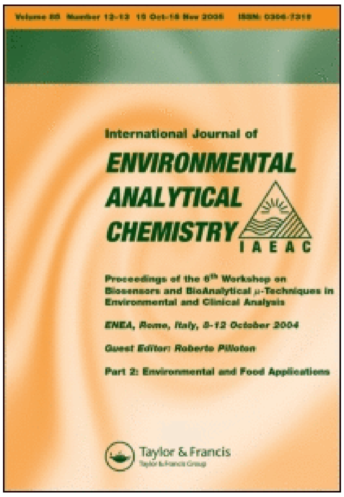

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# Influence of Wet Storage of Spruce Wood on Groundwater Quality: Investigations by Water-Chemical Methods, Pyrolysis-Fieldionization Mass Spectrometry and Luminiscent-Bacteria Bioassay

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# INFLUENCE OF WET STORAGE OF SPRUCE WOOD ON GROUNDWATER QUALITY: INVESTIGATIONS BY WATER-CHEMICAL METHODS, PYROLYSIS-FIELD IONIZATION MASS SPECTROMETRY AND LUMINISCENT-BACTERIA BIOASSAY

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For groundwater below a wet-storage location for spruce wood, water-chemical analyses indicated a distinct pollution by inorganic and organic compounds. Due to the high ammonium concentration this groundwater was not suitable as drinking water. Using pyrolysis-field ionization mass spectrometry, a direct and fast molecular-chemical characterization of the organic constituents in the polluted groundwater was possible. No pretreatment except freeze-drying was required. The combination of water-chemical methods, analytical pyrolysis and bioassays allows to determine water quality and the organic constituents of dissolved organic matter with respect to toxicological properties.

**KEY WORDS:** Bioassay, dissolved organic matter, environmental hazards, groundwater, pyrolysis-field ionization mass spectrometry, toxicology.

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## INTRODUCTION

After windfall catastrophes it is often necessary to store and conserve large amounts of warped wood for months or years in order to relieve the timber trade. The safest methods to protect wood-raw material from depreciation over a long period of time represent techniques which preserve a high water content in the wood and thus prevent the spreading of fungal infections or the formation of chinks. At present the wet storage enables the most efficacious long-term protection of logs[1]. For some time this method has been used successfully in North America[2,3], Scandinavia[4] and East Europe. Likewise Karstedt *et al.*[5] and Arnold *et al.*[6] reported on good experiences with the wet storage of logs in Germany. However, up to now only few investigations were carried out to explore environmental effects of wet storage on surface- and groundwater quality[7]. Considering the novel water regulations (Germany, EEC) adequate analytical investigations are necessary especially in this field. In order to develop reliable analytical methods to examine the influence of wet storage of logs on groundwater quality, water samples were collected in the area of the Knüllwald forestry (Germany) and analysed by water-chemical methods, pyrolysis-field ionization mass spectrometry (Py-FIMS) and bioassays using luminescent bacteria and Daphnia, respectively.

In previous investigations we had shown that Py-FIMS can be used for direct characterization of dissolved organic matter (DOM)[8–10]. The only preparation step needed for such analyses is the concentration of water samples by freeze-drying. Since field ionization represents a soft ionization technique that preferably produces molecular ions, the mass spectra can be correlated with genuine chemical substances in the sample. Chemical analyses of water samples supply only indirect information on their ecological quality. Therefore, to determine the influence of water pollutions on living organisms, bioassays are increasingly employed.

## MATERIALS AND METHODS

The samples analyzed were taken in the area of the Knüllwald forestry (Hessen, Germany). From 1985 to 1987 and from 1990 to 1992 unbarked spruce wood was conserved on the investigated storage location (1.83 $m^3$ wood per $m^2$) using a closed, circulating irrigation system (40 l water per $m^2$ and day). The following samples were analyzed:

Sample A: brook water used for the irrigation of the spruce wood;
Sample B: groundwater collected below the meadow adjoining the wet storage location for spruce wood (depth 1.50 m); and
Sample C: groundwater collected directly below the wet storage location for spruce wood (depth 1.50 m).

The collected water samples were not filtered through a membran filter. Four water-chemical parameters were determined directly after the collection of samples using the following methods:

- electrometric determination of the pH-values using a glass electrode;
- electrometric determination of the electric conductivity using a conductivity electrode;
- spectralphotometrical determination of $[NH_4]^+$ concentrations after pretreatment with Neßlers reagent; and
- determination of the chemical oxygen demand (COD) with the cuvette test.

