thus leading to a stabilisation of organic matter in forest floors and mineral soils. Decrease in organic matter mineralization may have reduced the availability of P from organic sources.
- An increase in growing stock in German forests may have immobilized P in tree biomass, diluting P in the aboveground biomass or reducing its amount of turnover and availability.

Below, these hypotheses are being discussed on the basis of a critical literature review including data from the long-term studies. Moreover, there is very little compiled information on the use of other plant parts (leaf or needle litter, fine roots) to assess the P nutritional status of trees, which may be used as a better indicator. There is very little known information about the consequences on plant growth, decomposer activity and other ecosystem functions for various P levels in forest ecosystems. The review will consider some of them by including relevant data from the literature.

1.1 Changes in P supply in forest soils due to acidifying inputs.

Acidifying inputs can decrease the plant phosphorus status (normally observed in the foliage samples), which is related to acidification and Al toxicity causing a decrease in P supply in soils or reduced P uptake capacity. A number of soil processes may be associated to such changes in P availability and uptake through changes in vitality of the mycorrhizal fungi. Several studies conducted in temperate forests have presented evidence of phosphorus limitation in forest stands, where the availability of nitrogen was high (Binkley and Hogberg 1997; Harrison et al. 1999; Corbin et al. 2003; Brown and Courtin 2003). High N levels may result from natural or man-made atmospheric inputs or from fertilizer additions for experimental or management reasons.

(a) Natural or man-made inputs of acidifying substances.

Nihlgard (1985) proposed the hypothesis that forests will run into nutrient imbalances because of increased N deposition. Commonly N/P ratios in the foliage samples are used to assess the imbalances in P status. An increase in N/P ratios indicates an imbalance owing to low P uptake under high N input conditions. Linder (1995) suggested that the ratios between nutrients are much more important for judging the nutrient status than the concentrations themselves as the concentrations are influenced by the amount of non-structural carbohydrates in the leaves. Deficiencies of P in forest stands receiving high levels of acidifying atmospheric inputs have been reported in North America and Europe. For example, Bernier and Brazeau (1988) reported P deficiencies in sugar maple stands in Quebec and Mohren et al. (1986) and Houdijk and Roelofs (1993) in forests in the Netherlands, especially in Douglas fir stands. Harrison et al. (1999) reported that in the UK the poor canopy condition was related to P stress in beech, Scots pine and Sitka spruce stands. Polle et al. (1992) reported P deficiency in needles of three Norway spruce stands growing at three

altitudes in the calcareous Alps of Bavaria. Thomas and Büttner (1998) investigated foliar P contents in 18 mature stands of sessile (*Quercus petraea*) or pedunculate oak (*Q. robur*) in NW Germany, crown leaf loss had occurred. Most *Q. petraea* stands tended to have a P-deficiency. Salih and Andersson (1999) noted that *Picea abies* stands of SW Sweden were growth-limited by N and P and applications of N induced P and K deficiencies. Rodenkirchen (1998) observed severe P deficiency in young Douglas fir stands growing on podzols in the Black Forest area.

Some of the case studies are given below:

- **France**

  In a study on changes in foliar nutrient levels, Duquesnay et al. (2000) sampled 118 beech stands in 1996-97 and compared the analysed values with those obtained in 1969-71. Between the two sampling periods, concentrations of foliar N increased (+12%), whereas that of P, Mg and Ca decreased by 23, 38, and 16%, respectively. Ratios of N/P and N/Mg increased by 42% and 77%, respectively. This decrease in concentrations of P and cations was particularly marked for trees growing on acidic soils. They assigned this decrease in P concentration in the foliage of beech trees to increasing atmospheric CO_2 concentrations and acidification of forest soils. In a parallel study where the foliage concentrations of beech stands were monitored continuously for 5 years, a decrease in P levels was observed, which resulted in an increase in N/P ratios.

- **Switzerland**

  Flückiger and Braun (1998, 1999) reported an increase in nitrogen concentrations and a continuous decrease in P concentrations in the beech and spruce foliage, when these were analysed every 3 to 4 years between 1984 and 1995. The values of P decreased from 1.25 mg P/g in 1984 to 1.08 in 1995 in 51 beech stands in northwestern Switzerland, with an accompanying increase in the N to P ratios from 18.6 to 25.0. In one-year old needles of Norway spruce collected periodically from 15 different sites, P concentrations decreased from 1.07 mg P/g in 1984 to 0.90 in 1995 with N/P ratios increasing from 14.0 to 16.4 for the respective years. These reductions in P levels were associated with high inputs of N and an increase in soil acidity.

- **Netherlands**

  Mohren et al. (1986) reported that phosphorus levels in a Dutch Douglas fir stand exposed to increased N deposition were in the deficient range. Houdijk and Roelofs (1993) reported a significantly lower P concentrations in Douglas fir and pine forests in Netherlands, which were related to increased atmospheric N inputs. At most sites, foliage levels of P were in the deficient range especially that of

Douglas fir which suffered from absolute and relative P deficiencies. According to Van den Burg (1990) the increasing N deposition in the south-eastern part of the Netherlands is largely responsible for the present absolute and relative phosphorus deficiencies in current needles of Douglas firs, whereas in pine needles the calcium and absolute and relative magnesium contents were mostly affected. This contrasting behaviour among Douglas fir and pines was related to the preference of nitrate uptake by Douglas fir suppressing the uptake of P.

- **U.K.**

  Harrison et al. (1999) studied the effects of pollutants on beech, Scots pine and Sitka spruce stands growing on a range of comparable soils in the UK. They investigated the canopy conditions of the stands in relation to the possible role of P limitation. Use of a root bioassay and a resin-extraction procedure to assess the availability of P in surface soil indicated that a higher level of P stress in stands with the thinner canopy was observed in eight out of the nine paired stands of Sitka spruce, Scots pine and beech suggesting the need to monitor the acid inputs on affected plots;

- **Canada**

  For an area in central Ontario with high atmospheric N depositions, Grawdoski and Thomas (2006) reported that the annual stem growth of sugar maple (last 5 year average) was limited by available P levels measured by using the Bray 1 method. Variations in this measure of P availability in the surface soils explained 74% of variance in growth. Low P values were associated with low soil pH in the root zone.

- **Germany**

  Polle et al. (1992) found that foliar P in 3 Norway spruce stands growing at different altitudes in calcareous Alps of Bavaria were in the deficient range. Thomas and Büttner (1998) reported limiting values of P in the leaves of *Quercus petraea*. Heinsdorf and Branse (2002) followed element concentrations in pine stands growing in Brandenburg, Germany, between 1964 and 1999 and found no clear decrease of P in needles. Similarly Mellet et al. (2004) in their review of foliar concentrations in the context of the RECOGNITION project found no clear evidence of P decrease in the foliage of conifer stands, especially that of pine.

(b)   Field and laboratory studies under controlled conditions.

There are a number of case studies in the literature, where acidifying substances were applied to forests either under field conditions or under controlled laboratory conditions in order to determine the changes in the nutrition of trees and/or soil P

availability and supply. The acidifying substances were either applied to the canopy or to the soil. The acidifying substances included commonly sulphuric acid, ammonium or other forms of N and sulphur. Many of those studies point to changes in the phosphorus status of plants and soils, some of them from different countries are included below:

- In Scotland, Carreira et al. (1997) reported the effects of acid-misting applied to a Sitka spruce (*Picea sitchensis* (Bong.) Carr) canopy at Glencorse on soil P availability, pH, and tree P nutrition. The acid mist treatments (H_2SO_4 plus NH_4NO_3 at pH 2.5 at two doses) had been found (Sheppard et al. 1995) to induce a significant ($p < 0.05$) reduction in stem diameter growth when compared to control trees. However no visible injury symptoms to the tree canopy were observed. Acid-mist treatments significantly reduced the water-soluble P content in forest litter, labile inorganic P (resin-extractable) and phosphate concentrations in equilibrium soil solution ($p < 0.01$) in the surface soil. The labile organic P content and P sorption capacity of the surface soil however were increased compared to soils under control trees. For assessing plant P status, a root bioassay technique was used, which provides a measure of the nutrient demand of the tree relative to its supply from the soil (Harrison and Helliwell 1979). The results indicated clearly that acid-misted trees were under P nutritional stress (Carreira et al. 1997). Subsequent research has clearly linked such nutritional stress to marked changes in the patterns of P availability and P cycling induced by soil acidification.
- In Denmark, Gundersen (1998) observed critically low P concentrations (0.6-1 mg P g-1) in a mature Norway spruce plantation at Klosterhede, which received 35 kg N ha^{-1} as ammonium nitrate annually in addition to the ambient N deposition of 15-20 kg N ha^{-1} yr^{-1}. These low foliage P values were associated to low activity of fine roots and mycorrhizae due to high N stress. The effect was however enhanced due to drought conditions that occurred at the site.

In a number of studies on pine and spruce trees in Germany, conflicting results of changes in foliar phosphorus concentrations were reported. For example Sauter (1991) reported an increase in P levels in the foliage with an increase in the atmospheric inputs. A number of other studies found no change (Prietzel et al. 1997, Heinsdorf and Branse 2002). It may however be noted that in individual years large deviations from the mean of longer periods have frequently been reported for foliar concentrations of several minerals (Sauter 1991, Prietzel et al. 1997, Stefan et al. 1997, Heinsdorf and Branse 2002, Mellet et al. 2004), which may be one of the main

reasons of such results. Another reason may be due to the special characteristics of the investigated sites.

1.2 Decrease in the decomposition of organically bound P and retention in the litterlayer under forests.

Meiwes et al. (2002) described the changes which have occurred during the last three decades in the litter layer of a beech and a spruce stand in the Solling area, Germany. The periodical sampling on the two sites indicated that the weight of litter increased from 48 to 111 t ha^{-1} in the spruce and from 34 to 56 t ha^{-1} in the beech stand. Using a regression model an annual increase was calculated to be 999 kg C ha^{-1}, 42 kg N ha^{-1}, 1.8 kg P ha^{-1} and 3.2 kg Ca ha^{-1} for the spruce site and a smaller increase of 347 kg C ha^{-1} a^{-1}, 21 kg N ha^{-1} and 2.5 kg Ca ha^{-1} for the beech stand. However, the increase in P was not statistically significant for the beech site, which may be related to a number of factors including the high variability in the amount of P due to irregular seed mast years in the periodically taken litter samples. If the total amounts of P in the annual litter fall are considered, the amount of P retained in the litter layer is a significant fraction of the total. This fraction is thus removed from the cycling fraction, and may affect the P status of spruce (and also of beech) stands.

Meiwes et al. (2002) suggested three reasons for the decrease in decomposition of soil organic matter in the litter layer causing its continual accumulation which are directly related to high atmospheric deposition of acidifying substances and N: (a) changes in the microbial activity as shown by the reduced CO_2 evolution from the litter layer (Jandl and Sletten 1999, Moloney et al. 1983, Miltner and Zech 1997, Schinner and Sonnleitner 1997); (b) reduction in decomposition processes due to heavy metal toxicities, especially to soil fauna (von Tyler 1992, Wolters 1991, Wolters and Schaefer 1994); (c) reduced decomposition of lignin components in litter owing to complexation with N (Berg 2000, Berg and Matzner 1997, Berg and McClaugerthy 2003).

Berg and McClaugherty (2003) postulated the formation of less degradable lignin compounds under high initial N levels in the litter may result from two reaction mechanisms. (a) There may be a reduction in the formation of lignolytic enzymes, and (b) chemical changes may occur, where lignin incorporates N and undergoes condensation reactions. Berg (2000) reported that a positive relationship existed between retardation in the decomposition of litter and its N content. An increase in N

content from 4 to 13 mg g^{-1} increased the fraction of non-degradable litter component from about 10% to 50 %. In the samples collected on a transect from Sweden to Italy, Persson et al. (2000) showed that the rate of CO_2 development decreased with an increase in N content or with narrowing of C:N ratios of the litter. Yanai et al. (2001) conclude in their literature review that in northern coniferous forests N fertilization resulted in higher forest floor contents due to lower decomposition rates. Olsson et al. (2005) demonstrated that fertilization can reduce the autotrophic and heterotrophic respiration in boreal forest ecosystems and Fog (1988) reported a reduction in decomposition of organic matter after N fertilization.

Pare and Barnier (1989a) investigated the origin of phosphorus (P) deficiency previously observed in declining sugar maple (*Acer saccharum* Marsh.) at several sites of the Quebec Appalachians. The investigation included litter layers and soils originating from 10 maple stands with foliar P concentrations ranging from 0.85 to 2.36 mg • g^{-1}. It was concluded that under the conditions now prevailing in the Quebec Appalachians, the nature of the humus form may have a major influence on P nutrition of trees. Stands growing on soils with a moderately acid Ah horizon (mull) exhibited low foliar P concentrations, while those growing on soils associated with a mor humus had adequate P nutrition.

In a study on the soil nutrient status of 50 stands of *Fagus sylvatica* in Lower Saxony, Germany, which occurred on 13 acidic to basic bedrock types (including limestone, sand, claystone, sandstone, loess and glacial deposit) Leuschner et al. (2006) identified the amount of exchangeable Al in the mineral soil as the key factor controlling the accumulation of C in the litter layer (OL, OF, OH). With increasing acidity in soils and increasing N:P ratios (19 to 59 mol mol-1) in the litter layer from basic to acidic soils, a possible P limitation in beech forests might occur.

1.3   Changes in the growth patterns of trees

Owing to high atmospheric inputs of N, growth patterns in trees may have changed leading to high productivity of woody components (Spiecker et al. 1996). This would increase the retention of P by woody components. Normally the annual values of P retention will be small but considering it a long-term process significant amounts of labile P may be removed from the cycling fractions of P. Such changes may decrease the amount of P turnover through aboveground and belowground litterfall.

The frequency and the amount of mast production has increased in recent decades probably due to increased N atmospheric inputs and high vitality of trees. This may increase the amount of P required for the growth in beech forests, which may be 2-3 times the amount of P required during mast years when compared to non-mast years. Bauhus (1994) reported for a beech stand in the Solling area that the concentration of P in seeds (4.8 mg g^{-1}) was more than 5 times that in leaves (0.9 mg g^{-1}).

That phosphorus can become growth limiting during vegetation succession was shown conclusively by Wardle et al. (2004) who studied six long-term chronosequences, in Australia, Sweden, Alaska, Hawaii, and New Zealand. During succession, ecosystem development occurred; but in the long-term absence of catastrophic disturbance, a decline phase eventually would follow. The decline phase was associated with a reduction in tree basal area and an increase in the substrate nitrogen–to-phosphorus ratio (in the litter layer), indicating increasing phosphorus limitation over time. These changes were often associated with reductions in litter decomposition rates, phosphorus release from litter, and biomass and activity of decomposer microbes.

1.4   Possible causal mechanisms of decrease in P status of trees

A number of causal mechanisms have been proposed to explain the association between the appearance of P deficiencies in forest trees receiving high atmospheric inputs of acids and nitrogen. Some of these are given below: (i) Soil acidification is hypothesised to cause an increase in the inorganic P sorption capacity of the soils and concomitant decreases in P solubility (Van Breemen et al., 1983; Pare´ and Bernier 1989b). (ii) Soil acidification may reduce the rate of organic P mineralisation (Harrison 1982; Pare´ and Bernier 1989a). (iii) High atmospheric N inputs may enhance the tree demand for other nutrients (especially P), potentially resulting in nutritional imbalances (Nihlgard 1985; Binkley et al. 1989). (iv) P uptake may be reduced due to a decrease in fine roots and mycorrhizal associations (Arnebrant and Soderstrom 1992, Gundersen 1998) due to high acidity and high levels of N in soils. However, the establishment of clear linkages between observed P deficiency symptoms and any of the proposed causal mechanisms has been difficult in the above-cited, field-based studies describing 'natural' variability.

2. PHOSPHORUS IN PLANT COMPONENTS

2.1   P in plants: role, uptake and distribution in trees

Phosphorus is an essential element required for the energy metabolism in plants. Phosphate esters act as energy carriers in various metabolic pathways. It is a constituent of nucleic acids and membranes. Phospholipids play an important role in integrity and functioning of membranes. Phosphorylation and dephosphorylation of proteins are crucial for signal-transduction pathways in plants. Phosphate homeostasis in the chloroplast regulates the transport of phosphorylated sugars across the membrane and synthesis of starch. Major biochemical processes such as photosynthesis and respiration are activated by inorganic phosphate (Pi) or its organic derivatives. Many recent reviews give comprehensive information on this subject (Abel et al. 2002; Marschner 1995; Ryan et al. 2001; Smith et al. 2003).

Phosphorus is taken up by plant roots as phosphate anions (Pi), the exact ionic form is however not well known, but for acid soils it is considered H_2PO_4. P occurs in a number of inorganic and organic forms in the soil. It also occurs in different ionic species in the inorganic forms depending upon solution pH and dissociation constants of various forms. In a recent review Raghothama & Karthikeyan (2005) observed that acquisition of P by plant roots involved high-affinity Pi transporters as entry points for Pi in the roots. Plants show the ability to adapt and thrive under phosphate limiting conditions by regulating at the level of transcription of high-affinity phosphate transporters, by activating biochemical mechanisms (release of organic acids and phosphatases) and by altering root morphology and mycorrhizal symbiosis that lead to increased acquisition of phosphate from both inorganic and organic phosphorus sources in the soil (Harrison 1999, Franco-Zorrilla et al., 2004, Lynch 1995, Schachtman et al. 1998, Vance et al. 2003)

The concentrations of P are highest in the growing and most active parts such as leaves and fine roots. The fractions of total P in trees may range from 10-44% in leaves and 9-35% in roots respectively (van den Driessche 1984, Khanna and Ulrich 1991). But the highest concentrations of P are probably found in the fruit and seed components. For example, the mean P concentration (from 1990-2002) in the leaves of a beech stand at Zierenberg was 1.33 mg P/kg and that of fruiting components which included seeds and pods was 1.66 mg P/kg (Khanna et al. personal communication). In common stands the highest fraction of the total amount of P is

usually present in the leaves. In very old stands, woody components may have accumulated the highest amount of P among all the other tree components. The annual accumulation of P was highest in needles and living branches of spruce after application of P in fertilizer (Nielsen and Wiklund 1995).

