

Determining the agricultural ammonia immission using bark bio-monitoring: comparison with passive sampler measurements

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Bark samples of spruce, pine and oak trees were collected at two sites in southern Bavaria which are characterized by high agricultural ammonia emissions. The samples were taken using a recently developed bark sampling device which removes a defined layer of the bark. The bark was then analysed for ammonium concentration in order to reflect the environmental ammonia immission. The measured bark concentrations decreased with rising distance between the sample trees and the ammonia source. This applied (i) to measurements inside a closed forest stand ranging from forest edge with high immission to forest interior with much lower immission, and (ii) to the open field where single-standing trees were sampled. Comparing the ammonium concentrations among the three different tree species revealed significant correlations. Thus, it could be shown that old spruce trees are as usable for bark bio-monitoring as the traditionally used pine and oak trees. The ammonium concentrations of the bark were significantly correlated to measurements taken by ammonia passive samplers at the same locations. These results indicate that bark samples may be used for a standardised monitoring of airborne ammonia load. A major advantage of the technique is the determination of the long-term accumulative ammonia load using a single measurement.

1 Introduction

1.1 General considerations and problems of bark monitoring

In recent years, tree bark from different tree species has been rediscovered for the monitoring of airborne pollutants. The pollutants accumulate on the outermost cork layer of the bark which is exposed to the air. By analysing the pollutant concentration in the bark, the environmental air pollution surrounding the trees can be determined.

Bark monitoring started in Sweden^{1,2} and Eastern Europe.^{3–6} It was used to determine heavy metal,^{7,8} acidity and sulfur pollution around industrial emitters.^{9–12} A literature review was written by Walkenhorst.¹³ Recently the method was extended to organic and inorganic compounds such as nitrate, ammonium, polycyclic aromatic hydrocarbons (PAH), semivolatile organic compounds (SOC), and even the isotopic composition of elements was added.^{10,14,15}

Tree bark is an ideal natural adsorbent as it is dead tissue that does not grow anymore, unlike mosses, lichens, leaves or needles. Exposed to the air for years, it is an indicator for the air pollutant concentration. For bark monitoring it is advantageous to use different tree species in order to find enough adequate sample sites, as tree species have different mean exposition times of their bark. For example, oak trees expose their outer bark layers for at least 5–8 years until it is weathered or scaled off, whereas pine bark has an exposition interval of 1 to (max.) 2 years.

The precise standardisation of the sampling conditions poses a technical problem. The thickness of the removed bark layer has to be defined by technical means as the pollutants show a steep gradient from the outermost layers to the inner parts.¹⁶ Therefore a recently developed bark sampler was used to take the samples.^{17,18}

Volatile substances, like ammonia, usually establish an equilibrium between the air and the bark surface. They are integrated into the bark much faster than non-volatile substances such as heavy metals. But as ammonia is transformed rapidly into ammonium at moisture contact it counts as a non-volatile and accumulative substance.

1.2 Validating ammonium bark analysis by comparing the values to ammonia passive samplers

Ammonia concentration in the ambient air is usually determined using the wet annular denuder system AMOR/AMANDA,¹⁹ developed by the Netherlands Energy Research Foundation (ECN). Extended measurements with passive samplers are necessary to get an overview of the widespread distribution of the immission load. This is strongly supported by the European Union.²⁰ Compared with the wet annular denuder technique, passive samplers are cheap and easy to use.²¹ However, they still have to be exposed at daily, weekly or monthly intervals which implies additional logistics and expenses. Additionally, a minimum time frame of six months of continuous measurements is necessary for reliable results. In contrast, bark bio-monitoring requires only a single sampling, no previous preparation of the site is needed and the laboratory effort is limited to the analysis of one sample per site. If the ammonium concentration in bark can be used to determine the ammonia concentration in the air, this presents a breakthrough in the monitoring of ammonia air pollution loads.