Prior to Py-FIMS analyses, the water samples were freeze-dried immediately after receipt (3h). The Py-FI mass spectra were recorded using a double-focusing Finnigan MAT 731 mass spectrometer. The heatable/coolable direct introduction system with electronic temperature-programming (IGT Instrumente- and Geräte-Technik, 53804 Much, Germany) adjusted at the +8kV potential of the ion source was used. About 3 mg of the freeze-dried samples was pyrolyzed in the ion source of the mass spectrometer. The samples were heated in high vacuum from 50 to 650°C at a heating rate of approximately $0.5°C * s^{-1}$. About 60 magnetic scans were recorded for the mass range 16 to 1000 Dalton during heating. These single spectra were integrated by the Finnigan MAT SS 200 data system, resulting in a summed spectrum for each measurement. Three replicates were carried out for every sample and the obtained summed spectra were averaged to one survey spectrum. The total ion intensity (TII, in counts $* 10^6$) of the replicated measurements was normalized to 1 mg sample, averaged and plotted versus the pyrolysis temperature resulting in the Py-FIMS thermogram (see upper right in Fig. 1). Detailed descriptions of Py-FIMS methodologies have been published[8,11]. The identification of the pyrolysis products was based on studies of extracted humic fractions[12] and soils[13–15] using low- and high-resolution Py-FIMS measurements, Curie-point pyrolysis gas-chromatography/mass spectrometry, extensive NIST, Wiley and in-house library searches. Recently, tentative assignments for identification of the major signals in Py-FI mass spectra of humic fractions and soils were published[12].

The luminescent-bacteria bioassay was carried out according to the German standard method (DIN 38412, part 34). The test organism was *Photobacterium phosphoreum*. The inhibition of emitted bioluminescence after an incubation period of 30 minutes (inhibitory effect $H_{30}\%$) for the original water samples was used as criterion for their acute ecotoxicity. The bioassay with a representative of the aquatic crustaceae was carried out according to the German standard method DIN 38412 part 30 with *Daphnia magna*, *Straus*, as test species. In this acute immobilisation test different dilutions of the resuspended lyophilisates of the water samples B and C were tested for acute toxicity within 24 hours.

## RESULTS AND DISCUSSION

### *Water-chemical analyses*

The results of water-chemical analyses are presented in Table 1. The pH-value and electric conductivity are indicators for inorganic water components. The German drinking-water regulation[16] provides pH-values between 6.5 and 9.5. The pH-values of the analyzed water samples were within these limits except the groundwater below the adjoining meadow which

**Table 1** Chemical and ecotoxicological characterization of water samples collected in the area of the wet-storage location for spruce wood Knüllwald (Hessen, Germany)

| *Parameter* | *Unit* | *Sample A*[1)] | *Sample B*[2)] | *Sample C*[3)] |
|---|---|---|---|---|
| DOC[4)] | mg * $l^{-1}$ | 4.2 | 1.8 | 19.6 |
| *Water-chemical analyses* | | | | |
| ph | | 7.8 | 6.4 | 7.7 |
| electric conductivity | µmS * $cm^{-1}$ | 254 | 126 | 764 |
| $[NH_4]^+$ concentration | mg * $l^{-1}$ | 0.09 | 0.41 | 4.0 |
| chemical oxygen demand | mg * $l^{-1}$ | 4 | 3 | 23 |
| *Luminescent-bacteria bioassay* | | | | |
| inhibitory effect | $H_{30}$% | 10.8 | 7.8 | 10.6 |

1) brook water used for the irrigation of the spruce wood
2) groundwater collected below the meadow adjoining the wet-storage location for spruce wood (depth 1.50 m)
3) groundwater collected below the wet-storage location for spruce wood (depth 1.50 m)
4) dissolved organic carbon

had a pH-value insignificantly lower than 6.5. The wet storage of logs led to an increase of the pH-value in the groundwater and improved the groundwater quality concerning this parameter. According to the German regulation[16] the electric conductivity of drinking water must be <2000 µS * $cm^{-1}$. Usually, non-influenced, natural waters have an electric conductivity <250 µS * $cm^{-1}$. About 30% of drainage of the investigated brook is used agriculturally, the rest is wooded. Thus, the higher electric conductivity of the brook water compared to the groundwater below the adjoining meadow is likely due to an anthropogenic influence on this surface water. Directly below the storage location, wet storage of spruce wood led to a distinct increase of electric conductivity in groundwater. However, the limit of electric conductivity in drinking water was not exceeded.

The $[NH_4]^+$ concentration reflects the microbial decomposition of proteinaceous substances of plants and animals in water samples. Usually, the concentration of ammonium ions in a non-influenced forest brook water is <0.3 mg * $l^{-1}$. In Germany, at most 0.5 mg * $l^{-1}$ $[NH_4]^+$ are allowed in drinking water[16]. The wet storage of logs caused a relatively high accumulation of proteinaceous substances in the groundwater and deteriorated the water quality strongly. In particular, due to the high $[NH_4]^+$ concentration, the groundwater below the wet storage location is not suitable as drinking water.