Given the function of P in leaves and needles and the importance of foliage as a P reservoir in forest ecosystems, the use of Critical Ranges of P concentrations in the foliage is the most commonly used method of assessing the P status of forest trees. However, there are many limitations to its use. The most important one is that the critical range values do not represent a unique P state of plants but vary significantly among tree species, tree age, foliage age, seasons, and are influenced by water or other stresses and many other site (chemical and biological processes) and plant factors (retranslocation, other nutrient levels). In addition, there is often no well defined reference status of tree condition, which can be described as optimum for given site conditions for assessing the foliar data. Many values are commonly obtained from controlled nutrition experiments, or those which show evident problems in growth. Moreover, there is clear evidence that element concentrations alone do not fully characterize element status in plants and other additional parameters such as the element content and growth response. In addition to the Critical Range (CR) concept, other concepts such as Deviation from Optimal Percentage, Nutrient–Element Balance, Diagnosis and Recommendation Integrated System (DRIS) and the Compositional Nutrient Diagnosis (CND) have been usefully employed to assess the mineral composition of tree foliage. Because of its simplicity, wide acceptance and common use we shall use, despite its limitations, the Critical Range method for this review. The other much more complex tools such as DRIS have not been used for the important central European tree species across a range of site conditions.

Data on nutrient levels in the foliage have been compiled by a number of authors (Hüttl 1992, Krauß and Heinsdorf 2005, van den Burg 1986, 1990). This review will focus on the four most important tree species by area in Germany, *Picea abies* (spruce), *Pinus sylvestris* (pine), *Fagus sylvatica* (beech) and *Quercus sp.* (oak) and includes various factors which determine the foliar P levels in these species.

2.2 Commonly used critical P-values for tree nutrition

Different values are used in the literature to describe the nutritional status of foliage.

The foliage chemistry data are commonly grouped into ranges to define: (a) deficiency (low to very low values) where either the plants show clear deficiency symptoms, stunted growth or when supplied with the nutrient show growth or other plant responses, (b) sufficient nutrient supply (optimum values) where the amount of nutrient is adequate for plant growth and the growth rates are satisfactory or good and do not respond or only to a small extent to fertilisation, (c) high nutrient supply (luxury consumption) where other nutrients may be limiting the plant growth, and (d) very high values leading to toxicity and reduction in growth. Of interest for this review are the first three groups of values (Table 1), as the very high values are not expected for P under natural site conditions in German forests. Krauß and Heinsdorf (2005) defined foliar data in five classes: 1-highly deficient with highly restricted growth, 2- deficient with low to medium growth rates, 3 –sufficient to optimal with good to very good growth rate, 4 – luxury with still very good growth but unstable, 5 – very high with depression in growth in some cases. The last group occurs rarely in nature, so for this review, we are presenting the critical P values of the remaining groups for comparative purposes in Table 1. The values for each group are given as a range with mean values in brackets. To interpret the differences between the nutritional ranges provided by the different authors, it is important to consider how they have been derived. For example Krauß and Heinsdorf (2005) pooled all available data for each species and divided the whole range of values into equidistant classes without considering possible different responses of young or mature stands. In contrast, van den Burg (1985, 1990) differentiated between young and old stands and defined the nutritional ranges not on the basis of statistical distributions but in terms of deficiency symptoms and growth responses in relation to foliage nutrient concentrations.

Foliage data given by Hüttl (1992) were used to evaluate the BZE-I data. In Table 1, median values obtained from the BZE-I analysis are given in brackets. Same values were used for spruce and pine and also for beech and oak. There is no indication whether the values are valid for only the mature stands.

For the grouping of foliar P values, van den Burg's data were grouped in the following manner to build classes : very low (classes 4+4.5), low (5+5.5). optimum (6+6.5), high (7+7.5) (very high values, class 8+8.5, had no or 1-2 values only). Ranges and median values for each class were taken for the comparison (van den Burg 1990). In Table 1 data for only the mature stands were included. For young stands the values were higher and are given in a separate table (Table 2). The range values (min-max) would include the outliers. In order to avoid the outliers, one could have chosen 10% / 90% or 25% / 75% as shown for the box plots. However for comparison purposes this set of data seems befitting. Median values for optimum

level class are given in brackets. From Table 1 the following observations of interest can be made:

(a) There is a huge variation in the individual values for assessing the deficiency and/or sufficiency levels, especially for the conifers. For example, the BZE-I report (BMELF 1997) used a P value of <1.2 mg/g as low (deficient) for spruce and pine needles, but according to Krauß and Heinsdorf, this value should be <1.0 for spruce and <0.79 mg/g for pine needles (Class 3 in their Table). However, P concentration values given by Krauß and Heinsdorf in class 4 (luxury) were very similar to those given by class 3 by others, reflecting the different approaches used to define the range limits.

(b) For beech and oak stands, BMELF (1997) used the P foliage concentration value of 1.3 mg/g for the upper limit of the low range to interpret the BZE-I data, whereas Krauß and Heinsdorf suggested values less than 1.14 mg/g and 1.27 mg/g for beech and oak leaves respectively. The values for oak leaves are relatively close in both cases.

Table 1: Some suggested critical ranges of P concentrations in the foliage to describe the nutritional status of mature stands of spruce, pine, beech and oak. Comparative critical values were grouped for deficient, sufficient, and high (luxury) amounts provided in the literature by various sources. Two values in brackets for Krauß and Heinsdorf refer to mean critical values for highly deficient and deficient categories. Two values for spruce and pine in van den Burg data are the range and median values of the low and very low categories. (+no samples for very low range in beech and oak sample collective of van den Burg)

	Deficient (low to very low)	Sufficient (optimum)	High (luxury)	Reference
Spruce	<1.2–1.4 (1.3)	1.4-1.8	1.8-2.0	Hüttl (1992) BZE 1
Spruce	0.5-1.4 0.6-2.0 (0.9) (1.2)	1.1-2.9 (1.7)	1.5-2.0 (1.8)	Van den Burg
Spruce	<0.71-1.00 (0.59) (0.84)	1.00-1.41 (1.18)	1.41-1.98 (1.67)	Krauß and Heinsdorf (2005)
Pine	<1.2–1.4 (1.3)	1.4-1.8	1.8-2.0	Hüttl (1992) BZE 1
Pine	<0.5-0.79 (0.40) (0.63)	0.79-1.26 (1.00)	1.26-1.99 (1.58)	Krauß and Heinsdorf (2005)
Pine	0.3-1.2, 0.6-2.0 (1.0) (1.2)	1.0-3.3 (1.6)	1.6-3.0 (2.1)	Van den Burg
Beech	<1-1.3 (1.2)	1.3-1.5	1.5-1.7	Hüttl (1992) BZE 1
Beech	<0.86-1.14 (0.75) (0.99)	1.14-1.52 (1.32)	1.52-2.01 (1.72)	Krauß and Heinsdorf (2005)
Beech+	1.1-1.6 (1.3)	1.2-1.9 (1.5)	1.0-2.8 (1.7)	Van den Burg
Oak	<1-1.3 (1.2)	1.3-1.5	1.5-1.7	Hüttl (1992) BZE 1
Oak	<0.96-1.27 (0.84) (1.11)	1.27-1.68 (1.47)	1.68-2.23 (1.94)	Krauß and Heinsdorf (2005)
Oak+	0.8–1.9 (1.3)	1.2-2.8 (1.7)	1.7-2.0 (1.9)	Van den Burg

2.3   Factors influencing the foliage P concentrations in trees

Species

Phosphorus concentrations in the foliage differ among various tree species, commonly high P values are found in deciduous trees and low in coniferous species. For example, using the data from stands which describe the optimum or sufficiency levels of P in the foliage, Krauß and Heinsdorf (2005) suggested that the different species can be grouped into the following the order:

(a) High range (>2 mg P/g) in *Populus balsamifera, Tilia cordata, Carpinus betulus and Betula pendula*

(b) Medium range (1.5 to 2 mg/g) in *Quercus robur, Pinus strobus, Larix decidua, Pseudotsunga menziesii*

(c) Low range (1.0 to 1.5 mg P/g) *Quercus rubra, Fagus silvatica and Pinus nigra, Picea abies, Pinus sylvestris*

Thus the four species being considered more closely here could be ranked in the following order of declining foliage P demand: Oak > Beech > spruce > pine, with very little difference between spruce and pine in their P foliage concentrations.

If the median values given in Table 1 for the optimum range are considered (van den Burg data), the four species follow the order: Oak = spruce > pine >beech with very little difference among the species. In fact, while considering the forest foliar chemistry surveys on level I sites of 16 European countries (1995 survey), an expert panel decided to consider three classes for pine and spruce (<1.0, 1.0-2.0, >2.0 mg P/g), for beech (<1.0, 1.0-1.7, >1.7 mg P/g) and for oak stands (<1.0, 1.0-1.8, >1.8 mg P/g) (Stefan et al 1997 (EC-UN/ECE)), which does not differentiate much between the species. Interestingly, the expert panel decided not to assign specific names or descriptions to these classes in order to avoid misinterpretations or wrong conclusions.

Tree age

The data compiled by van den Burg (1985, 1990) differentiate between mature and young stands and those from experiments, presumably seedlings or saplings from greenhouse trials, for a large number of cases (Table 2). The range in the concentration of P is very high for each group of trees with much overlap. However, when the median and the mean values are compared, it shows that there are many

outliers in the data set. Median P values in the different nutrition classes of the young trees were much higher than those for mature trees in spruce, somewhat higher in young than mature trees in beech and oak, but no difference was observed between the mature and young pine trees for their foliar P concentrations. In all cases, the experimental plants had higher P concentrations than the mature and young trees, except for beech where the number of cases was too low to for a comparison. This variability in foliar P concentrations with tree age is an important factor to consider, when the foliar samples for the next nationwide forest soil survey (BZE-II) are taken.

Table 2: Foliar P data of mature, young and experimental trees as described by van den Burg. Statistical parameters are provided for the optimum growth class (class 6+6.5) and the values are given in mg/g. (n refers to the number of individual cases included, sd = standard deviation).

Species	Age	n	mean	sd	median	min	max
Spruce	Mature	151	1.78	0.43	1.70	1.10	2.90
	Young	52	2.38	0.57	2.25	1.40	3.80
	Experiments	62	2.48	0.64	2.50	1.00	3.80
Pine	Mature	112	1.72	0.41	1.60	1.00	3.30
	Young	74	1.66	0.34	1.60	0.90	2.70
	Experiments	42	1.96	0.43	2.00	1.00	3.10
Beech	Mature	25	1.52	0.16	1.50	1.20	1.90
	Young	32	1.73	0.57	1.70	0.80	3.00
	Experiments	4	1.18	0.26	1.25	0.80	1.40
Oak	Mature	43	1.81	0.44	1.70	1.20	2.80
	Young	62	2.01	0.53	1.85	0.90	3.00
	Experiments	8	2.00	0.34	2.00	1.50	2.50

Needle age and foliage condition

Commonly older needles from previous years have lower concentration of P than the current year needles. The difference in the P concentrations of current and older needles depends upon the ages of the needles being compared, the P status of the site and genetically controlled factors driving withdrawal patterns of the stand. For

example the compiled data from BZE-I sites for spruce showed that 3-year old spruce needles had 30 to 40 % lower values of P than the fully developed needles from the current year (Fig 1). The difference between 1st- and 3rd year needles were surprisingly constant across the whole range of needle P concentrations in spruce (BMLEF 1997). In another data set shown in Table 5, foliar P levels in ten spruce stands were measured continuously for 10 years. Three years old needles had 66 to 82 % of P present in the one year old needles. Five year old needles had further reduced P levels (range 47% to 70%). The amount of P re-allocated from 5 year old needles to the youngest cohort of needles equated to 30 to 50 % of the content in the current year needles. The withdrawal was not related to any measured site property. Similar results were also obtained for one and two years old needles of Scots pine.

Soil characteristics

In a study of 49 stands of European beech (60-or more years-old) in the Werdenfelser Land region where the canopy conditions were monitored, Ewald (2000) analysed foliage and soil samples from 8 sites for nutrient composition. Sites could be divided into 2 groups. Moderate P levels were found in trees from well-developed mineral soils, and extremely low P levels (0.6-1.0 mg/g) in immature carbonate soils where total P levels in soils were low and Ca saturation very high. Very high N/P ratios of 30 or more were associated with low P levels. Phosphorus was a critical element in the nutrition of beech in the calcareous Alps, which may be partly responsible for poor vitality of this species in mixed mountain forests. Foliar P values in beech forests on calcareous bedrocks are commonly low when compared to acid soils. As the availability of protons is required to release P from rock minerals it is possible that low foliar P values on calcareous bedrock may result from the high buffering of most of the protons by carbonates which renders less protons available for silicate weathering.

Highest values of foliar P are found in spruce and pine stands on bedrocks of basalt type (bedrock type 8 – median value of P in the current needles of 1.5 mg P/g) and the lowest on the calcareous type (bedrock type 1 – median values were 1.2 mg/g for spruce and 1.3 mg/g for pine (BMELF 1997).
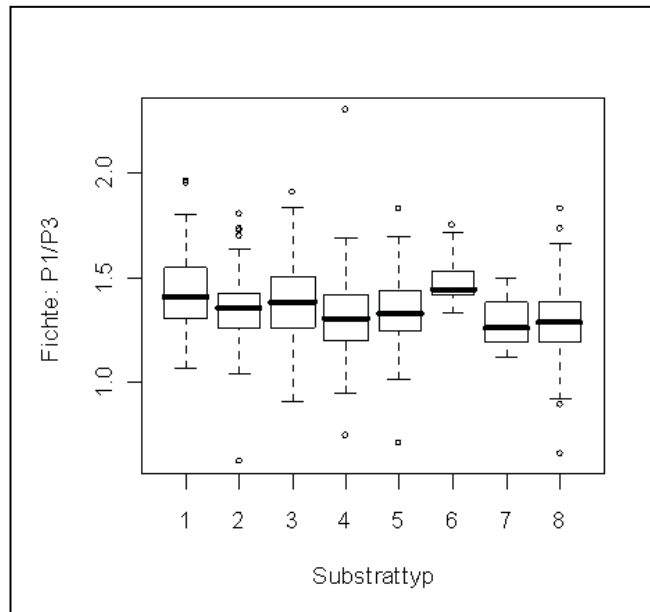
Fig 1. The ratio of P in current year (P1) and 3-year old (P3) spruce needles on sites grouped in to 8 different types according to soil parent materials.

Fertilizer additions

Addition of P fertilizer commonly increases the P in the current foliage and old needles, though the changes would depend upon the time of P application in relation to the period of growth. For application of N it was shown that an increase in N concentration of the current year needles of *Pinus radiata* occurred when it was applied at their initial growth period (Crane and Banks 1992). The longevity of the high concentrations of P in the needles can be observed for a long time as shown later from the data obtained from the fertilizer experiment at Oerrel (Table 7). However, it appears that the P retention properties of soil will determine the availability of P to plant roots and thus the longevity of high P values in the foliage. This is discussed in detail in section 2.7.

Retranslocation patterns in plants

Retranslocation of nutrients especially of P is quite well known and examples of this have been discussed above where more than 50% of P in the current year needles of spruce will be retranslocated to younger needle cohorts as they become older. A significant amount of P is also withdrawn when leaves or needles are shed. From beech leaves 50% or more of P is withdrawn. This retranslocation of P may occur

mostly during periods of active growth, making it important to chose the sampling period carefully for collecting needles for nutrient assessment. There are two common hypotheses pertaining to the fraction and amount of nutrients re-absorbed from leaves.

(a) The first one considers that the amount of nutrient resorption increases as an inverse function of soil nutrient availability (Grime 1979; Chapin 1980; Berendse & Aerts 1987). Nutrient resorption from senescing leaves is therefore expected to be more highly developed on sites of low fertility.

(b) The second hypothesis considers that resorption is influenced by sink strength within the plant (Nambiar & Fife 1991) so that resorption efficiency is positively correlated with plant growth rates, because the production of new tissues constitutes a strong nutrient sink. However sink strength is unlikely to explain the strong resorption shown by many deciduous trees in autumn where carbohydrate flux from leaves (i.e., source-sink interactions) may govern the retranslocation rather than the hydrolysis of nutrient-containing fractions.

