Stable isotopes as a tool to trace back the origin of wood

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Abstract

The natural variation of stable isotopes can be used to trace back the origin of wood. Especially the D/H and the $^{18}O/^{16}O$ ratio are suitable tools. This results from the isotopic fractionation of the stable isotopes of hydrogen and oxygen within the global water cycle. Each location has a characteristic isotopic composition of the precipitation and consequently of soil and ground water. Both isotopic ratios are closely correlated. Additionally in the needles as well as leaves the isotopic composition is enriched due to the fractionation during the transpiration of plants. Therefore reference samples from the regions of intensive timber logging are preferred, such as from Northern Europe or South East Asia. The WWF has supplied Agroisolab GmbH with 1651 samples of slices from trunks across Northern Europe, and with 487 core drills from South East Asia. In Northern Europe especially the D/H ratio of organically bound hydrogen can be used to trace back the origin of timber, but together with the $^{18}O/^{16}O$ ratio the regional origin can be examined more exactly. In the tropics the conditions seem to be more difficult. Other elements as sulphur have been therefore included successfully. To apply such elements as nitrogen or sulphur new methods have been developed and have to be improved in future. Beside tracing back the geographic origin the method can also be applied to control the declaration, e.g. whether the timber has been cut under legal conditions. Reference samples and data bases are necessary to fulfil this request. The composition of stable isotopes of biomass is mainly the result of that observed in the vicinity. This isotopic composition is stable and varies between different locations. Therefore the method is called "isotopic fingerprint".

Keywords: stable isotopes, wood, origin, tracing, Europe, South East Asia

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1 Introduction

The basic idea to localize a sample of unknown origin stems from the observation of the fractionation of the both stable isotopes of hydrogen and oxygen in the global water cycle. From the distribution of temperature and from the movement of air masses results a distinct and in recent times constant pattern. Both mechanisms are often closely connected one to the other. The resulting so called "meteoric water line", first published by Craig 1961 (see the paper of Förstel within this issue), and afterwards subsequently confirmed (Daansgard 1964), is a result of this correlation. But a model which could explain this very close correlation completely has not been offered until now. Each deviation from the meteoric water line results form specific situations as intensive evaporation of closed basins. The isotopic enrichment of the stable isotopes of water reservoirs which have a slow flow through the basin will be governed by the fractionation during evaporation.

Tracing back the geographical origin of a sample the so-called continental effect plays an important role. As a result from subsequent precipitation and evaporation two opposite effects result in a decrease of the content of the heavy stable isotopes of water vapour crossing the land masses. During the formation of precipitation, a condensation process, the heavy isotopes are preferred to form the rain droplets. The subsequent evaporation at the other hand is a fraction step which leaves back mainly the heavier stable isotopes. Consequently the water vapour from evaporation has a decreased content of the heavy stable isotopes of hydrogen and oxygen. The continental effect is a result of the incomplete balance of precipitation against evaporation.

Water, and also its stable isotopic composition, is the substrate where biomass is formed. Building up biomass needs the material from its direct environment. That means also, that the process of biosynthesis has to use and therefore to reflect the isotopic composition of its environment. The law of mass balance is not only valid for elements, but includes their stable isotopes also. But the formation of some materials like lignin needs the atmospheric oxygen also. The $^{18}O/^{16}O$ ratio of cellulose is assumed to result mainly from an equilibrium between water and the carbonyl groups which happens during biosynthesis (Sternberg 1989, Sternberg and DeNiro 1990). Therefore the proportion of cellulose and lignin may determine finally the $^{18}O/^{16}O$ ratio of the wood (Gray and Thompson 1977, Keppler et al. 2007). The big reservoir of air oxygen is isotopically homogeneous and its $^{18}O/^{16}O$ ratio is enriched (DOLE effect).

Wood is a well-studied material in the past and today because of two reasons. The first reason is the stability of this material whereas in the past the focus has been set on cellulose, may be taking into account the experiences and techniques from the pulp and paper industry, as demonstrated by the historical publications. The second interest has arisen from the fact that wood in the temperate and cold areas is formed during the annual growth season and stored in visible and separate tree rings like a calendar. This fact is used as a tool of dendrochronology. Additionally the variations of the stable isotope composition of oxygen and hydrogen were used to reconstruct palaeoclimate.