Thus, we aimed to (i) enable a standardised bark monitoring, (ii) test different tree species for their usability, and (iii) validate the ammonium bark analysis by comparing the results with the already established passive sampler technique. Concerning the second point we focused especially on testing spruce trees, as those are widespread in southern Germany. Successful use of

Table 1 Description of the sampling locations and the results of the bark analyses.²² *n* = Number of trees per location and species, CC = cumulative circumference in m, trunk band width by sampling ~ 0.5 m, * = replicate sample

Sample plot	Site	Location of the sample trees	Number of individuals and cumulated circumference per species and plot						Ammonia concentration in bark			Adjusted concentration of ammonia in bark for tree type using spruce as reference				
			Spruce		Pine		Oak		mg NH ₄ ⁺ per g bark			mg NH ₄ ⁺ per g spruce bark				
			<i>n</i>	CC	<i>n</i>	CC	<i>n</i>	CC	Spruce	Pine	Oak	Spruce	Pine	Oak	Plot mean	Std. error
1	Pielenhofen	Forest transect: forest edge	3	3.0 m			3	3.0 m	1.43		0.57	1.43		1.34	1.38	0.066
2	Pielenhofen	Forest transect: 50 m to edge	3	3.3 m					1.12			1.12			1.12	
4	Pielenhofen	Forest transect: 400 m to edge	3	4.2 m	3	3.8 m			0.72	1.44		0.72	0.59	0.65	0.094	
5	Pielenhofen	Forest transect: 800 m to edge	3	4.1 m	3	3.8 m			0.27	0.43		0.27	0.29	0.28	0.017	
8	Pielenhofen	Forest transect: 1.5 km to edge	2	2.4 m	3	4.5 m	3	3.6 m	0.29	0.51	0.08	0.29	0.32	0.22	0.28	0.050
6	Pielenhofen	Open field	3	4.2 m	3	3.9 m			1.14	3.32		1.14	1.13	1.14	0.005	
7	Pielenhofen	Open field	3	4.2 m	3	2.6 m			0.76	0.81		0.76	0.81	0.78	0.034	
9	Pielenhofen	Open field					2	4.6 m			1.17			2.7	2.70	
11	Ottobeuren	Forest edge	2	2.4 m			3	3.0 m	0.67		0.20	0.67		0.49	0.58	0.124
13	Ottobeuren	Forest edge	3	2.7 m			2	2.2 m	0.59		0.27	0.59		0.65	0.62	0.045
12	Ottobeuren	Inside forest: 150 m to edge	6	3.8 m, 3.0 m*			1	1.2 m	0.57, 0.51*		0.28	0.57, 0.51*		0.67	0.59	0.084

old spruce trees would extend the application of bark bio-monitoring remarkably.

2 Methods

2.1 Site description

According to Ibrom *et al.*²³ the background level of ammonia immission in unloaded areas of Germany amounts to approximately 1 µg NH₃ m⁻³, while highly polluted areas show immission loads of about 15 µg NH₃ m⁻³. In order to cover different levels of ammonia loads, samples were taken close to a poultry farm (Pielenhofen site, point source) and at a site characterized by diffusive agricultural emission (Ottobeuren

site, non-point source) in southern Bavaria. Frequent application of liquid slurry to grassland resulted in mean ammonia concentrations of 5–10 µg NH₃ m⁻³ at Ottobeuren in 2000. In contrast, mean ammonia concentration reached values of more than 25 µg NH₃ m⁻³ at Pielenhofen. At both sites samples were taken from old spruce dominated forests (70 and 100 years old) with single pine and oak trees. Plots were chosen where spruce grew together with at least one of the two other species. In order to cover the ammonia gradient within the forest, samples were taken directly at the forest edge where the immission is highest and in different distances from the edge.²⁴ Additionally, samples from exposed, separate trees were taken at the Pielenhofen site around the emission source. A description of the sampling locations is given in Table 1 and in Fig. 1(a) (Pielenhofen) and Fig. 1(b) (Ottobeuren).