Interactions with other nutrients and the use of P/nutrient ratios

Interactions among various nutrients should be considered both in the plant and in the soil. It has been shown (Sterner and Elser 2002) that stoichiometry of major elements (C:N:P) may be a major ecological driver from gene to biospheres. Constancy in the N:S ratios has also been reported in many ecosystem components. Of interest for this review is the N:P ratio in the leaves, litter layer and soils. A high N/P ratio in leaves is commonly interpreted as P limitation to plants. For litter layers, the N:P ratio above which P becomes limiting for biological processes relative to N is considered to be 16:1 (Redfield 1958) which may lead to reductions in litter decomposition rates, phosphorus release from litter, and activity of decomposer microbes. Wardle et al. (2004) used this ratio on six long-term chronosequences to report that a decline of natural forests, which is often observed in the long-term absence of catastrophic disturbance, may arise through increasing limitation by P and reduced performance of the decomposer subsystem. Leuschner et al. (2006) studied properties of soils under 50 beech stands and observed that N/P ratios in the litter layer increased with an increase in soil acidity which they ascribed to the possibility of P deficiency in these stands.
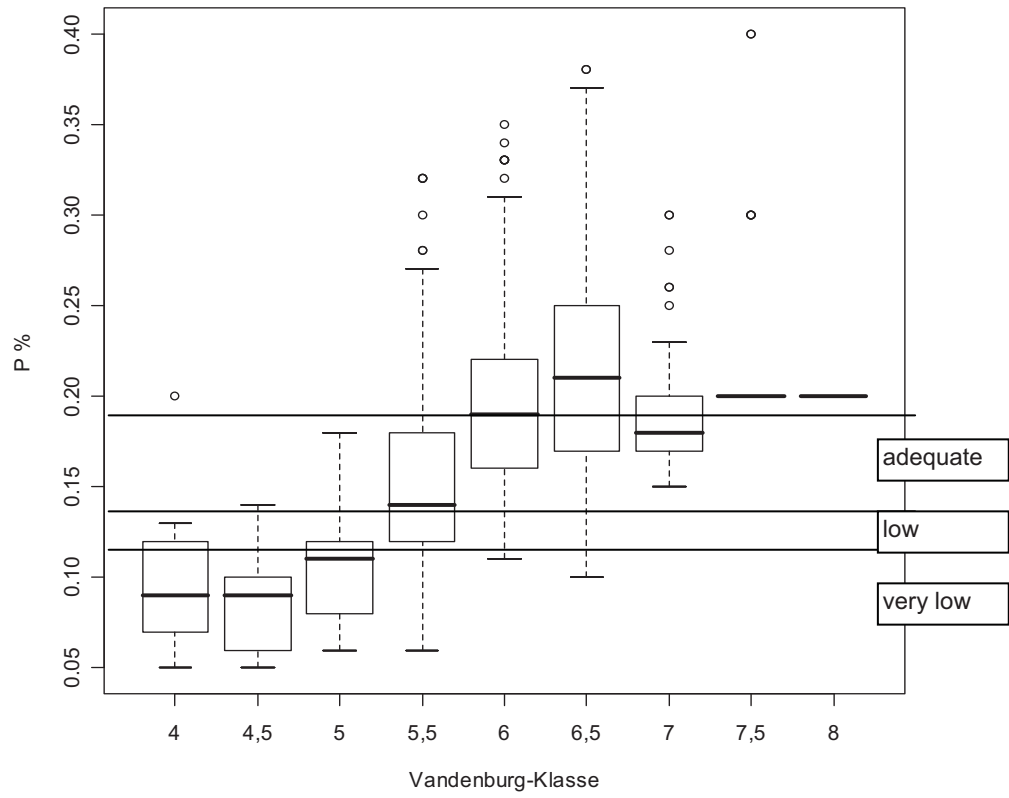
2.4 Analysis of van den Burg data sets for important German tree species

Background – van den Burg (1985, 1990) compiled from the literature concentrations of different elements in the foliar samples of many tree species and grouped them according to the reported deficiency, toxicity, or growth response, also in relation to fertiliser additions. The data for four important species for forestry in Germany were digitised and evaluated for P levels for this report. It is relatively a large data set (524 cases for spruce, 481 for pine, 103 for beech and 194 for oak). Each species was categorised separately for the age of trees, which included mature stands, young age stands and small saplings or seedlings used in controlled experiments. Critical ranges of foliar P values were grouped into five categories and each with a transitional category for comparison purposes: a) very low values, where the plants show severe deficiency symptoms, b) low values, when growth is nutrient-limited and increases with small to moderate doses of fertiliser, (c) optimum values, where the growth rates are satisfactory or good and would increase only if high amounts of fertilizer were added, (d) high values indicating luxury consumption, where other nutrients may be limiting the plant growth, and (e) very high values leading to toxicity and reduction in growth. The transitional categories were grouped to the respective lower category level for providing the number of cases in each category in Table 3. However, they were kept separate in the figures shown.

The number of cases in the categories of high and very high foliar P levels is small as one would expect that under natural conditions P is mostly limiting. There are however certain tree species which grow only under very low P levels and an application of P may lead to toxic levels in their foliage. Similarly the number of cases in the category of very low levels is small. Most cases are seen in the optimum category. The data were plotted as box plots for each of the four species. The upper limits of nutrition ranges "very low", "low" and "adequate" used in the BZE-I report (Table 1) were marked to see how far those values correspond to the categories suggested by van den Burg. For spruce, pine and beech (Fig 2 – 5) the values for the low category corresponded quite well with the class 5.5 of van den Burg. 5.5 is transitional between categories 5 and 6. The very low categories (<1.2 mg/g for spruce and pine and <1.0 for beech respectively) were slightly higher for 4.5 class of van den Burg. Oak values were not corresponding well, which may be related to very few cases in van den Burg's data set. The results obtained here provided confidence in the values used in the BZE-I which came to the conclusion that foliar P levels indicate its wide spread deficiency in German forests .

Table 3: Number of cases included for each species and age class in van den Burg's collective. M=Mature, Y=Young, E=Experiment.

Species	Type	Very low (4+4.5)	Low (5+5.5)	Optimum (6+6.5)	High (7+7.5)	Very high (8)	Total
Spruce	M	24	89	151	42	1	307
	Y	12	32	52	10	0	106
	E	10	32	62	7	0	111
Pine	M	15	88	112	18	2	235
	Y	14	59	74	15	6	168
	E	5	24	42	7	0	78
Beech	M	2	13	25	5	0	45
	Y	1	16	32	0	1	50
	E	1	3	4	0	0	8
Oak	M	4	26	43	7	0	80
	Y	2	34	62	1	0	99
	E	0	6	8	1	0	15

Fig 2. Relationship between nutrient classes of van den Burg (van den Burg 1985, 1990) for Norway spruce and the critical needle P concentrations used in the nationwide forest soil survey.
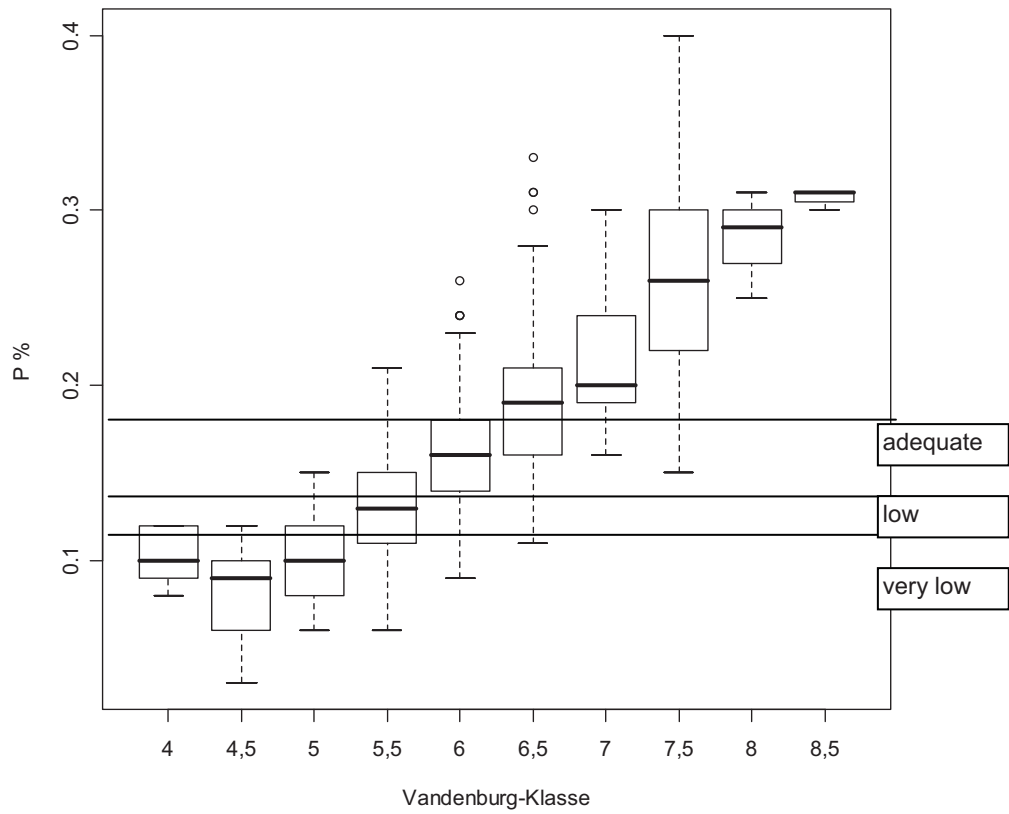
Fig 3: **Relationship between nutrient classes of van den Burg (van den Burg 1985, 1990) for Scots pine and the critical needle P concentrations used in the nationwide forest soil survey.**
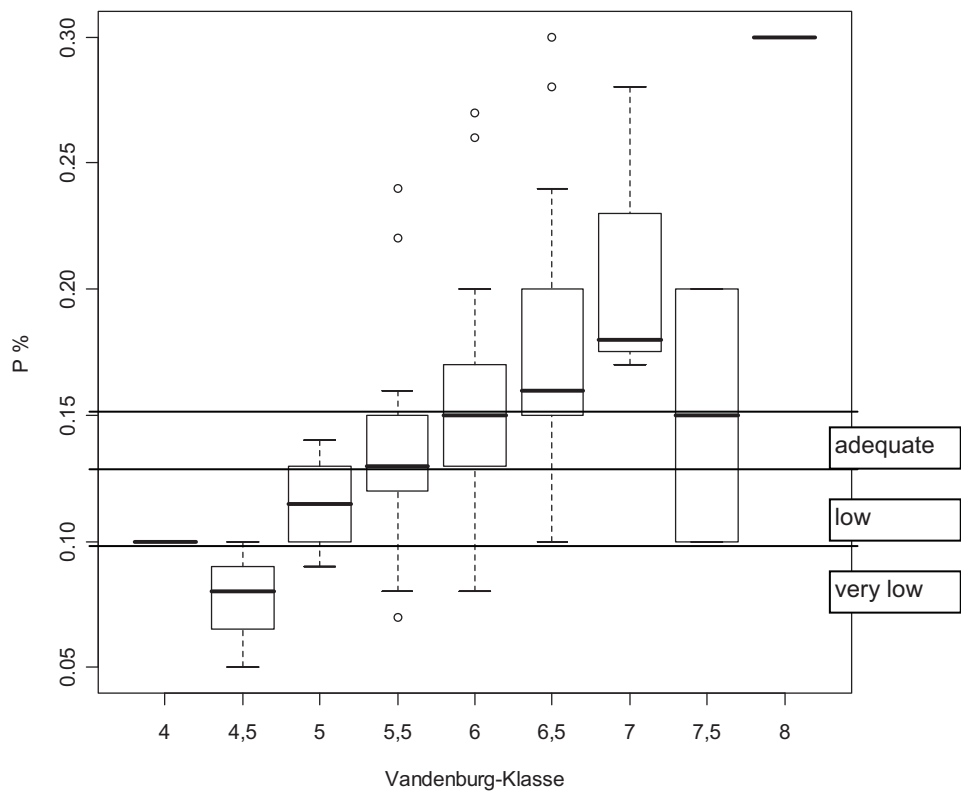
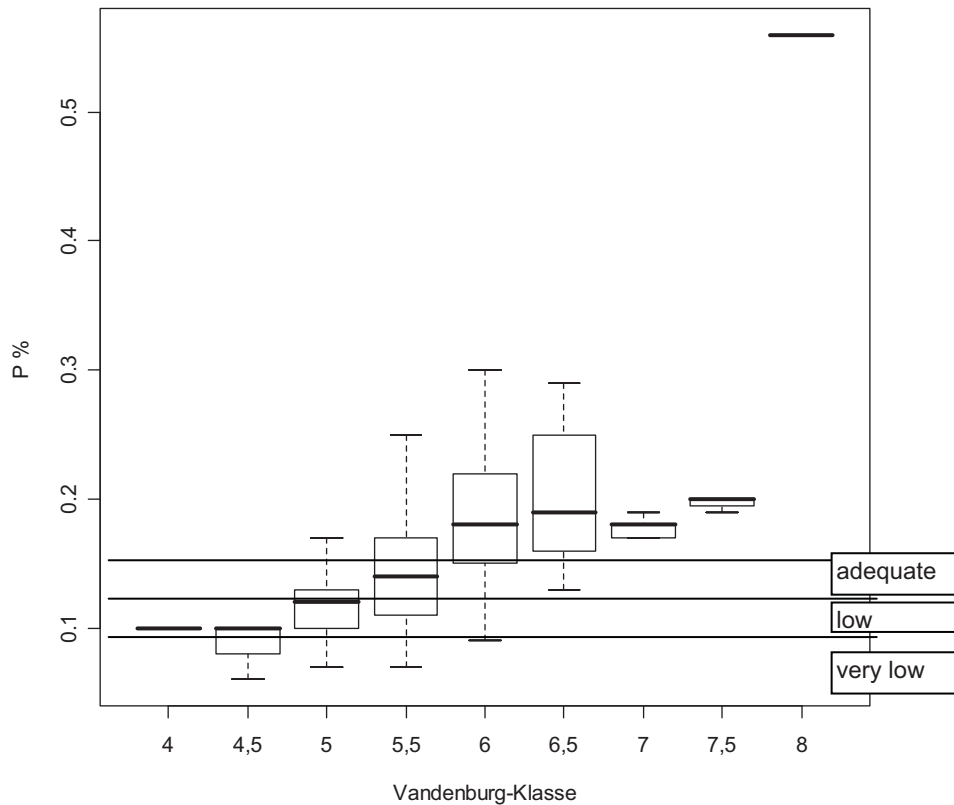**Fig 4:** **Relationship between nutrient classes of van den Burg (van den Burg 1985, 1990) for European beech and the critical needle P concentrations used in the nationwide forest soil survey.**

Fig 5: **Relationship between nutrient classes of van den Burg (van den Burg 1985, 1990) for oak and the critical needle P concentrations used in the nationwide forest soil survey.**

2.5 BZE 1 sites – Re-evaluation of data on foliage P and soil P parameters

Data from the BZE 1 study on P concentrations in the foliage samples covered a range of forest types. Most sites were occupied by conifer, spruce and pine forests. Deciduous forests, beech and oak are fewer in number. Foliage data from BZE 1 were compiled into P levels describing the P status of trees (Table 1) and were grouped according to the soils based on parent materials. The representation of the tree species in these groups describes the domination of spruce sites, followed by pine and beech and oak. Using the criteria of P levels in the foliage samples it can be observed that a

significant number of sites (59%) were containing low (< 1.2) to very low (<1.0) values of P in spruce which were equally distributed on the first 5 soil (bedrock) groups. For pines, there were 58% sites with low to very low values and for beech there were 58% sites with low P in the foliage. There were very few oak sites making it difficult to assess the actual P status of these forests. This high percentage of beech stands with low P values (canopy assessment data do not show that extent of foliage or productivity change) points to the possibility of high plasticity of beech to handle low P values. In addition to the many sites with low levels of P in the foliage there are many borderline cases which may develop into situations where P deficiency might occur under the on-going conditions of high N inputs and increased growth rates.

In order to investigate, if any of the site or stand parameters would explain the variation observed in the foliage P levels of each of the three tree species – spruce, pine and beech - regression trees were calculated. The method is described by an example given in Fig. 6. Figure 6 shows the proportion of variation in the amount of P in the humus layer as dependent variable, which is explained by all other independent factors that explain a significant part of the total variation in the dependent variable. Results in Fig. 6 indicate that variance in the amount of P in humus layer is best explained by the N content in the humus layer.
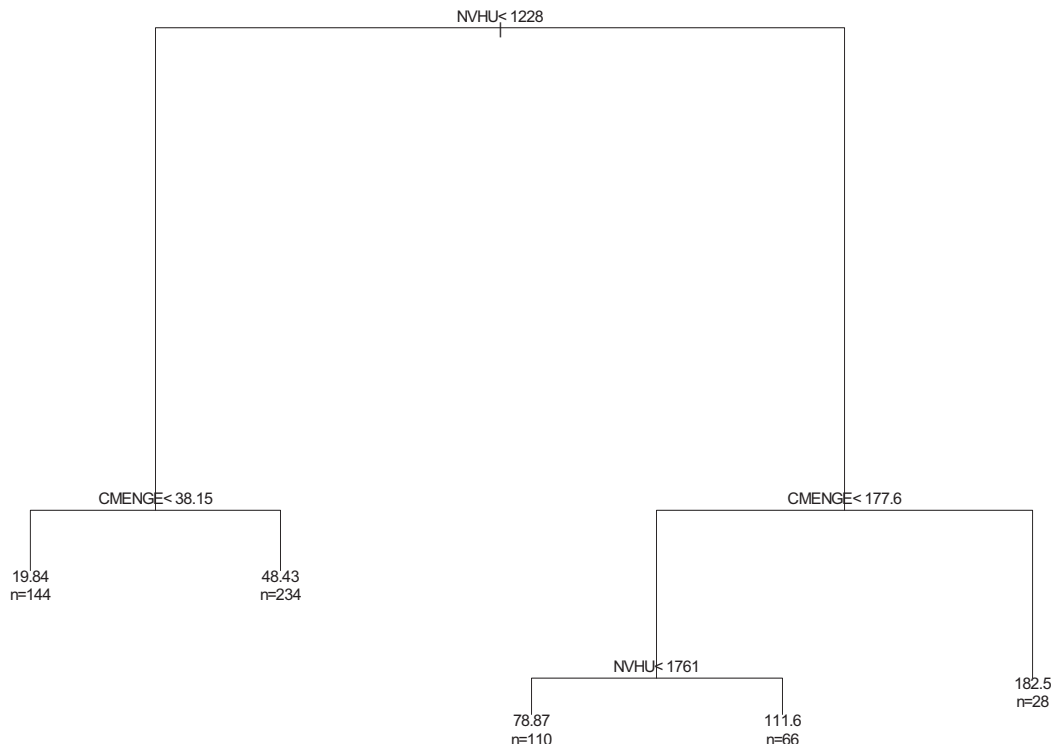
Fig 6: Spruce : Regression tree for the dependent variable P in the humus layer against all site and stand parameters available in the BZE-I data set (n = 587). Here only the influence of significant factors, N and C in the humus layer are depicted, which explain 55% of the variation in humus P, are depicted.