The COD is an indicator for the organic pollution of a water sample. Tannins, resins, sugars and lignins washed out of the wood or bark and humic substances originating from adhering soil to logs are possible sources for organic contaminations of the groundwater below the wet storage location. Thus, in this sample the COD was eightfold higher compared to the non-influenced water samples.

### *Pyrolysis-field ionization mass spectrometry*

The thermograms (normalized to TII in counts * $10^6$ per mg sample) for the three freeze-dried water samples are shown in Figures 1a-c (upper right). The thermal evolution of DOM was

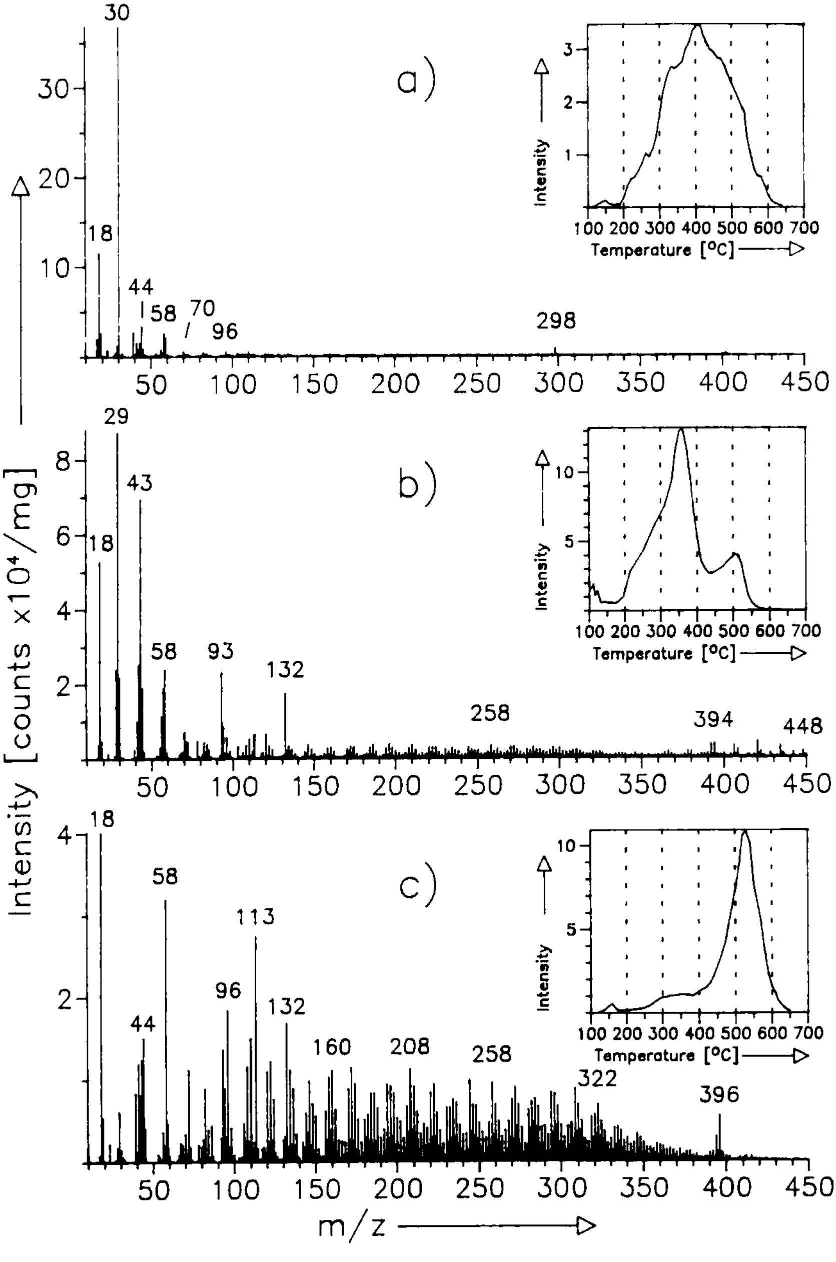

**Figure 1** Thermograms and Py-FI mass spectra of the freeze-dried dissolved organic matter of a) brook water used for irrigation of the logs (sample A), b) groundwater collected below the meadow adjoining the wet-storage location (sample B), c) groundwater collected below the wet storage location (Sample C).

observed for all samples analyzed over a wide temperature range. However, obvious differences in the temperature-dependent course of TII are discernible between non-influenced DOM samples (sample A and sample B) and the sample collected below the log-storage place (sample C). The distinct shifting of maximal TII during pyrolysis to the temperature range around 500°C indicates for sample C an enrichment of organic matter characterized by a higher thermal stability.

The DOM of the brook water used for the irrigation of the spruce wood (Figure 1a) gave a weak intensity. The signal pattern characterizing the naturally occurring DOM in the irrigation water shows relatively intensive signals for low-molecular weight fragments and compounds like m/z 30, 44, 58 and 70. In addition, weak signals of carbohydrates (m/z 96, 110) are observed.