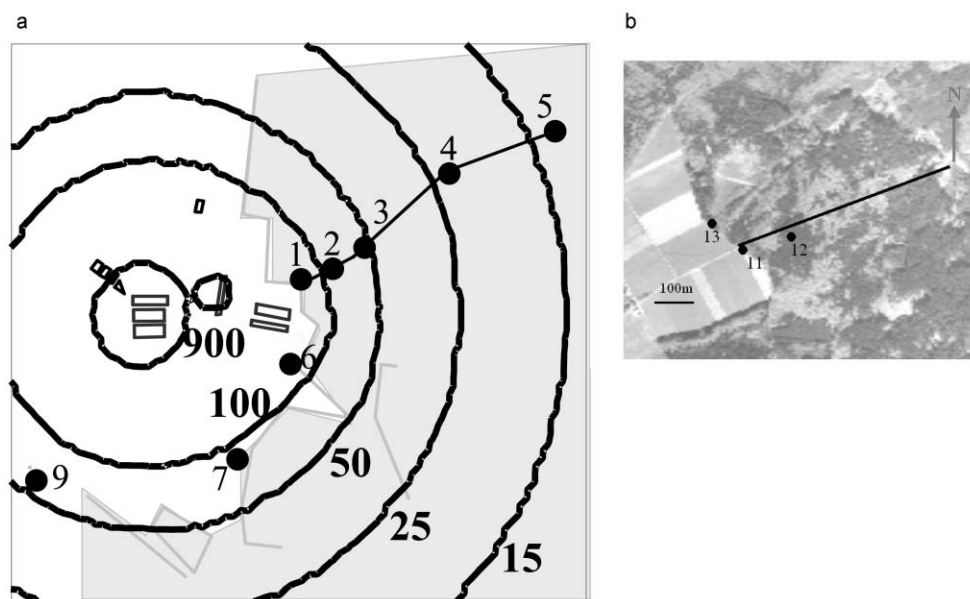


Fig. 1 a, Site map of the poultry houses in Pielenhofen including the numbers of the sampling plots, shape of the closed forest stand and the transect ranging from edge to interior (including the plot numbers 1–5 and 8 (not shown)). Plot numbers 6, 7 and 9 are located outside the forest in open field (compare Table 1) which means that single standing trees were sampled. The estimated deposition (according to²⁶) overlays the picture, reflecting a gradient of NH₃-immissions from 900 kg N ha⁻¹ year⁻¹ (around the housings) to 13 kg N ha⁻¹ year⁻¹. b, Site map of Ottobeuren. The plot numbering is comparable to Table 1. In contrast to Pielenhofen, samples were taken only from two plots at the forest edge and one plot in the forest interior.