The same type of regression tree analysis was carried out for a number of variables. The number of variables (with continuous values) available for testing are given below (no variable with discrete values was included in the regression tree, variable with continuous values were included in the analysis). The variables included were: concentration of elements in the foliage (N, P, K, Ca, Mg, Mn, S) and the ratio of P concentrations in 1-yr and 3-yr needles of spruce. For the litter layer, only values of element stores for C, N, P, K, Ca, Mg, Mn were available, for 0-10cm soil depth values for pH, base saturation and amount of acid cations on the exchange complex were available. For 0-30cm soil depth, stores of elements for Corg, N, P, K, Ca, Mg,

Mn, Al, Fe and for the ratios C/N,C/P,N/P, Ca/P,K/P, Mn/P were included. Three site factors altitude, mean annual temperature and mean annual precipitation values were also included in the analysis.

Table 4 below gives the variables for which the regression trees were built and the number of variables, which had gone into the analysis. None of the variables showed any relationship to P concentrations in leaves or 1-yr and 2-yr old needles. The only useful relationship was between amount of P in the litter layer, which appeared to be related to the amount of N in the litter layer.

Table 4: Variable for regression tree analysis for Spruce sites (P1 and P3 refer to 1-yr and 3(2)-yr needles, PVHU and NVHU refer to amount of P and N in the litter layer, PV and C refer to amount of P and C in the mineral soil, ratios for different elements are given in wt/wt).

Predicted parameter	Variance explained	No. of variables included	Independent variable 1 (% variation explained)	Independent variable 2 (% variation explained)
P1/P3	-	31		
P1	o	31	PVHU (5)	C/N (5)
P3	-	31		
PVHU	++	40	NVHU (45)	C (10)
PV	-	40		
C/N	-	42		
N/P	-	40		
Ca/P	+	40	Al/P (40)	
K/P	-	40		
Mn/P	-	40		

2.6   Changes in P concentrations in the foliage and leaf litter during the last 10 years at Level II sites in Lower Saxony (NS)

Foliage

It has been previously pointed out that P data obtained by one time sampling of foliage may not provide useful information about the P status of a forest stand. The main reason for that is the substantial temporal variation owing to many factors outlined previously in the review. Thus repeatedly taken samples over a number of years provide better information of any change in the foliar status. To assess, whether there may be a decline in foliar P nutrition, the temporal dynamics in P concentrations in the current year needles and mature foliage of 27 long-term monitoring plots in Lower Saxony were assessed statistically. For each site, annual or biannual P-concentration values were analysed using mixed linear models, which were fitted to all data for each species for a 10-year period. There were 10 spruce sites, for which the mean P concentrations of 1-year old needles and the relative proportion of 3-year and 5-year needles are given in Table 5. In addition, there were three pine sites, 8 beech sites and 6 oak sites (Fig 7-10). The older spruce needles had lower concentrations of P, 66-82 % in 3-yr old and 47–70% in 5-yr old needles when compared to 1-yr old needles. This represents a significant amount of P withdrawal, assuming the weights of 3- and 5-yr old needles have not increased, which is unlikely.

Table 5: Mean P foliar values in the current year old (1-yr) needles, and relative concentrations in 3-yr and 5-yr old needles to 1-yr old needles. Mean values represent 10 years of measurements.

Site	P in 1-yr old needles mg/g	Percent of P contained in 3-yr old needles %	Percent of P contained in 5-yr old needles %
HiKA	1.11	67	59
HiMA	1.18	70	57
HIMJ	1.31	82	70
LBKA	1.33	75	56
LBNH	1.39	77	70
LBSH	1.22	78	70
SLF1	1.38	74	62
SLFD	1.32	70	61
SPFi	1.36	72	55
WIFi	1.47	66	47

Foliar P concentrations of spruce showed a continuous decrease across all monitoring sites during the 10 year period of measurements. The mixed linear model (P<0.03) predicted a linear trend in the data for all sites, there were however site to site differences to be noted and the overall explanatory power of the model was low, indicating the high temporal variation in the data. The single plot deviation from the overall trend (random part of the model) was relatively small for most cases. For Norway spruce sites, the model predicts an annual decrease in the concentration of P over a ten year period of 0.06 mg g^{-1} in the youngest needles. The decline was more pronounced in the older needles (data not included).

Similar to spruce, there was a significant decline in the foliar P concentration of current year pine needles across all three monitoring sites. The mixed linear model predicted a relatively high average annual decrease of 0.15 mg g^{-1}. At this rate stands could move from the lower end of the "sufficient" nutritional stage to the "very low" stage of P nutrition within two decades.

For beech and Oak stands there was a slight increase or no change in the foliar concentrations over the 10-yr period. The linear model was not significant for oak (p=0.74) showing that there is no temporal trend. The trend for beech has to be viewed with caution, since the distribution of data points along the time axis is not even, with many more observations in the second half of the 10-year period. Although the model is highly significant (p<0.001), the temporal trend explains only a small proportion of the overall variation in the data. This also points to the need to carry out this type of analysis on a wider data basis. In addition, it is difficult to identify any specific reason for the increase, except that the beech sites are very few (four of them are from Solling, out of which one had received high doses of nitrogen repeatedly added for a number of years, another one received lime and the third received lime + small amount of fertilizer). Oak sites had very high single plot deviation in two of the cases because very few measurements points were available.

In case the atmospheric depositions of acid and high N are related to changes in foliar P concentrations, then these are going to be more pronounced under spruce and pine than under deciduous trees. Spruce and pine stands receive much higher levels of atmospheric depositions due to higher interception in winter months. There are numerous cases in the literature which point to this relationship between high acid and N inputs and reductions in foliar P concentrations. Literature details have been given

in section 1 of this report.

In summary, we observed that long-term measured foliar P concentrations in forest stands of Lower Saxony point to a continuous decrease in spruce and pine stands. The reasons for this decline are unknown. There is no clear indication of any change in the foliar P concentrations of beech and oak stands. It must be pointed out that the number and type of sites investigated are small and probably not representative for the whole country to extend these results to all BZE sites. It will be prudent now to conduct similar analysis of foliage P concentrations for the Level II sites from different States, and possibly for a longer time period than 10 years, to better evaluate any changes in the foliar P status of forest stands in the country.
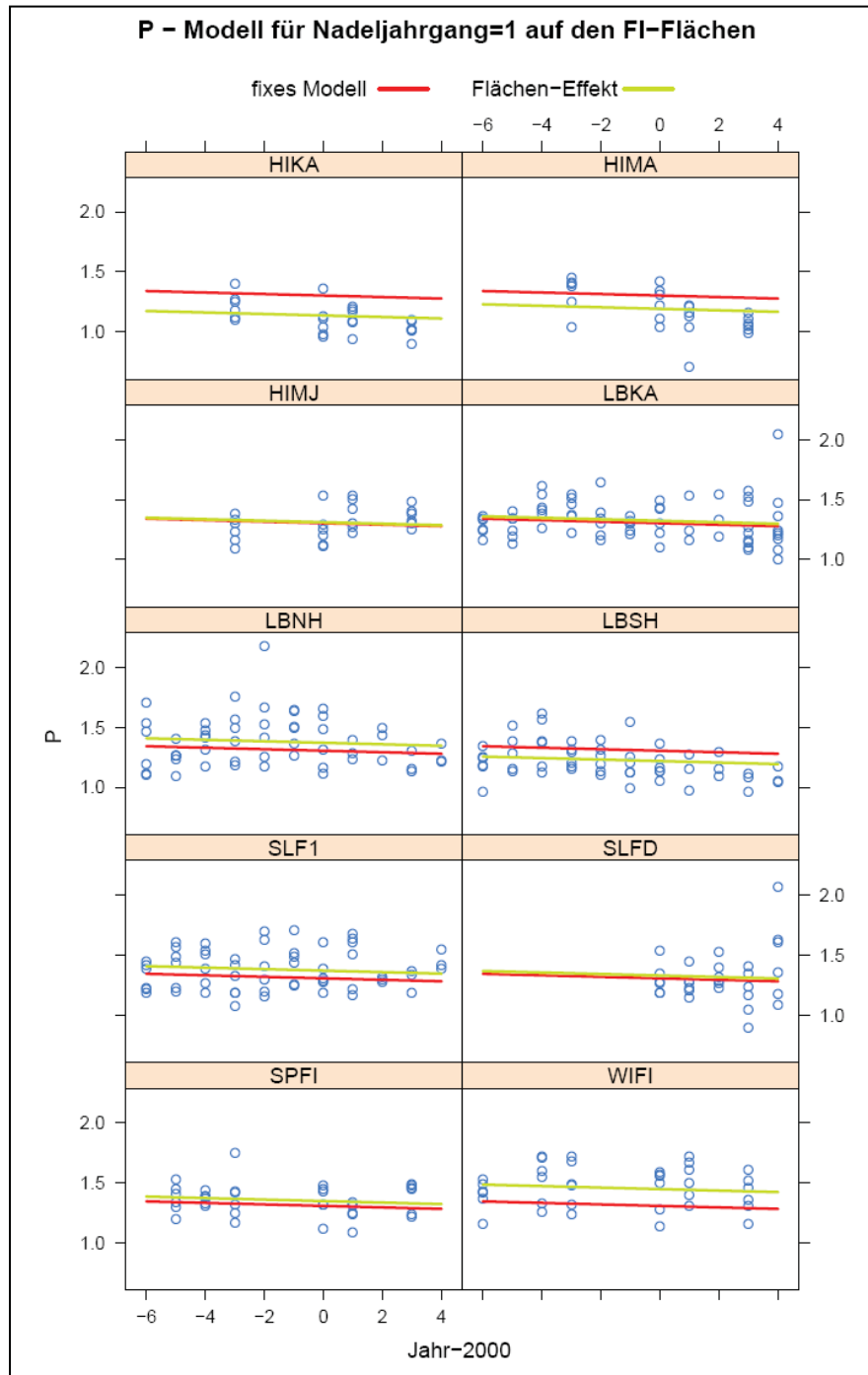
Fig 7: Mixed linear model describing the decline in P concentrations in 1 yr-old needles in Norway spruce at 10 sites in Lower Saxony. The year 0 on the x-axis equates to 2000. Dark (red) line: overall trend (fixed part of the model), pale (green) line: single plot deviation from the overall trend (random part of the model), circles = observed P needle concentrations. Model: P<0.03, n=404.
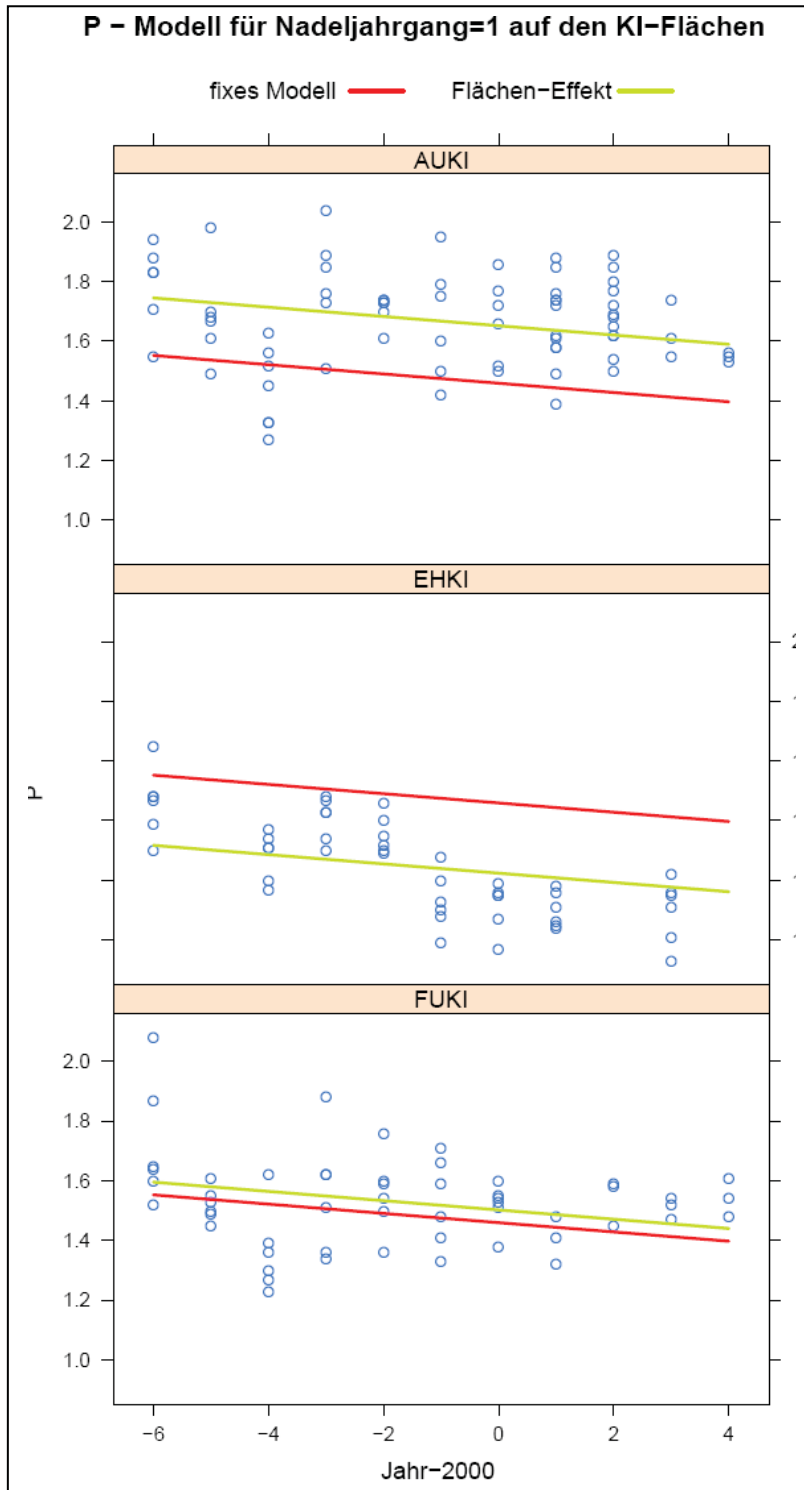
Fig 8: **Mixed linear model describing the decline in P concentrations in 1 yr-old needles in Scots pine at three sites in Lower Saxony. The year 0 on the x-axis equates to 2000. Dark (red) line: overall trend (fixed part of the model), pale (green) line: single plot deviation from the overall trend (random part of the model), circles = observed needle P concentrations. Model: P<0.05 , n=172.**
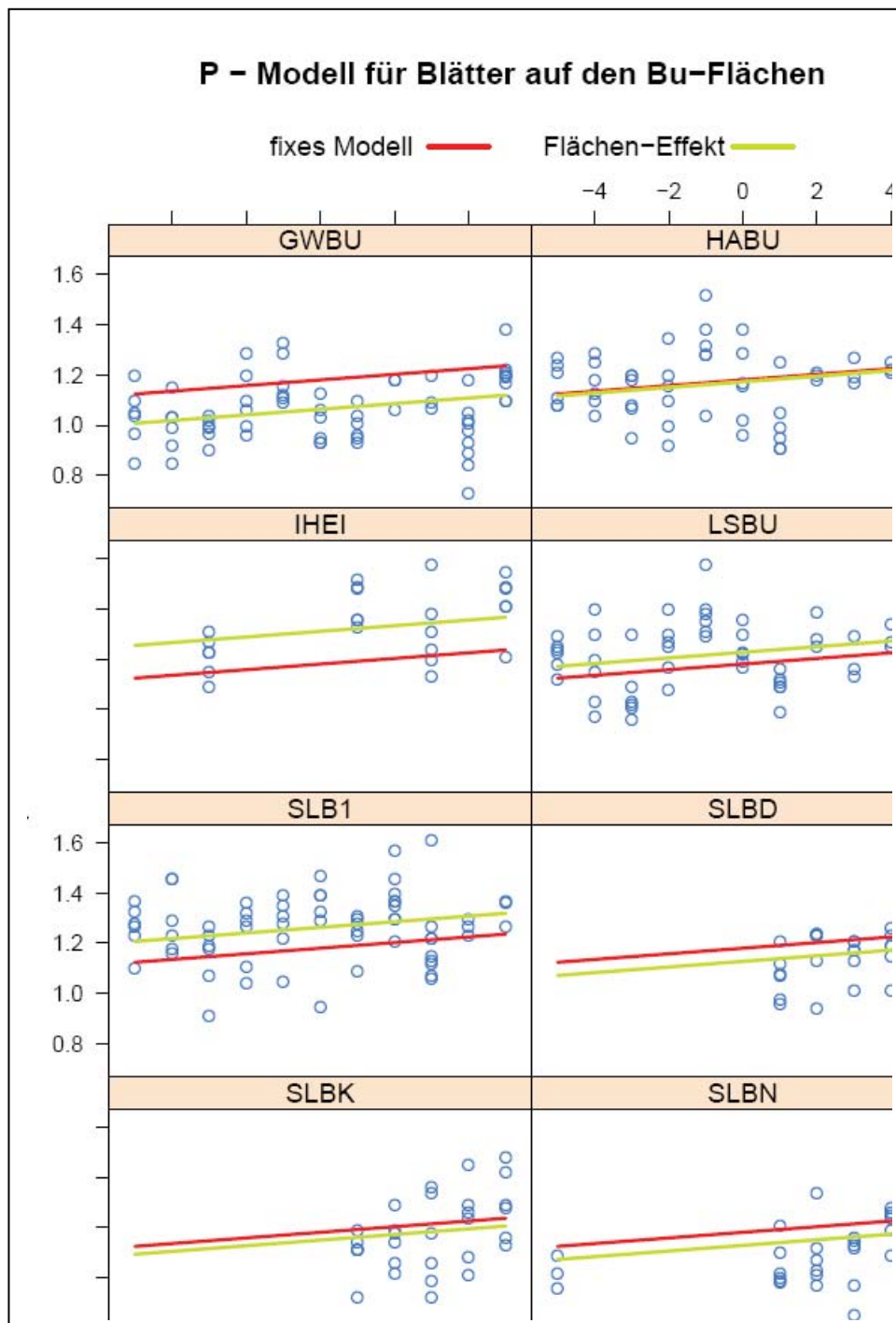
Fig 9: Mixed linear model describing the temporal change in leaf P concentrations of (Level II) European beech stands in Lower Saxony. The year 0 on the x-axis equates to 2000. Dark (red) line: overall trend (fixed part of the model), pale (green) line: single plot deviation from the overall trend (random part of the model), circles = observed foliage P concentrations. Model: P<0.001, n=357.