One main problem of the methods to trace back materials to their origin, valid not only for the stable isotope method, is the availability of reference samples. The WWF has enabled this pilot study by an intensive support of material covering large areas of interest. From northern hemisphere forests slices of wood were supplied, from the South-East-Asian region core drills. The sampling strategy was adapted from a study of the $^{18}O/^{16}O$ ratio in German groundwater (Förstel and Hützen 1983). The precipitation is deposited unchanged into the soil and finally into the groundwater. Tap water usually originates from groundwater and can be used as a representation of the isotopic composition of local precipitation. Exceptions are samples from river bank filtrate if the river originates from an area far away from the site of observation, mostly in mountains of high altitude. i.e. of low isotopic content of precipitation.

In the case of wood the local tap water is not sufficient to serve as an indicator of the isotopic composition of cellulose. The biochemical precursors of cellulose are synthesized in the water of needles or leaves. During the uptake of water through the roots and the mass transport in the stem no fractionation can be observed, but in contact with the air the transpiration is a typical step of fractionation. The basis is the local D/H- and $^{18}O/^{16}O$-ratio of the precipitation, but an effect of enrichment is added. The fractionation depends on the physical conditions at the needle or leaf surface, mainly governed by the relative humidity of the air. Thus, two physically driven processes determine the final isotopic composition of the biomass formed: the global climatic conditions of groundwater and the local conditions of the contact of the plant with the environment. This rapid exchange between leaf and air water vapour can be seen by the observation the diurnal cycle of the isotopic composition of leaf water (Förstel 1978). The CRAIG-GORDON model of the exchange between a liquid surface and the wet air in contact gives a first approximation but is not sufficient to describe the enrichment exactly. One reason can be that the small-scale physical conditions at the boundary layer between needle or leaf and the air are not exactly known. These conditions cannot be measured exactly, e.g. the temperature of the leaf surface or the complicated geometry of stomates.

An important argument for the necessity of reference samples results from the experience that the officials and the courts are more convinced by direct comparison with real samples instead of data which have been calculated from models. This has been one reason to initiate this first screening.

2 Material and methods

2.1. Material

2.1.1. Northern European samples

Discs from stems or strong branches were collected covering nearly the whole area from forests of the Northern Europe, wooded mainly by coniferous forest. From each site about 5 samples were taken, in some cases not only from one species. In Schweden the sample sites were labelled on maps, the other ones by GPS. The use of GPS allows a very rapid and exact localisation of the site of collection and should be preferred as a method to report the data. In combination with Google Earth® an overview of the data points can be obtained quickly and even in some cases the scale can go down to single trees in plantations.

The Swedish samples have been wrapped in plastics which unfortunately have allowed the growth of fungi at the wet surface. Therefore the samples were cleaned by removing down the upper surface. The other samples have been dried and wrapped in paper bags for mailing. Most of the samples were collected from spruce (*Picea abies* (L.) KARST), some from pine trees (*Pinus sylvestris* L.) and others from birch (*Betula sp.*) at the same site. Therefore the number of samples and of sites does not correspond to each other multipliying the number of sites with the factor 5 (Table 1).

Table 1:
Number of samples collected across Northern Europe, mostly spruce

Country	Number of samples	Number of sites
Finland	199	23
Sweden	305	25
The Baltic	119	19
Poland	144	17
White Russia	69	15
Northwest Russia	815	134
Sum	1651	233

Annual variations between the tree rings are a common tool of paleoclimatology, but previous tests have demonstrated that at least 6 tree rings are sufficient to get a representative value of the isotopic composition of a sample. In routine analysis the material was obtained by sampling sawmill dust across the whole cleaned disc, drilling a radial trace across the whole surface of the sample. If a sample did not include at least 10 annual rings it was omitted.

The sawmill dust is ground to a fine powder by a ball mill and an aliquot afterwards cleaned by extraction with first methylen chloride followed by methanol in a Soxhlet extraction procedure, each step lasting about 4 hours. After drying overnight at 70º C the samples are ready for further treatment.