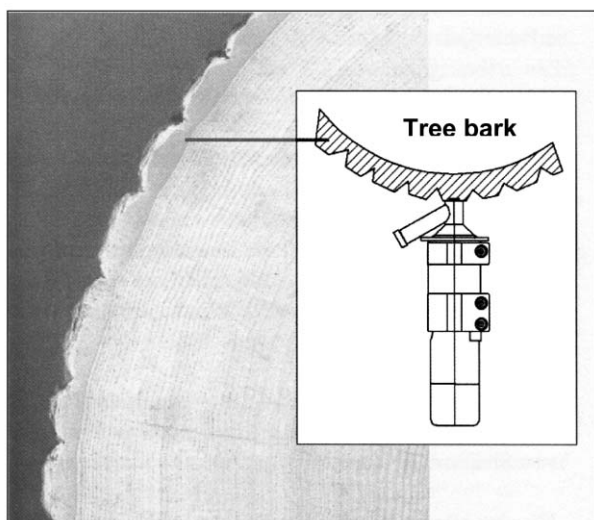


Fig. 2 Technical description of the bark sampling device.^{14,17,18}

2.2 Sampling of the tree bark

Twenty-two bark samples from spruce, pine and oak trees were taken at a stem height of 1.2–1.7 m using a bark sampler recently developed (Fig. 2) by the Ökologiebüro in Bremen.^{17,18} The bark sampler supports a standardised removal of a predefined thickness of the outer tree bark layer for different tree species while maintaining comparable and favourable analytical conditions. As a consequence, sampling could be reduced to few replicates extending the usable sampling sites. This method was successfully validated in a field study for 55 elements, 17 PAH and isotopic ratios of S and Pb.¹⁴ The coefficient of concordance (CC) as a measure of reproducibility gave a mean value of $14\% \pm 5\%$, from which $9\% \pm 8\%$ had to be attributed to the analytical methods.¹⁴ Oak, pine, lime tree, ash, poplar and maple were regarded as suitable tree species.

The sampler consists of a special coated high speed cutter and supports a standardised removal of the outer bark layer, in this case 1 mm. The samples are taken with rpm setting of $15\,000\text{ rev min}^{-1}$. The bark sample is directly milled and transferred into a polypropylene bag. Sampling was standardised at chest height and around the stem in order to cover all wind directions equally. Only trees older than 70 years with ripe bark structure and of good shape were chosen. Samples were taken from areas free of structured lichens, mosses and stem flow. To reach a good reproducibility, at least 30 g of bark material were collected per sample, covering a cumulative trunk area of at least 2 m^2 .

2.2.1 Chemical analysis of tree bark samples. Ammonium concentration was determined using bark extracts (6.25 g bark–25 ml 1% K_2SO_4 w/w) of the dried ($30\text{ }^\circ\text{C}$) and milled homogenised bark samples. Measurements were performed with a gas-sensitive ammonia electrode (Type NH 500/2, WTW Germany) with a precision of $< \pm 2\%$. Internal standards added during the extraction indicated recoveries of $92 \pm 5\%$.^{25,15}

2.3 Passive sampler monitoring

The passive sampler monitoring was achieved using ventilated diffusive samplers developed by the Institute of Balneology in Munich. The sampling method was tested in an international field inter-comparison.²¹ The ventilated sampler contains an impregnated filter of sulfuric acid. The ammonia analysis was done using the Berthelot reaction. Once exposed to the environment, the sampler's optimal interval for gathering data is at intervals of 1, 2 or 4 weeks; thus, our sampling intervals ranged from 2 to 4 weeks over a six month period. The detection limit lies at $0.05\text{ }\mu\text{g m}^{-3}$ per week.²²

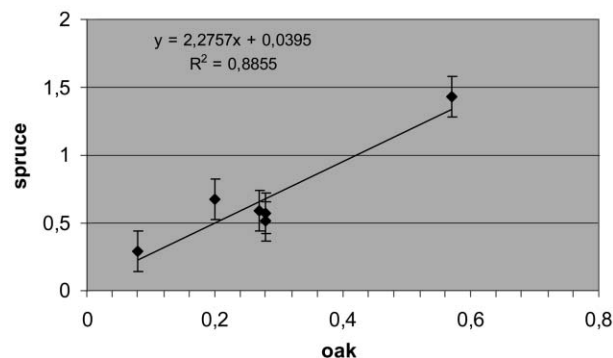


Fig. 3 Results of the regression analysis between spruce and oak for the ammonia concentration of the bark [mg NH_4^+ per mg of bark]. The bars indicate the standard error of regression. The r^2 of the correlation is significant at $p < 0.01$. The error of the coefficient a is ± 0.41 , of $b \pm 0.13$.

2.4 Data analysis and statistics

Data analysis and graphs were produced using MS Excel and its statistical analysis functions (add-ins). The relation between ammonium concentrations of spruce and pine or spruce and oak was analysed by linear regression. The statistical significance of the relation was tested using the square of the correlation coefficient (r^2). The standard error of the regression and the significance, p , of the regression parameters were estimated. Using regression equations, the ammonium concentration values of pine and oak were adjusted to the spruce values and expressed as “adjusted concentration of ammonium in bark” [$\mu\text{g NH}_4^+$ per mg spruce bark]. The individual values of the tree species were combined to mean values for each plot and the standard errors were calculated.