Fig 10: . Mixed linear model describing the temporal change in P concentrations in leaves of oak stands (Level II) in Lower Saxony. The year 0 on the x-axis equates to 2000. Dark (red) line: overall trend (fixed part of the model), pale (green) line: single plot deviation from the overall trend (random part of the model), circles = observed foliage P concentrations. Model is not significant: P=0.74, n=198.
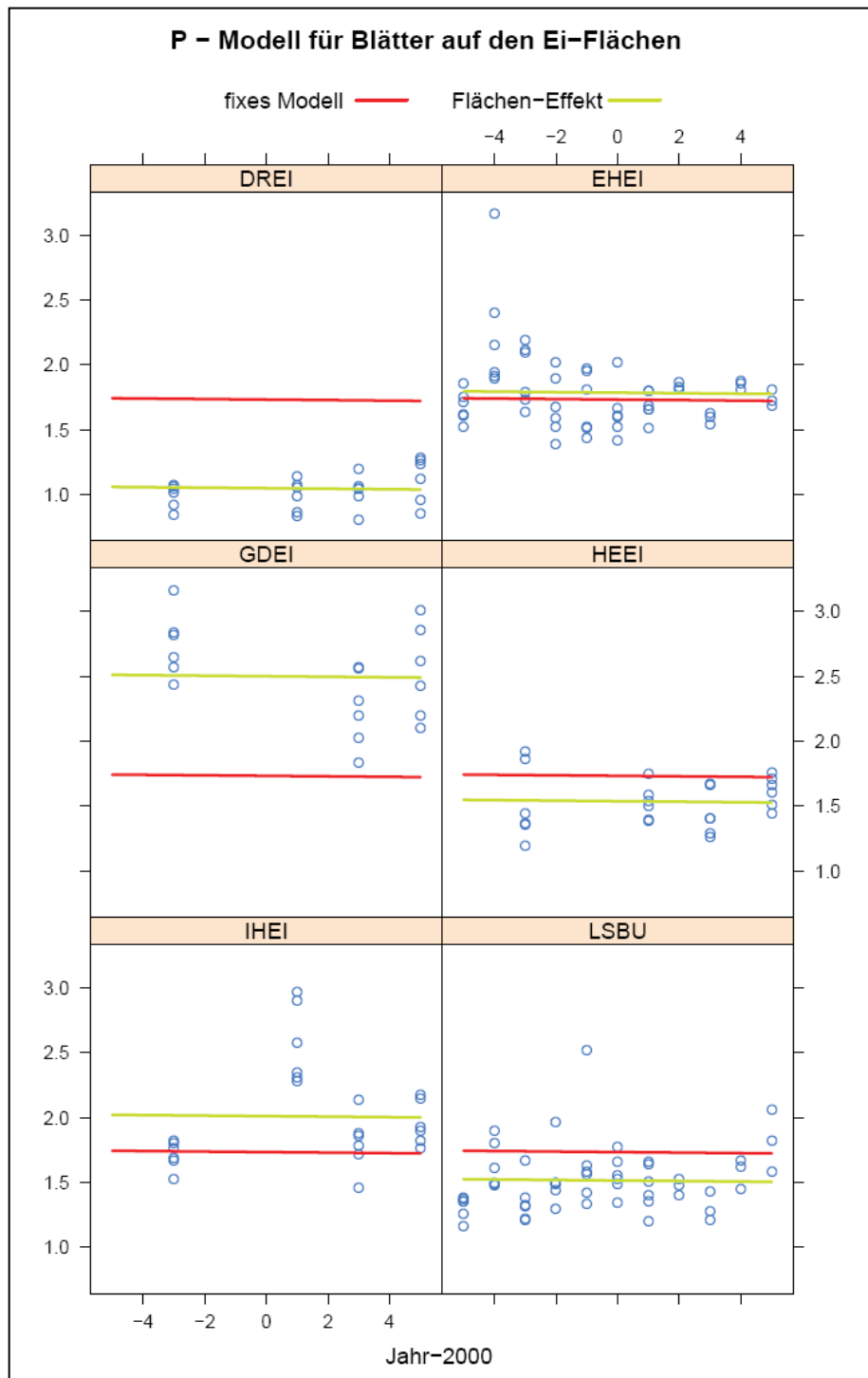
Leaf litter

Leaf litter was not measured in all the 27 stands, where the foliar P concentrations were measured but only in 13 stands which were located on 10 different sites (Table 6). Based on the analysis of these data, we can make the following observations:

- Mean P concentrations of the spruce needle litter (collected at the end of the growing season) were much higher (0.73 to 0.82 mg P/g– unfertilized plots) than of the pine litter (0.40 – 0.41 mg P/g).

- Beech showed much greater variation in leaf litter P concentrations (range of mean values 0.44 –0.70 mgP /g), than the other species. Lowest values of P concentration in the leaf litter were found on the calcareous Göttinger Wald site (GWBU). However, among the beech sites, this stand has one of highest wood productivity values, probably indicating high plasticity of the beech with respect to nutrient requirements. The green foliage on this site had also values in the low range (0.98 to 1.18 mg P /g).

- Only one oak site was continuously monitored for 14 years and showed a very high mean value of 1.10 mg/g in the leaf fall samples (ranging from 0.78 to 1.44). The highest value of P concentration in the oak leaf litter on this site is higher than the critical value for the live foliage sometimes recommended as low.

- The fertilized sites, spruce - SLFD and beech –SLBD, which received small amounts of N, K and liming in 1970's, had lower litter P concentrations than the unfertilized adjacent stands.

- In contrast to foliage, no temporal trends in the concentration of leaf litter were evident (data not shown) for this restricted data set from a few sites for each tree species. This lack of change in P concentrations of leaf litter cannot simply be related to any lack of changes in P status of plants. The leaf litter values cannot always predict such changes. However it is highly probable that the withdrawal patterns of P may be better indicator of changes in the P status of trees, though it was not possible to test this assertion due to small number of sites for each tree species. This can be tested when data for leaf and needle fall from Level II sites of different States are available for evaluating changes in P status of trees.

Table 6: Concentration of P (mg/g) in the leaf litter of various tree species measured at different sites, n refers to the number of years, data presented refer to the samples collected at the end of the growing season; se = standard error.

	Site	n	min	max	mean	se
Spruce	LBKA	11	0.66	1.06	0.82	0.03
	LBNH	12	0.62	0.83	0.70	0.02
	SLF1	14	0.58	1.01	0.73	0.03
	SLFD	13	0.46	0.73	0.55	0.02
	W128	4	0.64	0.78	0.73	0.03
Pine	AUKI	8	0.29	0.55	0.41	0.03
	FUKI	12	0.26	0.61	0.40	0.03
Beech	GWBU	14	0.30	0.62	0.44	0.03
	HABU	12	0.42	0.79	0.59	0.03
	LSBU	14	0.49	1.00	0.70	0.04
	SLB1	12	0.12	1.10	0.70	0.08
	SLBD	12	0.35	0.97	0.64	0.06
Oak	EHEI	14	0.78	1.44	1.11	0.05

2.7 Foliage analysis data from long term P fertilizer experiments

Fertilizer P application increases the foliar P levels and it can remain effective for a long time depending upon changes in soil P availability, biochemical P cycling and re-allocation patterns in trees. We provide here the long-term foliar P data measured periodically in a spruce stand on poor sandy soil at Oerrel, Lower Saxony. The stand received 45 kg P/ha in 1929, and a second dose of 41 kg P/ha in 1956 as slow release fertilizer (Basic slag or Rhenania phosphate). Surface soil layers were sampled and analysed in the 1960's, which indicated that there was no change in total soil P content. Most of the applied P had been incorporated into the cycling fraction and any small difference between the control and P fertilizer treatment was not detectable in

the soil. However the differences in the foliar P levels as shown in Table 7 were significantly higher in the P treated trees (1994 sampling). As the soil at this site is expected to be low in P fixation capacity, most of the P may be stored either in the vegetation or in the litter layer, which has grown to 6-7 cm depth (moder - raw humus type). There were big variations in the absolute values of P in the foliage samples collected at different times, which may be related to seasonal differences (for example, 1961 was a very wet year and the foliage showed high P values in all treatments).

Results in Table 7 clearly show that P levels in 1-yr old needles have remained high for a long time after P applications. The high temporal P variation in the samples indicate the difficulty involved in using single absolute values of the foliar P for assessing P status of the stand. If we use 1.2 mg P/g as the critical foliar P value, this site appears to have sufficient P but it showed a positive response in foliar P levels when fertilizer P is applied. Unfortunately, P was not applied in isolation but unlike in a fully factorial design only in combination with other nutrients. It is therefore impossible to attribute growth responses of treated stands to P application.

In another long-term fertilizer experiment where 70 kg P/ha were applied to a spruce stand in 1953, a slight increase was measured of total soil P in 0-5 cm depth in 1998, but on all the treatments including those receiving P fertilizer, a decrease in P (and K, as K was not applied in the fertilizer) concentrations in the foliage was observed (v.Wilpert 2003). Foliar P values decreased from 1.3 –2.0 mg P/g in 60's and 70's, which were then lying in the medium to high range of foliar nutrition, to low values around 1.0 mg P/g in 1998. The relatively short term response to P fertilization on this site compared to Oerrel may be related to high P retention capacity of this soil leading to only a fraction of fertilizer used by the trees.

In the fertilization and irrigation experiment at Skogaby, SW Sweden, which was started in 1988 to study the effects of increased or decreased nutrient and water stress in a Norway spruce stand, Nilsson and Wiklund (1995) reported an increase in the P concentration in the current year needles from 1.2 mg/g in the control treatment to 2.0 and 2.2 mg/g in the treatments receiving P fertilizer Together with other nutrients and irrigation (96 kg P/ha in one treatment and 51 kg P/ha in the other treatment) . This increase in P concentration was also observed in the older age needles, litterfall, bark and wood components.

In another P fertilization experiment with Scots pine and Norway spruce in Norway

(Nilsen and Abrahmsen 2003) reported that even a very small amount of fertilizer P application (5.3 kg P/ha) applied annually (for 9 years to pine and 4 years to spruce stands), did not affect the growth, but increased P concentrations in the foliar samples (in current year and old needles) and changed the N/P ratio.

Table 7: Analysis of foliar samples (current year needles, mg P/g) from a spruce stand at Oerrel which received different fertilizer treatments. The experiment was started in 1929. The foliar data for 1956, 1958, and 1961 are taken from Seibt and Wittich (1965), and for 1994 from Mindrup and Meiwes (1995). Fertilizer was applied periodically for many years (total amounts until 1970 were Ca 1929 kg/ha, Mg 19 kg/ha, P 86 kg/ha, K 218 kg/ha and N 217 kg/ha). Lup refers to planting of lupin for atmospheric N fixation and for improving litter quality.

Treatments	N	P	K	Ca	Mg
1956					
Control (nil)	11.6	1.0	5.9	1.9	0.8
NPKCa	15.6	1.4	6.3	3.9	0.9
Lup. PKCa	13.5	1.6	6.9	4.9	1.3
PKCa	13.1	2.0	7.6	5.0	1.0
N-KCa	17.3	1.4	4.2	4.7	1.0
NP-Ca	17.6	1.8	4.2	4.8	0.9
NPK	17.0	1.6	7.3	3.0	0.8
1958					
Control (nil)	13.7	1.1	4.8	2.9	0.8
NPKCa	13.9	1.8	5.9	5.1	1.2
Lup. PKCa	13.0	1.7	5.5	5.9	1.1
PKCa	13.0	1.7	7.2	6.6	1.1
N-KCa	14.1	1.4	7.1	5.5	1.1
NP-Ca	13.6	1.8	4.6	6.9	1.1
NPK	14.1	1.7	6.4	3.7	0.8
1961					
Control (nil)	13.8	1.9	8.7	4.0	1.1
NPKCa	14.4	2.5	9.1	6.2	1.4
Lup. PKCa	14.2	2.1	8.7	7.4	1.7
PKCa	14.6	2.3	9.2	6.7	1.5
N-KCa	14.8	1.7	8.7	8.4	1.5
NP-Ca	14.9	2.9	7.4	7.5	1.5
NPK-	15.0	2.5	10.2	4.5	1.2
1994					
Control (nil)	14.9	1.4	5.7	4.8	0.8
NPKCa	13.4	1.5	4.6	9.1	0.9
Lup. PKCa	15.1	1.8	4.4	9.5	1.1
PKCa	15.4	1.6	4.8	11.5	1.1
N-KCa	14.6	1.3	4.3	11.0	1.0
NP-Ca	15.3	1.7	3.5	9.6	1.2
NPK	15.6	1.7	5.9	6.3	0.7

2.8   Summary and Recommendations for use of foliar P concentrations.

The assessment of P levels in the foliage collected from BZE-I sites indicated low values on the majority of sites, which created concern for future tree nutrition, health and vitality of these ecosystems. There could be many reasons for the lower than commonly expected values of P in the foliage samples of some sites which have been discussed in the review. However, the one time measured values of foliar P concentrations should be viewed with some caution as many factors could affect those values. Some of these factors have been reviewed, and they include, tree species, site factors, tree age, needle age, fertilization, interaction with other nutrients etc.

In order to use the range of suggested critical values of P, the validity of these values needed to be tested with those given in the literature. For that the critical P ranges used in the BZE 1 report were compared with a very large data set on foliar nutrient concentrations grouped into various categories depending upon the tree growth responses and other plant indicators. This data set was originally assembled from literature by van den Burg (1985, 1990). The comparison of the critical P-values used to define deficiency ranges in the nationwide forest soil survey with those provided by van den Burg showed that the upper limits of the classes indicating low and very low P concentrations were not set too high for the spruce, pine and beech. The scanty data for oak did not allow a reliable evaluation of the critical ranges for foliar P.

Concentration of P in the current foliage is highly dynamic. In order to assess P status of trees frequent sampling taken over many years in succession would provide better information. Such a data set was available from 27 Level II sites in Lower Saxony which are continuously being monitored for the last 10 years. Trends in P concentrations of the current year needles and mature foliage were assessed by using mixed linear models. All the spruce and pine sites showed a continuous decline in P concentration in the foliage. Annual mean values of P reduction in the youngest needles were 0.06 mg g^{-1} and 0.15 mg g^{-1} for spruce and pine respectively. It seems therefore highly relevant that foliar P data from the continuous monitoring sites (Level II) from other States should be collated and evaluated by using similar type of model as was used for the sites of Lower Saxony. As the P withdrawal from older needles to younger needles and from live leaves to leaf litter may provide better information on the P status of the tree, it will be useful to explore these relationships by using the available data on leaf litter from the Level II sites from other States.

3. PHOSPHRUS IN FOREST SOILS

3.1   Introduction

Phosphorus occurs in many inorganic and organic forms in soils, but P is taken up by roots from the soil solution phase in the phosphate forms. The amount of phosphate in soil solution is commonly very low, which results from dynamic equilibrium between dissolution and precipitation processes of inorganic P forms, mineralisation and immobilisation of organic P forms and uptake by plant roots. Fig 11 describes in short the conceptual frame work of P dynamics in soils. The P concentration in soil solution determines the amount of P taken up by roots and mycorrhiza. It is described as the intensity factor determining the uptake and other adsorption and desorption processes. Low concentrations of P in the soil solution, which may be the result of kinetics of desorption reactions, would reduce P uptake by roots. On the other hand, high P concentrations in the solution phase, which may occur following P fertilization, would lead to adsorption processes, initially in the readily labile forms which then move into moderately or sparingly soluble forms. The moderately and sparingly soluble forms are also in equilibrium with the occluded forms, though many of these reactions have very slow kinetics. In addition, P bound in secondary and primary minerals may also become available through weathering reactions mostly involving protons and complexing agents produced by plants and microbes. Phosphorus taken up by the plants is partly reverted to organic P forms, which may remain in labile forms or be protected from further mineralisation. Mineralisation of organic P is carried out by enzymatic reactions through phosphatases. Production of phosphatases is related to root activities and the concentration of P in the solution or labile forms. Therefore, plants play an important role in P dynamics of soils, especially in forest ecosystems.