The DOM of groundwater collected below the meadow adjoining the wet-storage location (Figure 1b) shows also relatively intensive, low-molecular-weight signals, e.g. at m/z 28, 29, 42, 43, 57, 58 and 70. In addition signals indicating carbohydrates (m/z 72, 96, 110, 132) and nitrogen-containing compounds (m/z 83, 93, 113) are observed. Compared to sample A, signals in the mass range above m/z 132 are more abundant. This indicates a natural enrichment of lignin subunits, lipids and alkylaromatics in the groundwater under a meadow.

The DOM of groundwater collected directly below the wet-storage location (Figure 1c) gave a Py-FI mass spectrum indicating a complex DOM structure in the groundwater below the wet storage location. In the lower mass range prominent signals for low-molecular-weight fragments like m/z 42, 43, 44 and 58 are observed. Signals at m/z 72, 82, 96, 110, 132 and 162 refer to carbohydrates. N-containing compounds are indicated by m/z 67, 81, 113, 117 and 131. Phenolic structures (m/z 94, 108, 110, 120, 122, 124) and monomeric lignin subunits, probably coniferyl alcohol and its derivates (m/z 124, 150, 152, 164, 166, 180, 182), syringyl units (m/z 168, 192, 194, 198), sinapyl aldehyde (m/z 208) and sinapyl alcohol (m/z 210) are clearly discernible. Signals at m/z 270, 284, 296, 300, 310, 312, 314, 326, 330, 340, 342 and 356 indicates lignin dimers with phenylcoumaran structures. Likewise, lignin dimers with biphenyl structures (m/z 246, 260, 272, 274, 286, 300, 312, 316, 328), diarylpropane structures (m/z 272, 302, 332) and resinol-type structures (m/z 298, 328, 358) refer to the enrichment of lignins in the groundwater below the wet storage location.

The translocation of tannins is indicated by pyrolysis products with phenol and benzene structures (e.g. m/z 134, 146, 160). Alkylaromatics, originating probably from translocated humic substances and proposed as their structural building blocks[17], are indicated by m/z 192, 206, 218, 232, 246, 260 and 274. In addition, the signals at m/z 170, 184 and 198 arise likely from tri-, tetra- and pentamethyl-naphthalenes, whereas m/z 220 and 234 are due to tri- and tetramethyl-phenanthrenes. Observed lipid-derived structures represent n-$C_{12}$ to n-$C_{16}$ alkyl diesters (m/z 230, 244, 258, 272, 286), n-$C_{18}$ to n-$C_{24}$ fatty acids (m/z 284, 298, 312, 326, 340, 354, 368), sterols (m/z 394, 396) and homologeous series of alkenes and alkanes starting with m/z 280 and 282, respectively.

Generally, Py-FIMS shows that the DOM of the groundwater below the wet-storage location is enriched with lignin and tannin subunits as well as lipid-derived structures compared to the non-influenced water samples. According to Hempfling and Schulten[10] these compounds of DOM are pyrolyzed at higher temperatures. Thus, the enrichment of lignins, alkyaromatics and lipids corresponds with the relatively high thermal stability of DOM in the groundwater below the log location.

### *Luminescent-bacteria bioassay*

To assess the ecotoxicological effects of the groundwater contamination below the wet storage location with inorganic and organic compounds, the water samples were investigated by bioassays using *Photobacterium phosphoreum* and *Daphnia magna, Straus*, respectively. The results of the luminescent-bacteria bioassay are shown in Table 1. Not one sample exceeded the toxicity limit of 20% inhibitory effect after 30 minutes incubation. An elongation of the incubation period to 60 minutes did not change this result. A comparison of samples A, B and C shows only small differences in the bioluminescence inhibition of *Photobacterium phosphoreum*. Using *Daphnia*, no significant acute toxicity was determined for the samples B and C within 24 hours incubation likewise. Thus, results of bioassays indicate that the wet storage of unbarked spruce wood on the storage location Knüllwald did not cause a toxicological pollution of the groundwater.

## CONCLUSIONS

The described study represents the possibilities of a combined, integrated analysis of groundwater quality using water-chemical methods, analytical pyrolysis and bioassays. As shown, Py-FIMS allowed a fast and sensitive molecular-chemical characterization of major constituents of water-chemically determined organic pollutions in water samples. Thus, Py-FIMS indicated that the groundwater below the investigated wet storage location was enriched with lignins, tannins and humic substances. However, according to bioassays the polluted groundwater was not toxic for luminescent bacteria and *Daphnia*, respectively.

Further experiments with leachates of forests and waste disposals but also surface water of lakes and rivers appear promising and will be the topic of future work.

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