2.1.2. South East Asian Samples

In South East Asia samples from the Western islands of Indonesia, from Kalimantan, from Vietnam and from Western Malaysia and were collected on the behalf of the WWF (Table 2). The samples from Vietnam were kindly supplied by Prof. Finkeldey University of Göttingen. They were used to study the effect of different species at one location.

Table 2:
Summary of the samples collected in South East Asia.

Region	Number of samples	Number of sites
Kalimantan	203	39
Brunei/Sarawak	32	8
Western Malaysia	34	7
Sabah	78	16
Sumatra	80	18
*Kalimantan**	*20*	*10*
Vietnam	40	4
Sum	487	102

** Two samples were drilled at a close distance from the same trunk to test the variability within the wood.*

From south East Asia only 10 cm long cores from drilling were available. Two cores collected from the same tree at a short distance from the trunk vary only within the methodological and statistical scattering.

2.2. Methods

A special technique compares a sample with an internal reference during each measurement, the isotopic ratio mass spectrometry IRMS. Additionally each set of samples is compared not only at the beginning and at the end with a laboratory internal reference material, but also within each run.The laboratory standards are calibrated against internationally distributed standard materials and reported as deviation from there data as δ-values as

$$\delta = \frac{{}^{18}O/{}^{16}O_{(\text{Probe})} - {}^{18}O/{}^{16}O_{(\text{Standard})}}{{}^{18}O/{}^{16}O_{(\text{Standard})}} \cdot 1000$$

$$\delta = \left(\frac{{}^{18}O/{}^{16}O_{(\text{Probe})}}{{}^{18}O/{}^{16}O_{(\text{Standard})}} - 1 \right) \cdot 1000$$

The water of timber may be changed during the transportation. Therefore cellulose will be isolated and used as a memory of the local isotopic composition. To avoid effects of an isotopic exchange between foreign water and the hydrogen of –OH groups these groups are deleted by nitrification (Epstein et al. 1976, Dubois 1984, Brendel et al. 2000, Loader et al. 2003). Agroisolab GmbH has developed a specific furnace (silicon carbide) which can be run at high temperatures above 1500º C without an increasing background.

Carbon and nitrogen are measured by a conventional elemental analyser which converts the biomass to the simple gases carbon dioxide and nitrogen. To avoid problems resulting from the different content of carbon and of nitrogen within the biomass the inflow of carbon dioxide has to be reduced by a diluter. Nowadays the connection between sample preparation and mass spectrometer is achieved by an open split system.

The measurement of the isotopic ratio of sulphur $^{34}S/^{32}S$ is more difficult because of the very low concentration of this element in the matrix. The sulphur has to be converted to a form which enables the concentration and extraction from a bulk of material. Sulphur is an indicator of fertilisation and immission situations as well of the close distance to the sea. A first application is presented for samples in Borneo.

Figure 1 gives a general overview of the methods which have been applied for this study. Latest results have shown that for recent wood nitration is not necessary.