The correlation between the adjusted ammonium concentrations of the bark and the ammonia immission measured by the diffusive passive samplers was tested using the data of all plots by linear regression analysis. R^2 , significance, p , and the standard error were also calculated.

3 Results

3.1 Tree bark biomonitoring

The results of the regression analysis revealed significant relations between the tree species concerning their ammonium concentration. Fig. 3 shows the relationship between the ammonium concentrations in bark of oak and spruce. Compared to oak, spruce accumulates more than twice the amount of ammonium. Concerning pine and spruce, the opposite is true (Fig. 4). Pine accumulates about three times as much as spruce does. In both cases the correlations are significant on $p < 0.01$. Old spruce

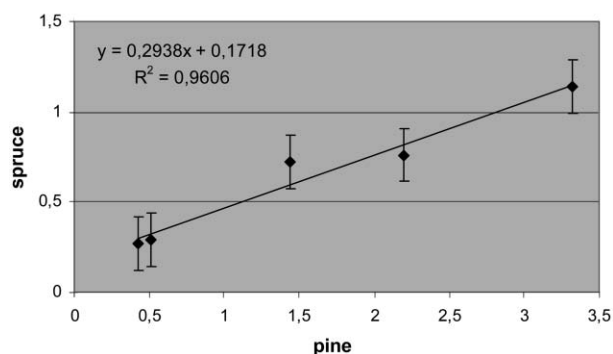


Fig. 4 Result of the regression analysis between spruce and pine for the ammonia concentration of the bark [mg NH_4^+ per mg of bark]. The bars indicate the standard error of regression. The r^2 of the correlation is significant at $p < 0.01$. The error of the coefficient a is ± 0.41 , of $b \pm 0.13$.

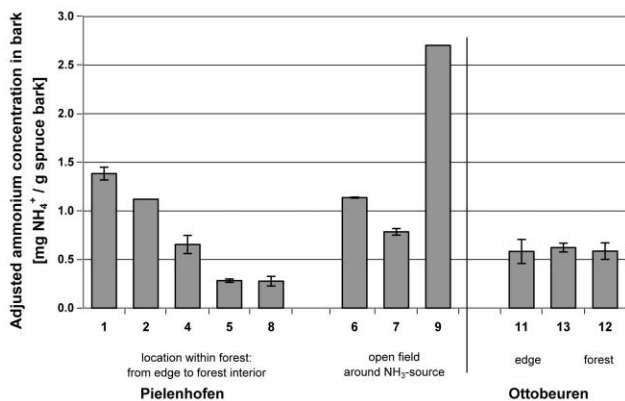


Fig. 5 Adjusted values of ammonium concentration in bark for species type at the sites of Ottobeuren and Pielenhofen [NH_4^+ per mg of spruce bark]. The index shows the mean values over all tree species at the plots with standard errors (see Table 1).

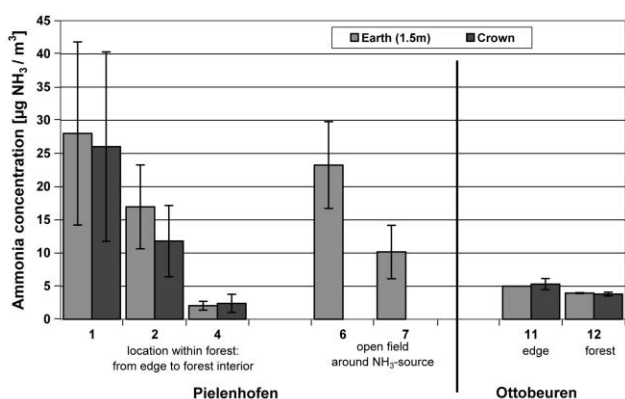


Fig. 6 Ammonia concentration obtained with the diffusive sampler technique at the Pielenhofen and Ottobeuren site. The plot numbering is directly comparable to Fig. 5 and refers to Table 1.

trees can be used as successful for the bark monitoring as pine and oak.