In agricultural systems, where plants need high amounts of P over a short growing period, contributions to the supply of P by mineralisation of organic P is commonly considered to be of low significance. However, in surface layers of forest soils, organic P may form the dominant fraction of P in most cases, but the amount and rate of its mineralisation have been rarely studied. Harrison (1982) argued that owing to the high amount of organic P in forest soils, mineralisation of a small fraction of about 1% of organic P in the surface 5 cm depth layer would supply sufficient P for annual uptake. Bauhus and Khanna (1999) reported in their review about microbial biomass in forest soils that microbial P can account for 13% to 23% of total P in the mineral soil and forest floor layer respectively. Nutrients in microbial biomass are considered

to be a potentially highly dynamic pool. Given the considerations of Harrison (1982), it is clear that the turnover of microbial biomass alone can contribute a large proportion of P required for plant uptake.

The conceptual model of P dynamics in forest soils is difficult to describe in terms of either the forms involved or their solubilities or the kinetics of the reactions. For example it is well recognised that in soils of high pH inorganic P is predominantly bound to Ca, whereas in acid soils it is bound to Al, Fe or Mn. Ulrich and Khanna (1968) noted that soil pH was a major factor determining the relative abundance of different inorganic P forms in 230 forest soils of northwest Germany (mostly from Lower Saxony). However other factors such as organic matter content, soil depth, amount of calcium carbonate, waterlogging and fertilization modified the relative proportions of P forms. Soils with lime potential (A pH-0.5pCa refers to the ratio of activities of H and Ca in solutions calculated as negative logarithms of each . It is considered a better measure of soil acidity than pH alone.) values of >6.52 had on an average 62% P as Ca bound, < 1 % as Al- and Fe-bound and only 7% as organic P. Acid soils with less than 2% C (lime potential of about 2) had on average 28% organic P, only 5% P as Ca bound, 7% as Al bound and 19% as Fe bound.

Therefore the forms of readily, moderately or sparingly labile fractions depend to a large extent upon the pH of the soil. Consequently the chemical methods employed to distinguish those forms should also depend upon soil pH. However, the definition of these forms is based on the concept of decreasing solubility as one proceeds from readily labile fractions of P to those present in the primary and secondary minerals. Thus the methods have been accordingly developed to account for this solubility. When soil samples are extracted sequentially, the first easily extractable fractions belong to readily labile forms. This is followed by increasingly stronger extractions to extract moderately labile and sparingly labile forms, and then succeeded by the occluded P fraction and finally the P in primary and secondary minerals (Hedley et al. 1982, Tiessen and Moir 1993). In a similar way the organically bound soil P occurs in many different chemical forms, which differ in their degree of polymerisation and thus further transformations. Their detection and analysis needs special chemical methods. For simplicity, they are conceptually grouped into two or three fractions – P present in microbial biomass, easily mineralisable P or labile organic P, and fraction of P protected from mineralisation. By disregarding their chemical forms it is possible to use specialised methods to measure the amount of P present in these three organic fractions, which are still difficult to determine especially in organic matter rich forest soil. However as alternative on can determine organic P in the solutions obtained by
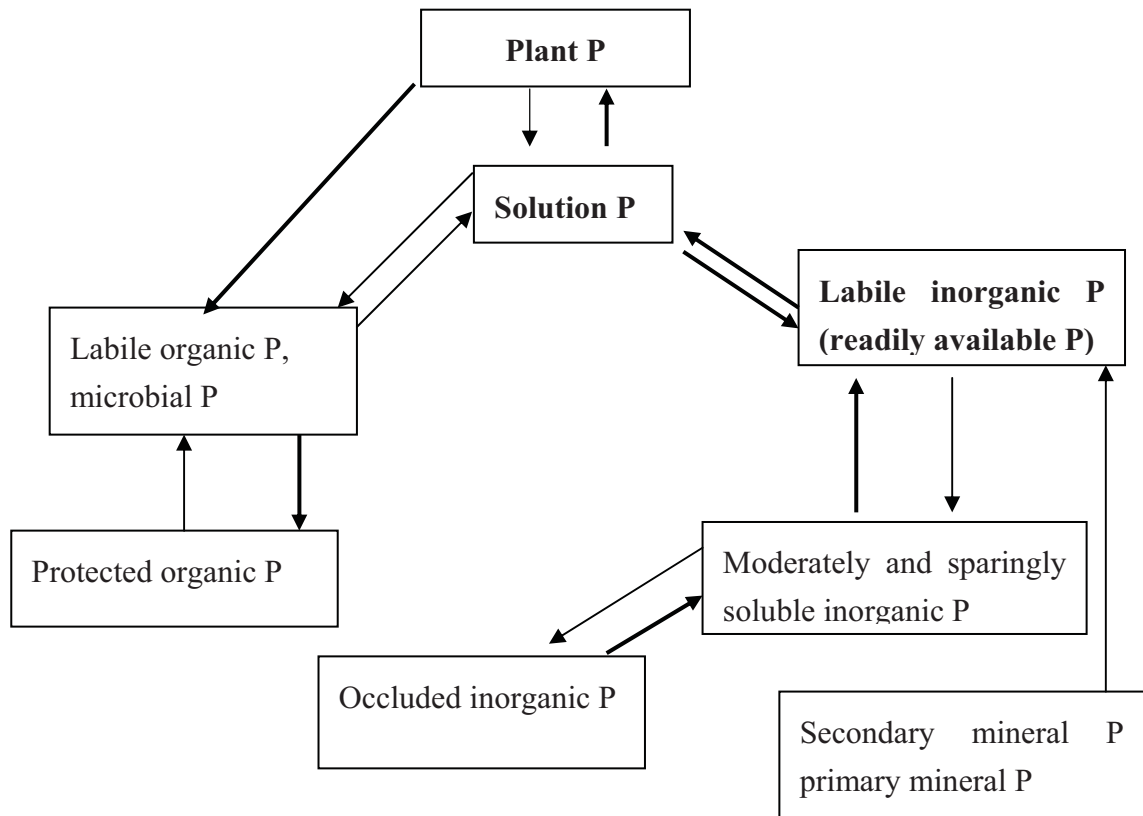
sequential extraction scheme of extracting inorganic fractions, assign a degree of lability to each of the organic fraction (Tiessen and Moir 1993). Table 8 shows one such sequential fractionation method for agricultural soils, which has also been widely used for research purposes for forest soils. We shall discuss the use of these methods for assessing changes in the forest soils of Germany.

Sequential extraction methods are highly resource consuming. As can be seen in Table 8, 7 different extractions and analyses are required to quantify the different P fractions. Therefore these methods are commonly reserved for research purposes, but are probably not suitable for routine monitoring purposes, where large numbers of samples are involved (e.g., BZE). However, there are potentially two alternatives available:

(a) to develop pedo-transfer functions suitable for calculating these different fractions in soils from soil parameters that are simple to analyse (e.g. Total P or C in the soil) (Ulrich and Khanna 1968, Ulrich 1972), and

(b) to develop a purpose-based analytical method such as to determine available P, where specific chemical extraction procedures are employed. A typical example of this approach is the wide use methods for quantifying available soil P in agriculture. These soil testing methods are specifically designed for recommending suitable doses of fertilizer inputs to crops. The most commonly used methods are outlined in Table 9. These methods include simple extraction with water (water extracts from soils which have accumulated high amounts of P through fertilizer inputs in easily dissolved forms), mild exchange of P present on solid surfaces (anion resin methods), mild extractants using anions (lactate methods Egner and Riehm, bicarbonate method by Olsen et al; fluoride methods – Bray; acid methods – Mehlich; and many others), methods described by Kuo (1996). To predict fertilizer demand of annual crops in agricultural soils, the amount of P obtained by chemical extractants is related to plant P uptake, which is measured through biomass growth and P concentration in plant tissue. Through suitable regression and other statistical methods, critical soil test values are then derived. Evidently, the purpose and usefulness of such methods for forest soils are highly questionable. Firstly, the annual P uptake is extremely difficult, if not impossible to quantify, since new tree tissue can also be built with P that has been stored within the tree or mycorrhiza, or has been retranslocated from ageing or senescing tissues. Thus the system is much more buffered against short-term fluctuations in P supply from soil. Secondly, owing to the fact that P is commonly

not applied to stimulate short-term growth where crop production cycles span many decades, soil analyses are carried out to determine the medium- to long-term P supplying capacity of forest ecosystems. Hence, there is a need to review the currently available methods used to assess their limitations and advantages with regard to this objective.

This review will consider a number of issues raised in the introduction, which will then lead to suggestions for the development of appropriate methods for future studies where medium- to long-term changes in the P status of forest soils are to be investigated.

Fig 11 : A conceptual model of phosphorus dynamics in forest soils

Table 8 : Sequential extraction procedure to define soil P fractionation and their lability with respect to P uptake (Modified from Hedley et al. 1982)

Extraction step	Lability and fractions
1. Resin Pi	Labile - soluble and exchangeable
2. NaHCO3 Pi	Labile - adsorbed
3. NaHCO3 Po	Readily mineralisable
4. NaOH Pi	Fe and Al – associated
5. NaOH Po	Slowly mineralisable
6. IM HCl Pi	Ca – associated
7. Conc. HCl Pi	Occluded P and secondary mineral P
8. Residual P – Pi and Po	Primary and secondary mineral P and organic P

Table 9: Commonly employed soil test methods to determine available P

Soil group	Soil pH	Most common P forms	Available P methods
Highly acid to acid	<6.0	Al-P, Fe-P, (Mn-P)	Bray 1 and 2, Mehlich 1 and 3, Anion exchange resin, lactate methods
Slightly acid to slightly alkaline	6.0 – 7.2	Al-P, Fe-P, (Mn-P), Ca-P, Mg-P	Bray 1 and 2, Mehlich 1 and 3, Anion exchange resin, Olsen, lactate methods
Alkaline to calcareous	>7.2	Ca-P, Mg-P	Anion exchange resin, Olsen, lactate methods

3.2   Factors affecting P status of forest soils

3.2.1   P concentration in soil solution : the controlling component of P uptake

Concentrations of about 1 mM P are commonly required in soil solution to supply P in adequate amounts to plants, however, P concentrations rarely exceed 10 µm (Bieleski, 1973). Moreover, P concentrations can vary over a wide range depending

upon soil and plant processes and the amount of P inputs. Among the several factors influencing the phosphorus concentrations in soil solution, soil pH, organic matter content, clay content, oxides of Fe and Al, carbonate content, uptake patterns of roots and microbes, and organic matter mineralisation are the most important ones. To describe changes in P concentration of the soil solution, sorption isotherms are used, which account for both intensity and capacity factors of P equilibrium in soils. These two factors and the kinetics of P release and uptake constitute important parameters for predicting the P supplying characteristics of soils for optimum plant growth. Any soil test that involves sorption isotherms is considered more accurate than conventional P analysis methods (Klages et al. 1988) as isotherms may include several factors mentioned above which influence the phosphorus dynamics in soil (Monterroso et al. 1996). P sorption isotherms describe the amount of P required to bring the concentration of P in the soil solution to an optimum level required for maximum plant growth.

Concentrations of elements in soil solution can be used to calculate the so called ' P-potentials' or 'Schofield's potentials'. These P potentials are related to lime potentials or pH values in the soil solution to obtain solubility diagrams. Such diagrams provide information on the predominant form of solid P which may be determining P concentrations in the soil solutions (Schofield 1955). One such diagram is given in Fig 12 which was taken from Ulrich and Khanna (1968). This figure is based on 230 forest soil samples from northwest Germany. All the values presented in the figure (pH, Ca, Al, P) were obtained in soil solutions by preparing saturation extracts of field moist soils.

The Fig. 12 shows a number of categories, where soils of distinct groups were combined. The groups were based on their soil pH (lime potential), calcium carbonate content, organic matter content, and soil depth (water logged soils, and those receiving fertilization were excluded). In soils of pH >6.8 and calcium carbonate of >2% of soil weight concentration of P in the soil solution was defined by Ca-P forms, which were more soluble than apatite but less than octacalcium phosphates. In contrast, in soils with <2% calcium carbonate, most samples lying on or around the octacalcium line, indicating that this form was determining the P concentrations in the soil solutions. There were very few samples in the transitional range of pH 4.5 –6.8 where Ca phosphates are changed predominantly to Al – phosphates. In soils of pH 3.5 –4.5, P concentrations in soil solutions are mainly controlled by aluminium phosphates which are more soluble than crystalline variscite but less soluble than amorphous aluminium phosphates. This is also true for strengite and other iron

phosphates at pH values <3.5. It may be mentioned here that liming may change the pH of the soil but would not change the Al and Fe phosphates in the soils to Ca phosphates.

Use of P concentrations in soil solution to predict P availability in forest soils has been advocated by many authors (recent review by Smethurst 2000), but in most cases such studies have been confined to comparison between fertilized and unfertilized treatments (Smethurst et al. 2001, Mendham et al. 2002). An important requirement for the successful use of P concentrations in soil solutions is the extraction of equilibrium soil solutions by using appropriate methods on field moist soils. Drying of soils for such studies should be avoided as it would normally show high values of P in the soil solutions which are associated with the lysis of microbial biomass (Sparling et al. 1994, Turner and Haygarth 2001; Styles and Coxon 2006).
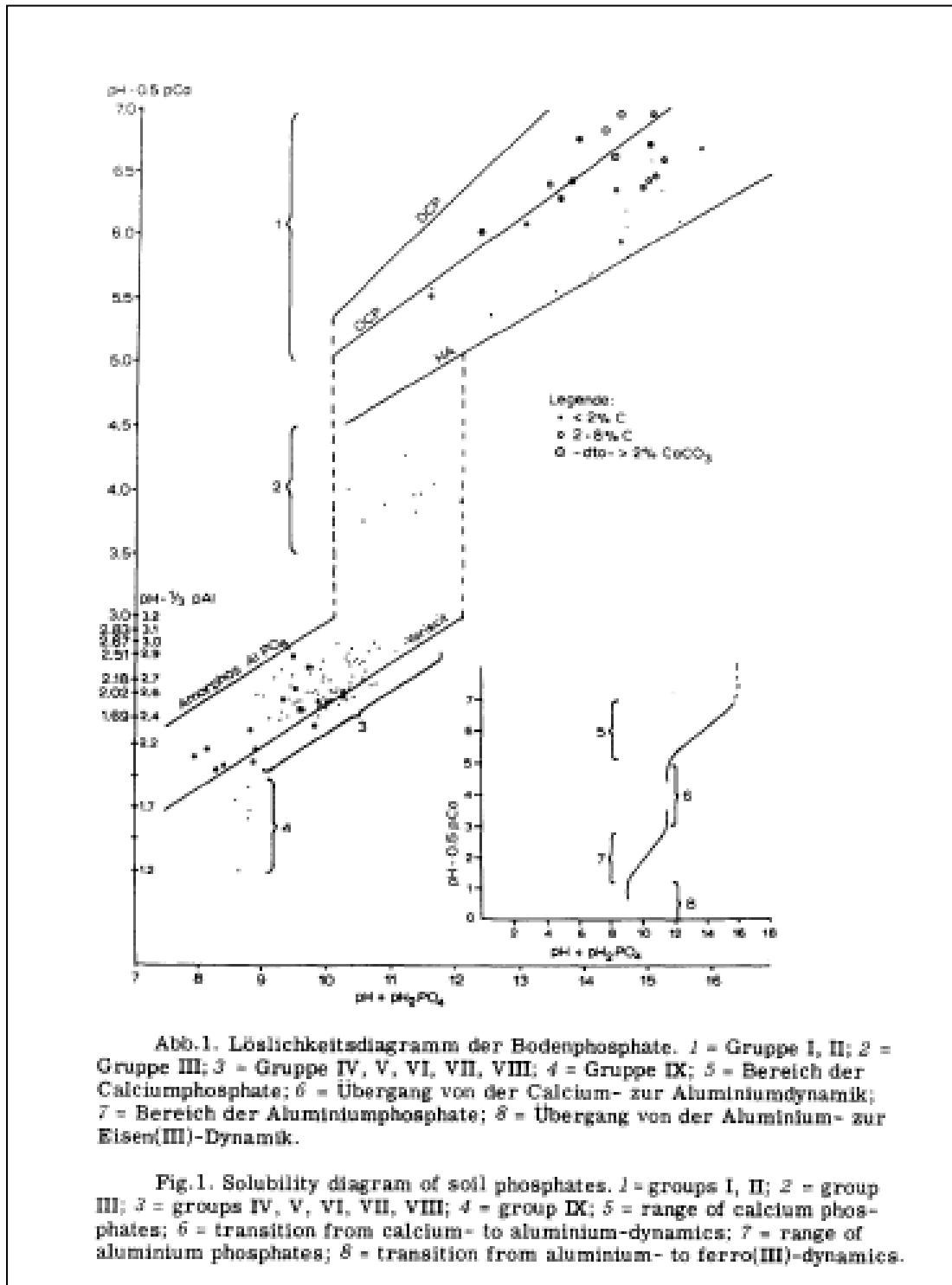
Abb.1. Löslichkeitsdiagramm der Bodenphosphate. *1* = Gruppe I, II; *2* = Gruppe III; *3* = Gruppe IV, V, VI, VII, VIII; *4* = Gruppe IX; *5* = Bereich der Calciumphosphate; *6* = Übergang von der Calcium- zur Aluminiumdynamik; *7* = Bereich der Aluminiumphosphate; *8* = Übergang von der Aluminium- zur Eisen(III)-Dynamik.

Fig.1. Solubility diagram of soil phosphates. *1* = groups I, II; *2* = group III; *3* = groups IV, V, VI, VII, VIII; *4* = group IX; *5* = range of calcium phosphates; *6* = transition from calcium- to aluminium-dynamics; *7* = range of aluminium phosphates; *8* = transition from aluminium- to ferro(III)-dynamics.