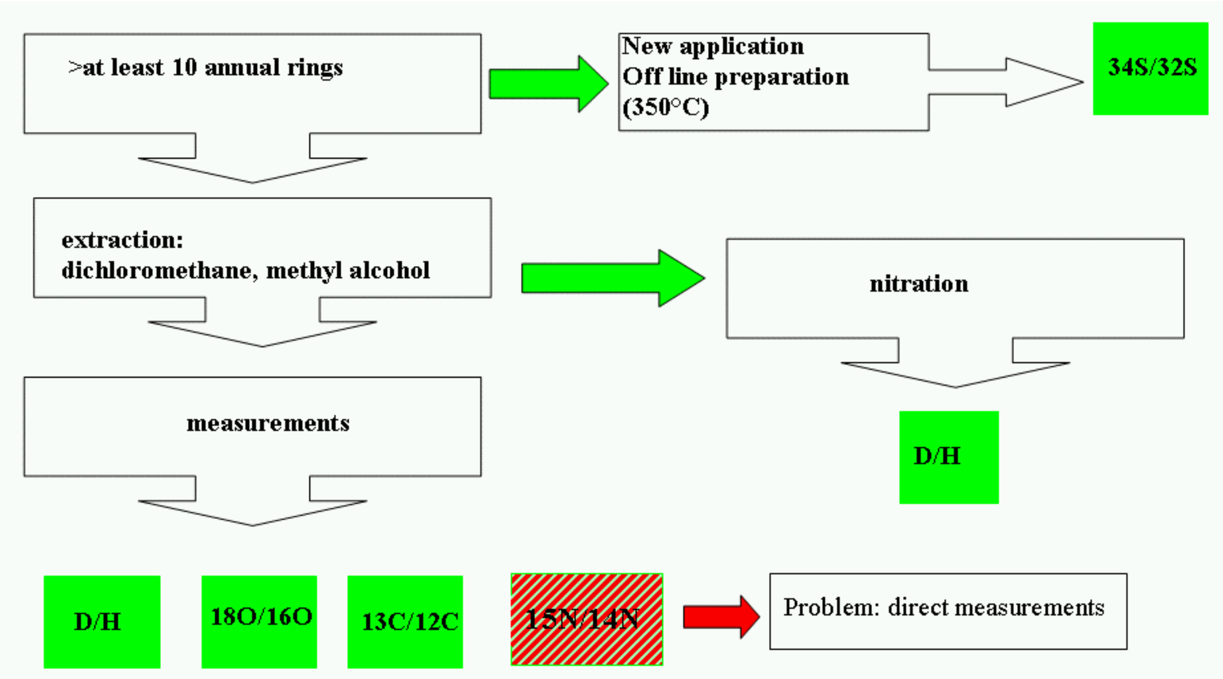

Figure 1:
Overview of the methods used for this study

3 Results

3.1. Northern European data

Northern Europe is originally covered by coniferous forests, so-called boreal eco-systems. Spruce and other species are the dominating species. This results from the en-vironmental conditions of cold winter seasons including a big amount of snow. The trees grow more slowly compared to the plants at warmer climates more south.

The $^{18}O/^{16}O$ ratios show only minor tendencies across Northern Russia. In contrast to that result a distinct pattern of the D/H ratios in wood will be seen (Figure 2) Two tendencies overlap each other, a decrease from southern towards northern regions due to the decrease of the temperature and from the west to the east as a result of the preferred direction of the movement of air masses across the continent (continental effect). A north-south profile is given for the data along the western border of Russia (Figure 3). The $^{13}C/^{12}C$ ratios may be useful for the identification of a certain batch controlling the paper documents.

Taking into account our experience with food political units may be too limited to catch larger tendencies. Figure 4 and 5 summarize the data of North East Europe and demonstrate the tendencies of the D/H and $^{18}O/^{16}O$ ratios: a decrease to the north and to the east, for $^{18}O/^{16}O$ this is symbolized by the colour of the dots from dark blue to yellow, for the D/H ratio from yellow to red dark. Both of the parameters, the temperature and the distance from the ocean determine the local isotopic composition.