Using these relations, the ammonium values were adjusted for the tree species and expressed as adjusted ammonium concentration in bark based on the spruce values. The results are presented in Table 1 for all plots and species. Afterwards, the data of all species were combined as mean values representing the ammonium immission load received by bark bio-monitoring. The results are shown in Fig. 5 for all sample plots. It can be seen, that the ammonium concentration in the bark decreases with increasing distance to the emission source. This strongly applies to the Pielenhofen site. In contrast, the differences between the forest edge and the interior concentration are not significant at the Ottobeuren site.

3.2 Comparison between the bark samples and the ammonia concentration measured via passive sampler

The results of the ammonia immission measurements using the diffusive samplers are presented in Fig. 6. The resultant plot is directly comparable to the results of the bark bio-monitoring in Fig. 5. Once again, the ammonia immission decreased with increasing distance from the source at the Pielenhofen site. This applies to the forest transect from edge to interior as well as to the open field.

Fig. 7 shows a comparison of the adjusted ammonium loads by bark biomonitoring and the ammonia concentration in the air measured by the passive samplers. The adjusted ammonium values by bark biomonitoring are significantly related ($p < 0.01$) to the ammonia concentration data in the air measured by

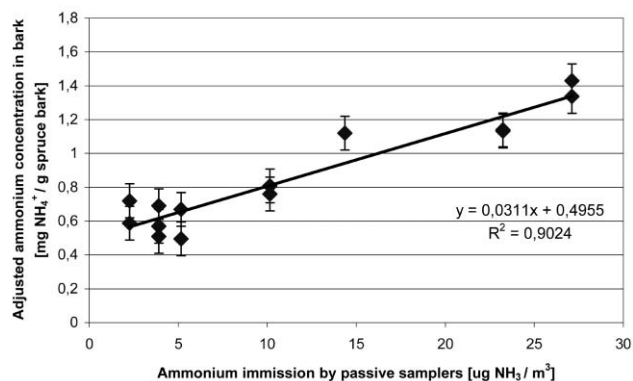


Fig. 7 Results of regression analysis between the adjusted ammonium concentration values in bark versus the ammonia concentration in the air by the technical based passive samplers. The bars indicate the standard error of the regression statistics. The error of the coefficient a is ± 0.0029 , of $b \pm 0.043$. The regression coefficients as well as r^2 are statistically significant at $p < 0.001$.

the passive samplers. Using the result of the regression analysis, a calibration curve may be determined in order to use bark bio-monitoring as an indirect method to estimate ammonia air pollution loads.

4 Conclusions

The presented results indicate that ammonium analyses of some tree bark types might be successfully used as a bio-indicator for ammonia pollution in future. With increasing importance of nitrogen pollution, especially with respect to nitrate leaching, simple measurement techniques for rural areas with high ammonia emissions will become more important over time.

It was shown that spruce trees older than 70 years are usable for bark sampling in the same way as the bark of pine and oak trees, which have been already used for a long time.^{13,14}

The ammonium concentration in the spruce bark was significantly correlated to the values of pine and oak. Thus, the 'tree species adjusted values' of ammonium concentration in the bark can be calculated by the regression terms using one species as a baseline. In our test spruce was used. The same results of bark analysis from different tree species can be achieved for ammonia using the bark sampling device.

The adjusted ammonium values of the bark of all species were significantly related to the ammonia concentration levels measured by the diffusive samplers. The significance of the data regression indicates that a calibration of ammonium in bark to ammonia in the air can be possible.

However, further investigations are necessary to support these results. An investigation at more sites covering wider amplitudes of NH_3 -immission loads would be interesting. A valid calibration might finally be achieved as this has already been done for elements like S and Pb using the log-normal base distribution of the data.¹⁴

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