Fig 12: Solubility diagram for P in forest soils of northwest Germany

3.2.2   Inorganic forms of P - desorption and retention processes

The forms and relative quantity of different P fractions in soils depend on a number of soil properties (described above), environmental conditions and management factors (biomass removal, fertilization, litter inputs, fire). Three parameters are considered important in defining the P availability in soils: a) the intensity of P retention in the solid phase (binding with respect to desorption processes), b) the capacity or the amount of P retained (amount of P in the binding forms which undergo desorption reactions, also described as labile P) and c) the kinetics of P release to soil solution. The intensity parameter is described by the P concentration in the soil solution (discussed above). The soil property controlling the relationship between the solid phase P and its concentration in solution is known as the buffering capacity. The solid phase P involved in this relationship is only a small proportion of the total P, and is known as labile P. It is usually measured by isotopic exchange, but this exchangeable P component does not include the sparingly soluble compounds that also get replenished by plant uptake. The buffering capacity is the ability of the soil solution to resist a change in its P concentration as P is removed by plant uptake, or is added in the form of fertilisers or organic materials. Relationships between the concentration of solution P and the amount of labile P (sorbed P) are experimentally obtained (also called sorption isotherms), and by fitting a suitable equation, such as the Langmuir, the total sorption capacity as well as the sorption strength can be determined. Buffering capacity determines the ease of desorption of labile solid phase P, its diffusion and thus its uptake. One very simple and widely used method to compare P sorption by different soils is to determine single point adsorption and calculate an index as was suggested by Bach and William (1971).

Following from the above, available P is a direct function of the quantity of labile P and an inverse function of buffering capacity, and the most effective methods of measuring available P (soil tests) are those which remove a proportion of labile P that is inversely related to buffer capacity (Holford 1997). The quantity of labile P in a soil that is required to construct the sorption isotherms is difficult to assess and many methods are used for that purpose. Among these, the use of the isotopically exchangeable fraction, use of anion exchange resins, or in recent years the use of Fe-impregnated paper are common. Ulrich and Khanna (1968) investigated the isotopically exchangeable fraction of a number of forest soils and reported the following general observation. When the amount of Al- and Fe-phosphates were low in soils, the fraction of them occurring as isotopically exchangeable tended to be quite high (60-80% for Al-P, and 10-30% for Fe-P) indicating a low degree of crystallinity

of these compounds under such soil conditions. Only under very high acid soil conditions did these P forms show a high order of crystallinity as evidenced by their low (<10%) isotope exchangeability. Most of P in such cases is poorly available to plants. How fast these changes can occur and whether the decrease in P status of soils may be a consequence of atmospheric inputs are questions which have not received due attention. Two other issues need mention here: (a) there is a lack of studies where the pattern of P desorption has been studied in the unamended forest soils. Most studies on P desorption have involved soils which were first experimentally enriched with P; (b) one should keep in mind that the quantity parameter involved in plant uptake will never be a defined value as it will be both time-specific and plant-specific.

3.2.3 Organic P forms - mineralization and immobilization processes

Organic P in forest soils occurs in many chemical forms (Harrison (1987). In leaf litter, organic P occurs as orthophosphate monoesters, diester phosphates and phospholipids. Through bacterial and fungal decomposition these are converted into inorganic forms of diphosphates, polyphosphates and phophonates (Cade-Menun et al. 2000, Turner et al. 2004, Koukol et al. 2006). To distinguish the various forms of phosphorus present in soil and organisms, ^{31}P NMR spectroscopy can be used (Cade-Menun et al. 2000, Turner et al., 2004).

In their review on microbial biomass in forest soils, Bauhus and Khanna (1999) reported that the mean amount of microbial biomass P in the mineral soils was 73 mg/kg (13.3 % of total P) as compared to 233 mg/kg (23% of total P) in the forest floor samples. These high values of microbial P indicate their potential to affect the plant uptake and other mineralization processes in soils. Sparling et al (1994) estimated an annual flux of 22 and 18 kg P/ha through microbial biomass in a *Nothofagus truncata* forest and *Pinus radiata* plantation respectively in New Zealand. These values are much higher than the amount of P required for vegetation uptake and therefore illustrate the potential contribution from this fraction.

For the extraction of organic P fractions in soils, similar extractants as used for inorganic P forms are sometimes used (NaHCO$_3$, NaOH, acid digestion). In some cases a good relationship between the total C and different organic P fractions is reported. This relationship between the two may be related to mineralization, or to sequestration or retention of C in soils together with P retention. The so called 'old' humus may contain less P than the newly formed humus (Bradtberg et al., in review).

Mineralisation of organic P does not follow the same pattern as N, whereas very little N is released during the initial phases of litter decomposition, causing the C:N ratio to increase in the decomposing litter, a significant amount of P is released, before it follows the same pattern of decomposition as for N.

3.2.4 P uptake - Role of rhizosphere and mycorrhiza activities

Presence of mycorrhiza may facilitate the uptake of P under acidified rhizosphere conditions. Gillespie and Pope (1991) reported that P plant uptake rates were similar at both pH 4.0 and pH 7.0 by non-mycorrhizal black locust (*Robinia pseudoacacia* L.), whereas in plants with mycorrhizal associations, the rate of phosphorus uptake at pH 4.0 was twice that observed at pH 7.0. Depending on the soil type five-fold differences in the P diffusion rates were observed in the six forest soils using desorption-isotherm buffer power assays. There are many studies in this special area of research and the Mycorrhizal Information Exchange (MIE) website at the following address provides the pertinent literature

(http://mycorrhiza.ag.utk.edu/).

The following issues should be mentioned in the context of this review:
1. Phosphate uptake is a diffusion processes which occurs a few mm around the fine roots and mycorrhizal filaments, thus the rhizosphere play an important role in the amount of P taken up by plants.
2. A number of rhizosphere processes would affect the solubility of inorganic P, the most important ones are the changes in pH, exudation of inorganic acids by roots.
3. Mycorrhiza play an active role in the uptake of P by intensive exploring of soil volume, and through exudation of acids and enzymes.
4. Phosphate being an anion, other anions will compete with its uptake. Thus interactions with other ions in the rhizosphere are important determining factors for P uptake.
5. Fine roots and mycorrhiza are highly sensitive to acid conditions and high levels of nutrients in the soil.

3.2.5 Use of soil tests – limitations and possibilities

Many chemical solutions are used to extract P from soils. With any extracting solution, four basic reactions are involved by which P is removed from the solid

phase: a) anion replacement to enhance desorption, b) complexing of cations binding P to release P, c) hydrolysis of cations binding P to release P and d) dissolving action of acids. Therefore, the selection of a soil test for P should depend on extracting P from certain chemical forms of interest based on the soil characteristics.

Some these methods are reviewed below:

Among the use of different extractants the use of water to extract P from soils is restricted to soils, to which very high amounts of P have been added and are present in easily dissolved forms in soils. This is not the case for forest soils in general. Only small amounts of soil P can be extracted by water creating problems in chemical analysis. However despite the very low absolute values obtained by water extraction, these values relate to the intensity parameter of P availability in soils and have been used in relating them to capacity parameters of soil P obtained by using other methods (see Ulrich and Khanna 1968). The limitations of its wide scale use are both the cumbersome extraction procedures to achieve equilibrium solution phases and the use of such methods for huge number of survey type soil samples.

One of the most common methods used for forest soils is the so called Bray method (Bray and Kurtz 1945). The extractant is a mixture of HCl and NH_4F, where F acts to complex the Al and Fe and the P bound to them is released. The amount of acid added is sometimes varied depending upon the form of P to be extracted. The extractant with low HCl concentration is called the Bray1 method. This method is specifically designed to be used in acid soils. Bray 1 and Bray 2 (high HCl concentration) methods are commonly employed for forest soils, especially those with high amounts of organic matter. This method has been used to show short term changes in the soil due to treatments such as fire (Romanya et al. 1994), soil heating (Serrasolsas and Khanna 1995), or fertilizer additions. However, Compton and Cole (1998) reported that alder stands which had higher P dynamics (uptake, litterfall content, resorption values) than Douglas fir stands, had lower Bray P value and total P in the soil, suggesting that the quantification of an available P pool alone does not adequately reflect P supply in forest stands. When nutrient pools are small, the flux through these pools, must be considered as well to obtain a realistic picture of nutrient supply from that pool.

For calcareous and alkaline soils the method commonly used employs 0.5 M $NaHCO_3$ solution at a pH of 8.5 to extract available soil P (Olsen et al. 1954). This extractant decreases calcium in solution (through precipitation of calcium carbonate), and thus

enhances the dissolution of Ca-phosphates. Moreover, this extracting solution removes dissolved and adsorbed P on calcium carbonate and other surfaces (Al- and Fe-oxide). As expected, this method would extract a significant amount of organic matter and thus P associated with it. In recent years, this method has been included in the sequential extraction procedure, where both the inorganic P and organic P forms extracted by this method are described as readily labile forms. There is very little evidence to show that the organic P fraction extracted by this reagent is readily mineralisable and can be treated in the same category as the inorganic P fraction. This method has been used to detect short-term changes in the amount of P in forest soils. For example, Bekunda et al. (1990) showed that changes in the amount of inorganic P owing to different forms of slash management at the time of plantation establishment could be measured by the $NaHCO_3$ method with good results, though not for organic P measured in the extract.

Solutions containing lactate and citrate anions are also extensively used to release P in soil test methods. These methods are based on the desorption and exchange of P from various soil components. In Germany, Scandinavia and many East European countries different versions of the lactate method which was suggested by Riehm (1947) are used. Of the two commonly used versions, CAL (calcium lactate and acetic acid at pH 3.5) dissolves less P than the DL (Double lactate) method. The method extracts comparatively low values of P from forest soils, when compared to soils from agricultural land uses, as can be been in the Fig 13 taken from Leinweber et al. (1993). Thus the usefulness of the method to detect small changes in P status of forests soils is highly questionable. This method may however be useful for assessing short term changes in forest soils, eg., after fertilizer additions.

Mehlich used a combination of HCl and H_2SO_4 acids (Mehlich 1) to extract P from soils in the north-central region of the U.S. which he modified (Mehlich 1984) to develop a multi-element extractant. Mehlich 3 extractant is a combination of acids (acetic and nitric), salts (ammonium fluoride and ammonium nitrate), and the chelating agent (EDTA). This is a commonly used method, also for forest soils in parts of USA. These methods as the other methods mentioned above provide useful results for specific short term changes in P status, but as shown by Richter et al. (2006) this method could not predict the long-term amount of P taken up by an aggrading pine ecosystem.

Use of anion exchange resin acting as a sink to extract P has been in use for a long time. In recent years an impregnated paper with anion exchange resin (Sharpley 2000)

or Fe-oxide impregnated paper (Menon et al. 1989, Chardon 2000) have also been used as a P-sink to determine available P in a wide range of soils.

Given the wide range of methods to test for different P fractions in soils, it is very important to select the right test for specific soils and target fractions. The soil properties affecting selection of the appropriate P test and recommended methods are outlined in the Table 9.

Da Silva and Van Raij (1999) reviewed different methods of measuring the available P content in agricultural soils. The methods considered were: anion exchange resin, Olsen, Bray 1, Bray 2, Mehlich 1, Troug, Egner, water, 0,01M CaCl2, iron hydroxide impregnated filter paper (Pi) and the determinations of the E and L values. Details about these methods are given by Kuo (1996). Average values of the goodness of fit for regressions between the soil test method and P uptake of plants and corresponding numbers of articles (in brackets) in which the method was considered were obtained, showed the following descending order: resin, 70% (34); E value, 68%(16); L value, 65% (8); Olsen, 54% (48); Bray 1, 50% (42); Mehlich 1,46% (25); Egner, 44% (9); Bray 2, 42% (19); Water, 42% (15); Truog, 38% (13); CaCl3, 36% (13), and Morgan, 32% (13). The results show that the anion exchange resin method was superior to other methods. It has the additional advantage that it can be used for both acid and alkaline soils, has probably the best theoretical basis, and does not overestimate the amount of available P as may be the case when insoluble P forms get dissolved by acids extractants.

Neyroud and Lischer (2003) compared the methods used for soil P availability across Europe which involved 16 different methods on 135 soils from 12 countries. Each European country was using its own method for the determination of phosphorus availability to plants, together with an appropriate interpretation scheme of the P status and fertilizer recommendations. The amount of extracted P decreased in the order $P_{total} > P_{oxal.} > P_{AL} > P_{Me3} > P_{Bray} > P_{AAEDTA}, P_{DL}, P_{CAL} > P_{Olsen} > P_{paper\ strip},$ $P_{AAAc}, P_{Morgan} > P_{H2O}, P_{CO2}, P_{CaCl2}.$ Isotopically exchangeable P was also measured. Even though all the methods reacted in the same way to increasing amounts of added P in several trials, there were wide differences between results obtained with different methods. The interpretation schemes for P status suggested that about 50 % of the tested soils were P-deficient.

Sibbesen (1983) ranked different P-tests on the basis of data from 29 published papers into three groups: best group: anion-exchange resin method; intermediate group:

water, and sodium bicarbonate methods; worst group: all acid methods including acetate buffer, lactate buffer, citric acid, Bray-1, Truog and Bondorff methods.
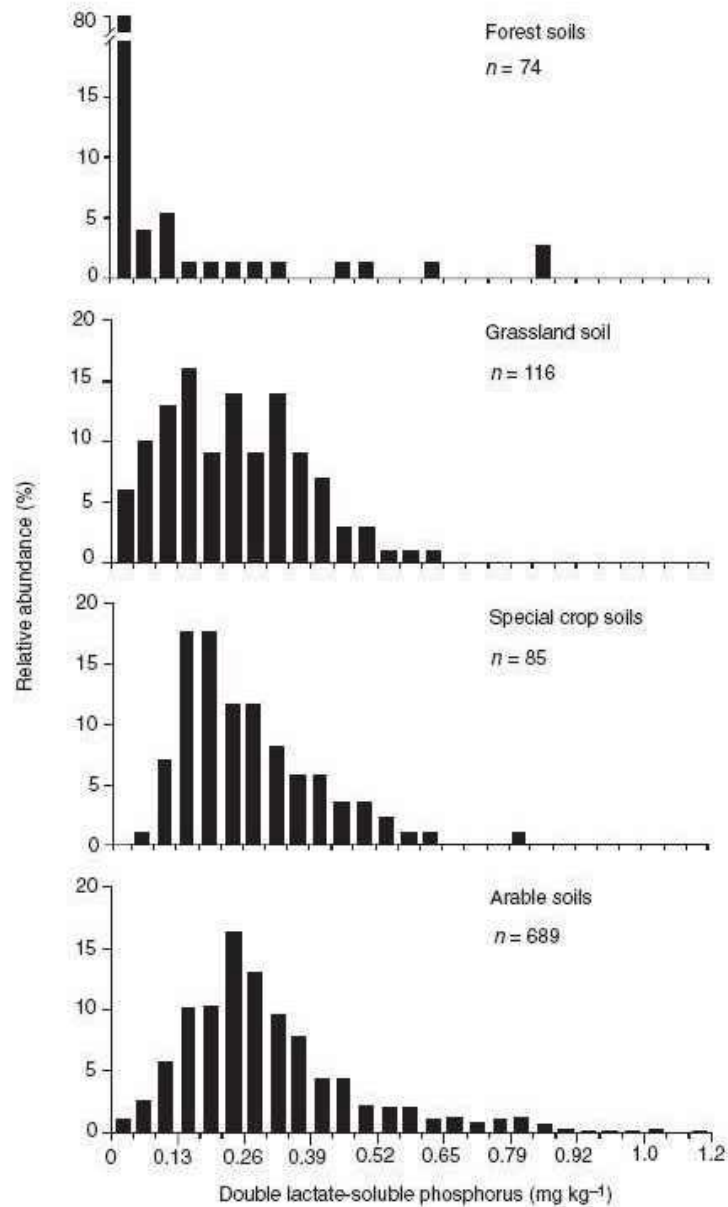

Fig. 2.3. Frequency distribution of soil phosphorus test values in a densely stocked area in north-west Germany (Leinweber et al., 1993).

Fig 13 : Frequency distribution of soil samples against double lactate soluble P concentrations in soils from different land uses. Values obtained for forest soils are very low

For the older compiled information on the use of soil test methods for forest soils refer to Ballard (1980). In their recent study (Mendham et al. 2002) compared different methods to distinguish fertilized and unfertilized sites for determining available P and suggested that the use of CaCl2 soluble P provided the best results with respect to the growth responses in Eucalypt plantations. Khanna (1994) evaluated various indices for measuring P status of forest stands by using both plant based and soil based parameters from Pine and Eucalyptus sites. Plant based parameters were P concentrations in the foliage, fine roots, and leaf litter, and plant bioassay (^{32}P uptake by roots) and phosphatase activity of fine roots. Soil based parameters included P extraction, anion exchange and Fe-impregnated paper, microbial P, phosphatase activity in soils, and P mineralisation under laboratory conditions. He concluded that P content in the fine roots, and Fe-impregnated paper may be most useful to assess P status of forest stands.

The soil test methods were developed by involving some basic soil chemical principles. Thus P extracted by these methods does not provide any arbitrary value but a defined fraction of soil P. Some of these methods have been used for forest soils, mostly to describe the P status in comparative situations, or to describe the immediate effect of fertilizer or other silvicultural treatments (fire, removal of harvesting slash, windrowing, addition of thinning slash). Absolute available soil P values obtained by any of these methods are difficult to calibrate for forest stands using growth or other responses and thus cannot be used to describe the long-term P supplying status of these soils.

There are two other main issues which should be addressed:
1. As forest soils contain high amounts of organic P, many of these methods which use high pH solutions will extract excessive amount of organic matter, creating problems in the measurement of inorganic P.

2. Many forest soils are highly acid and it is possible that the amount of Al complexing agent, e.g., F in Bray's method may be too low to release P from soils. However repeated addition of NH_4F solution in sequential extractions may overcome this problem, which arises because such methods were not developed for forest soils.