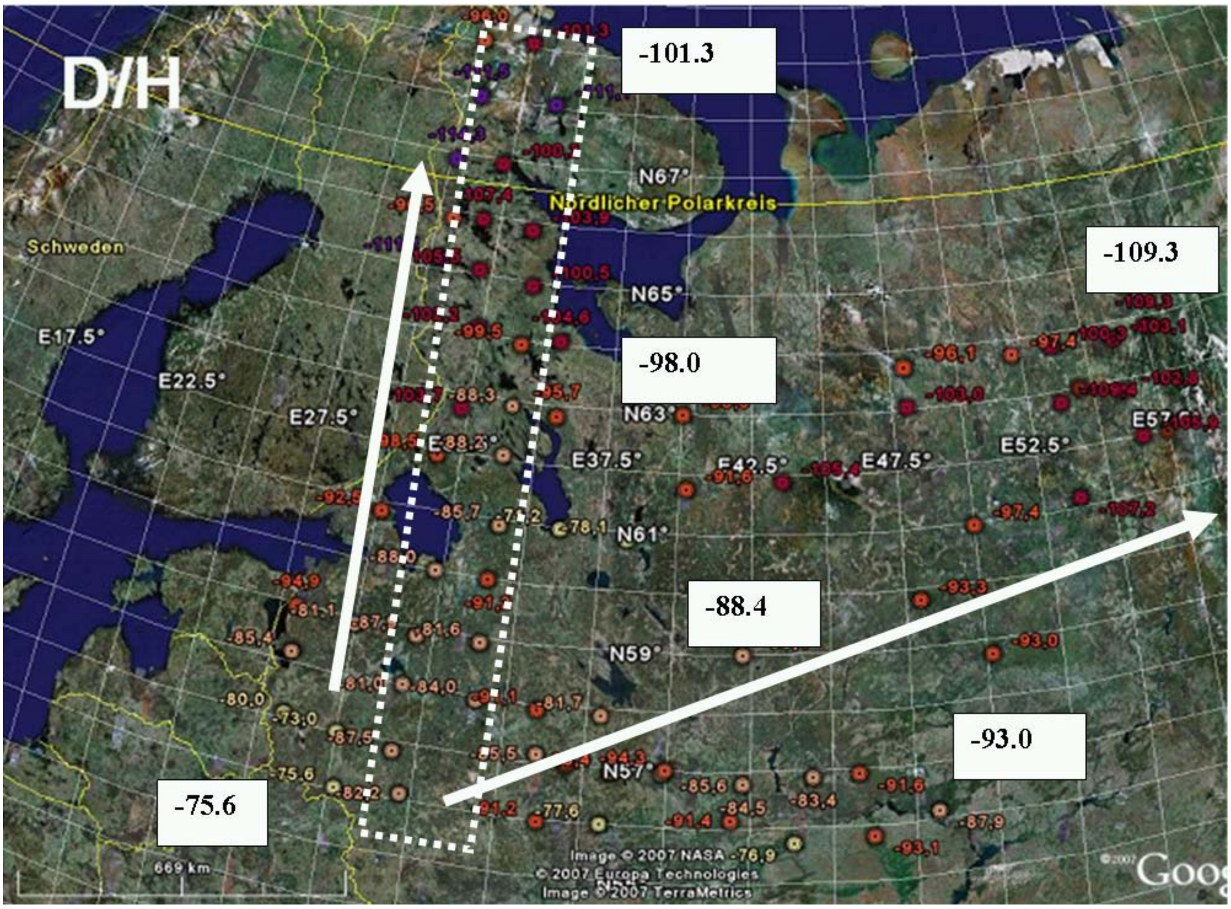

Figure 2:
Tendencies of the D/H ratio across Northern Russia. The dotted rectangle labels approximately the region of data which were used to demonstrate to south-north tendency (see Figure 3)