Table 10. Estimated transfers and changes in mineral soil P fractions after 28 years (soil depth – 0-60cm) following establishment of a pine plantation. Details of the method in the text and Table 8 (taken from Richter et al. 2006)

P flux or component	28-year change in soil P (kg/ha)
Total P changes in mineral soil (retention in vegetation and forest floor, minus atmospheric inputs)	82.5
Soil gains (+) and losses (-)	
Resin Pi	0
NaHCO3 – Pi	+22.0
NaHCO3 – Po	0
NaOH – Pi	-3.4
NaOH – Po	-22.8
1 M HCl – Pi	-52.2
Residual P	0
Total P (sum of statistically significant changes)	-63

3.2.5 Soil P measurement by sequential fractionation

A chemical fractionation method for P in soils was initially provided by Chang and Jackson (1957) which was later modified (Hedley et al. 1982) to better represent plant-available and non-plant-available P forms in soils (Tiessen and Moir 1993) (Table 8). This method is commonly modified to suit the aim of a study, site conditions and laboratory facilities. The fractionation also provides a valuable index of the relative importance of biological processes to soil phosphorus content across a soil weathering gradient (Cross and Schlesinger 1995).

The fractionation scheme involves the sequential extraction of (a) soluble and exchangeable P by anion exchange resin or iron oxide-impregnated filter paper strip (Menon et al. 1989); (b) readily available forms by sodium bicarbonate to removing the inorganic P (Pi) adsorbed to iron and aluminium surfaces, and organic P (Po), which may include P from lysed microbial cells, nucleic acids, phospholipids etc.; (c) moderately to strongly bound forms by sodium hydroxide which may remove Pi retained by iron and aluminium, and organic P stabilized partially as soil organic matter; (d) moderate to strongly bound to calcium by 1 M hydrochloric acid (HCl);

(e) strongly bound occluded Pi forms within sesquioxides by strong HCl; (f) highly resistant Pi in secondary and primary minerals.

The fractionation methods are very widely used with different levels of success to assess P status of forest ecosystems. We present here the results of three case studies:

(a) Compton and Cole (1998) compared P cycling between Douglas fir and red alder stands. Total ecosystem P in the alder stand was 69% of that found in the Douglas-fir stand (inherit site difference), but the alder stand took up 61% more P annually than Douglas-fir and also showed higher fluxes of P in litterfall (94%) and resorption (292%). But all the P extractable fractions, which are meant to represent available soil P, were lower under alder. They came to the conclusion that all static measures (pools) of available P do not appear to adequately reflect P supply in these forest stands.

(b) Binkley et al. (2000) investigated P dynamics in *Eucalyptus* and *Albizia* pure species stands, and also in 1:1 mixture of the two species. A P fractionation technique with a slight modification (Fe impregnated paper) was used instead of anion exchange resin to obtain easily desorbed P fraction - solution Pi. *Eucalyptus* had higher productivity, but both sites had similar amounts of P uptake at age 15 yrs. For most P-fractions there was no effect of tree species except HCl-P, which was lower in Albizia than Eucalyptus soil (HCO_3-Po was high in Albizia soil but NaOH was high in Eucalypts). However, solution Pi was high in Eucalypts.

(c) Richter et al. (2006) attempted to quantify changes in P fractions in an Ultisol during the growth of an old-field pine forest from 1957-2005. Soil sample were collected in 1962, 1968, 1977, 1982, 1990, 1997, and 2005 and different P fractions and available P using the Mehlich III method were determined. The net transfer of P from mineral soil into tree biomass and O horizons was 82.5 kg ha^{-1} over a 28 year period (Table 10). However, this did not diminish the amount of labile soil P (anion-exchange resins, and NaHCO3 and Mehlich-III extractants). Substantial decreases in slowly cycling Po and Pi associated with Fe and Al oxides and Ca compounds occurred during 28 years of forest growth, and these accounted for much of the P supplied to biomass and O horizons, showing the long-term dynamics of P in soils as discussed above (Fig 11). Changes in soil P are small in this aggrading forest (2.9 kg ha^{-1} y^{-1} over 28 yr).

3.3 Use of pedo-transfer functions to assess availability and the amount of available soil P

Pedo-transfer functions (PTF) are predictive functions for soil properties, which are not easy to measure but can be derived from other more-available, easily, routinely or cheaply measured soil parameters. McBratney et al. (2002) used the term 'soil inference system', where pedo-transfer functions are the knowledge rules for soil inference engines. A soil inference system takes measurements with a given level of certainty (source) and by means of logically linked pedo-transfer functions (organiser) infers unknown data with minimal inaccuracy (predictor). Pedo-transfer functions thus utilize different regression analysis and data mining techniques to extract rules for soil properties which are difficult to measure.

For this review we intend to consider the possibility of using pedo-transfer functions to assess the amount of different P forms in forest soils, which would enable the evaluation of long term soil P changes in forest ecosystems. Earlier attempts have led to regression relationships which were based on 12 different sites collected in Lower Saxony (Ulrich and Khanna 1972, Khanna and Ulrich 1969, Ulrich 1972). The basis of these relationships are described below in short:

- Total P (Pt) is considered to be a function of organic C in the surface soils which can be described by the equation Pt = a+b (%C). Here the assumption is that Pt follows the depth-wise distribution parallel to that of C and the parameter 'a' describes that fraction of P in soil, which does not undergo any biologically driven P transformation and translocations. The value of 'a' is thus based on the type of bedrock material, which was found to be 5 mg P /100g for silicate-poor diluvial sand (site - Meppen), 10 mg P/g for the diluvial sand which had medium amounts of silicates (site - Sprakensehl), 32 mg P/g for the soil from loess on sandstone (site – Solling). The value of 'b' in the equation can range from 2 to 7 depending upon the soil type and rooting depth. The significance of assessing the distribution of total P in soil in relation to organic matter content is indicated by the role of biological parameters in the transformation and translocation of P in a soil profile.

- Now assuming that occluded P fractions (P_{occl}) (which also includes secondary or primary silicates) are not taken up by the roots and are not involved in the retranslocation processes, one can define the fraction of occluded P as : P_{occl} / Pt x 100 = a+b log(%C). The values of parameter 'a' may vary from 30-45% and that of parameter 'b' which has negative values of 18 – 31. Ulrich (1972) suggested

that these values should be validated for different soil types, but as a first approximation a value of –25 can be used.

- By using the above values, Ulrich (1972) calculated the amount of mobilisable or labile fractions of P for two types of sites: (a) for diluvial sands with medium amounts of silicate content there may be 530 kg P /ha mobilisable P in 0-50cm depth and (b) for an acid brown earth developed from loess mobilisable P content in 0-25 cm depth may be about 1550 kg/ha.

- These values of mobilisable P are much higher than the small changes which are expected to occur in the short period of 10 or 20 years of tree growth or even during a period of one rotation. However P fractions may provide useful information on substantial losses associated with erosion of surface soils or long-term litter-raking activity where a significant proportion of organic or mobilisable P is missing (Ulrich and Khanna 1969).

It is evident from the above discussion that it is possible to develop pedo-transfer functions, but they cannot be developed based on the above given relationships for a small number of sites. Depth-wise distribution of different P forms from a wide range of soils will be required to test and develop such relationships further. In the context of BZE analysis this does not seem to be a practical way to follow.

3.4   Suggested method to assess changes in P status of soils

There are a number of issues and requirements, which need careful consideration before an appropriate method can be suggested for future use to assess changes in soil P reflecting the P status of forest ecosystems. In our view the most important issues are:

1. Short- versus medium- to long-term availability of soil P. It is important to understand that contrary to the agricultural systems, where only short term availability of P is of interest, forest ecosystems require both short- term and long-term assessment of availability and the amount of P available. To determine short-term changes it is possible to adapt some of the methods developed in agriculture. But for medium- to long-term changes forest-specific methods will be required.

2. The assessment of P availability will not always provide the amount that may be taken up by the trees as there are site and plant specific factors which determine

the amount taken up at each site. The assessment methods will always provide values which are optimum and comparable for different sites.

3. A number of plant factors such as the growth, withdrawal and reuse patterns for P will determine the amount of P required for uptake. For a complete assessment of P status of any specific site these factors, which describe the flux of P through the system, should be included in the observation.

4. Forest soils are rich in organic matter and mostly highly acid. Any suggested method should include these special characteristics of forest soils.

We have considered different alternatives and have come up with the following preferred option of a suitable method to study medium to long term changes in P status of forest soils in Germany.

Desorption of soil P by repeated sequential extractions using an anion based appropriate extractant

This method is based on the common observation that the amount of P extracted by an anion based mild extractant (or anion exchange resin) provides very low values for P, which are not related to the dynamics of P in the soil. They may provide information on short-term P changes in soils due to fertilization, litter changes, soil disturbance etc. but fail to provide information on the long-term changes in soil P. Adequate examples have been provided in the review to show that. This is primarily due to the fact that single measurements of P pools fail to capture the dynamics of P desorption from the soils which includes buffering capacity of labile P and the pattern of its release. This can be achieved by repeating the extraction of a soil which is carried out sequentially for sufficient number of steps so that the rate of P release starts to decrease and sufficient data points are available to assess the amount of desorbable P and the rate of desorption. An example of such a method is shown in Fig 14, where two forest soils were sequentially extracted for a number of times using Bray 1 extractant (commonly used for acid soils) (Serrasolsas et al. in review).

As shown in Table 11 , the two soils were similar in many characteristics but differed significantly in P values. Both soils were low in P retention capacities. P fertilisation experiments on the two sites showed no growth response in one (*Pinus radiata* plantation) but a big response in the other (*Eucalyptus* regrowth) stand. The pattern of P released by stepwise extractions was fitted using the equation $y = A (1-e^{-Bx})$ where y represented the cumulative amount desorbed for a cumulative x ml of

Bray extract. A is the total desorbable amount and B is the rate of desorption.
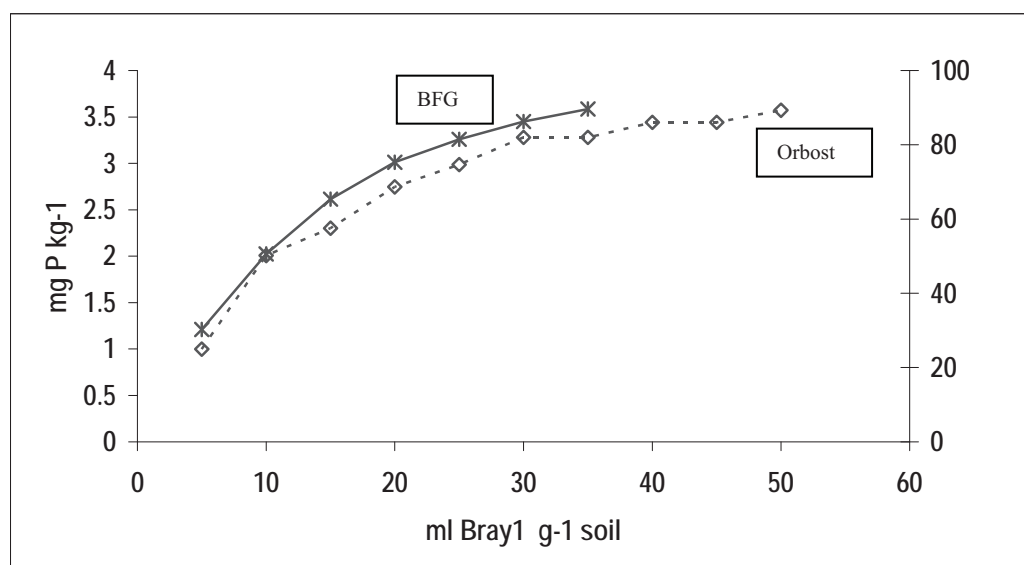
Fig 14 : Cumulative desorption of P from two sites, Orbost and BFG, (secondary Y axis) using Bray 1 extractant repeatedly.

Table 11: Data on soil characteristics, response to P application and a and b parameters from desorption equation $y = a(1-e^{-bX})$ are given. A refers to the total desorbable amount and B to the rate of desorption. (Serrasolsas et al - in review)

Sites	BFG	Orbost (Du)
Soil Type	Yellow podzolic	Yellow podzolic
Organic C (g/kg)	17	32
Total P (mg/kg)	252	68
Bray 1 – P (mg/kg)	30.2	0.46
A	96.6	2.9
B	0.075	0.034
P fertilizer response	None	Large

A number of extractants are available for desorption and an initial study would be required to decide one or more appropriate ones for the whole set of BZE samples. Among the methods available, an extraction with an anion resin method, where resin

is commonly saturated with HCO_3 is mostly used, but OH saturated resin is also used. Resin beads are packed in bags (Brewster et al. 1975, Sibbesen 1978, Bache and Ireland 1980) for such studies or more recently, anion exchange resin papers have been successfully used to desorb P from soils (Saggar et al. 1990, Schoenau and Huang 1991, Nuernberg et al. 1998, Sato and Commerford 2006). It appears that there is no experience on the use of anion resin papers to desorb P from organic rich forest soils of Germany.

A repeated extraction method has been suggested by others (Delgado and Torrent 1997, Bhatti and Comerford 2002,), but this has not been used for desorption of native P. Such a method will also provide parameters which can be used later for models involving kinetics of P desorption (Koopmans et al. 2004). A set of selected soils from BZE2 should be included for preliminary experiments and for obtaining desorption isotherms.

- **Further development of methods to assess desorption parameters for BZE2 samples**

The suggested method is resource intensive and not suitable for wide range of survey work. There are two possible alternatives which would require further experimental development:

(a) use of pedo-transfer functions to find relationships between easy to measure soil parameters and desorption parameters obtained from the sequential extraction procedures. A number of attempts have been made recently to find out if the adsorption and desorption parameters can be estimated by means of pedo-transfer functions (Borggaard et al 2004, Barros et al 2005). Barros et al (2005) considered the possibility of using pedo-transfer functions to assess the desorption and adsorption parameters of Cerrado soils. They considered clay content and the amount of labile P on soil surfaces to relate to Kd values of resorption and desorption isotherms. Phosphorus desorption was measured using anion-exchange membranes. Sorption was a function of soil clay content, and a pedo-transfer function for the soil partition coefficient was calculated with an $r^2=0.99$. Desorption and resorption were dependent on both the clay content of the soil ($r^2=0.59-0.99$) and the amount of sorbed labile P.

This procedure may not be useful unless soil parameters required for estimating pedo-transfer functions are available for each site, which in BZE 2 may not be the case. But

it may be still worth considering a trial for a restricted number of sites such as intensive monitoring (Level II) sites.

(b) The second possibility is to use surrogate measures such as near infrared (NIR) or mid infrared (MIR) spectroscopy and develop statistical models for which the data of selected samples for desorption set would be available. NIRS is a simple and cheap technique to handle a big set of samples as will be available for the BZE. There have been a number of studies reported in literature, where this technique has been tested for assessing P in the soil and plant samples. It has shown to be useful for studying retention of P by Al and Fe rich humus soils (Giesler et al 2005).It is routinely already used in some laboratories for C and N analysis.

In short the suggested development of a suitable method will include the following steps:

1. Preliminary experiment on a small set of samples from BZE collective to test the suitability of different anion based extractants including anion resin exchange methods. The subset of BZE1 samples that cover the wide variation in soil conditions encountered.

2. A set of suitable soil samples will be selected from BZE collective to develop desorption procedure including the fitting of the desorption isotherm to obtain the capacity and the rate functions. The number of samples will depend upon the different types of soil matrix to be included in prediction models.

3. This set of soil samples will be used for NIRS and/or MIRS analysis and appropriate calibration and validation models will be developed to obtain parameters of desorption isotherms.

4. All soil samples in the BZE collective will be analysed with NIRS or MIRS to predict the desorption parameters. Desorption parameters will then provide soil data to assess the status and changes in the P supply of soils.

3.5   Summary of P in Forest Soils

Dynamics of P in forest soils involve both the organic and inorganic fractions which are in different dynamic equilibria involving various processes of mineralization, immobilization, desorption, solubilisation, retention and uptake. It is therefore hard to

assess P status or any changes in P status of soils by using simple methods, rather the complex nature of interactions requires special techniques often involving a number of different methods. It was shown that P in the soil solution phase determines P uptake but it is the most dynamic component of soil P. Through solubility product diagrams it has been possible to assign the dominant inorganic forms of P which may be determining the concentrations of P in soil solutions. A conceptual framework is normally used to assign differences in the lability of different soil P fractions with respect to their availability for uptake. Sequential extraction methods are used to obtain P fractions which are differently labile. However, not the easily labile fractions undergo changes in the long term but in many cases the fractions of moderate to low turnover indicating the dynamic equilibria occurring among different forms of P. This creates a problem for selecting the suitable chemical fractions which could be extracted by appropriate methods. Consequently there are many different types of soil P tests which are used both in agriculture and forestry. Agricultural methods have been developed specifically to provide fertilizer recommendations for crops, and are thus of limited use to describe the long-term P status of forest soils. The limitations and advantages of various methods have been described.

We recommend a method including repeated extractions of soil P by using an appropriate extractant. The selection of extractant(s) would require some initial studies. Such a repeated desorption of P from soils will provide a capacity factor giving the amount of labile fraction and a desorption rate function which may be related to soil characteristics. Any change in those two parameters would then indicate a change in P status of soil. The development of the method should be done on a small but representative set of soils of the BZE collective. In order to save resources, for the rest of the samples these parameters may be obtained by developing suitable models using NIRS or MIRS techniques. The proposed method will still require a high level of resource commitment to be made available in future under the BZE program. Despite the major concerns of changes in P status of forest soils, this area of research has not received sufficient attention in the past.

4. ACKNOWLEDGEMENTS

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