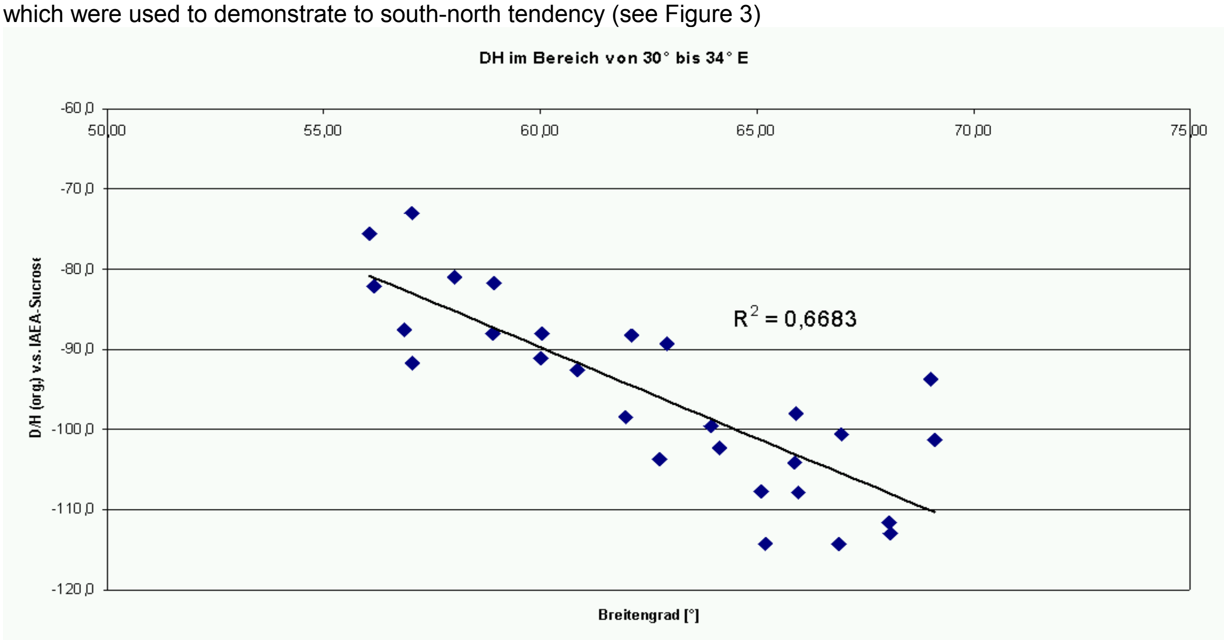

Figure 3:
D/H ratios along a north-south profile close to the western border of Russia (see Figure 2 dotted rectangle)

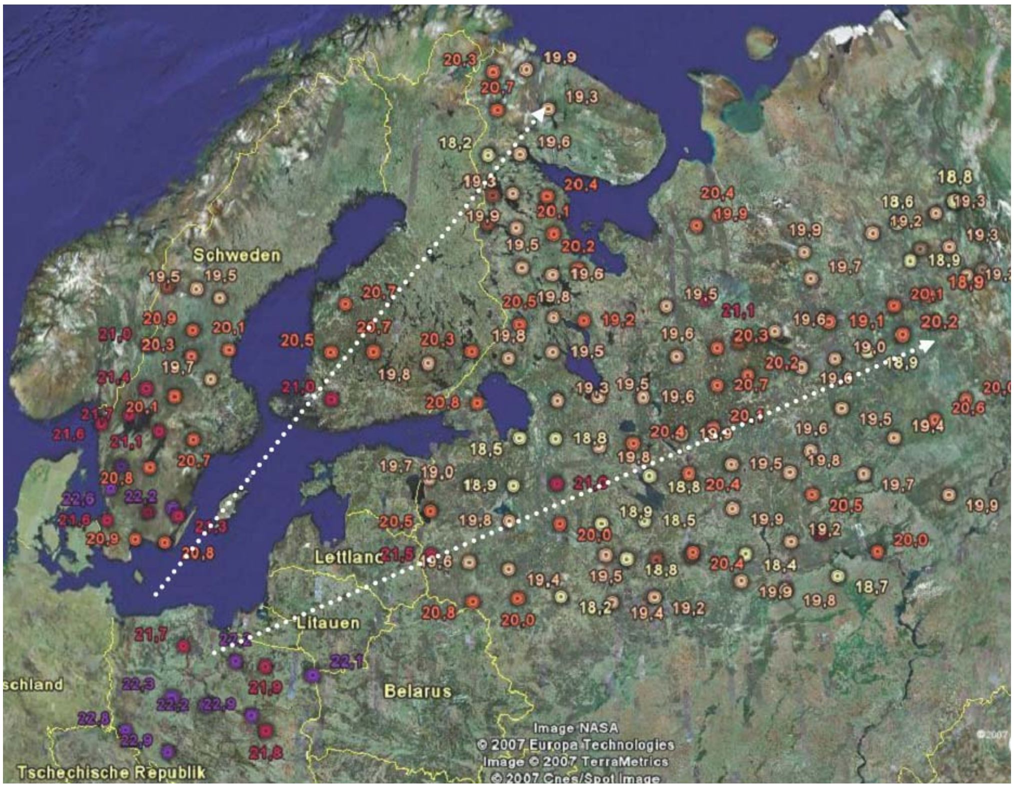

Figure 4:
Overview of the $^{18}O/^{16}O$ data from North East Europe. The decrease of the value of the $^{18}O/^{16}O$ ratio is symbolized by coloured points from dark blue to yellow. Map is generated by Google Earth®

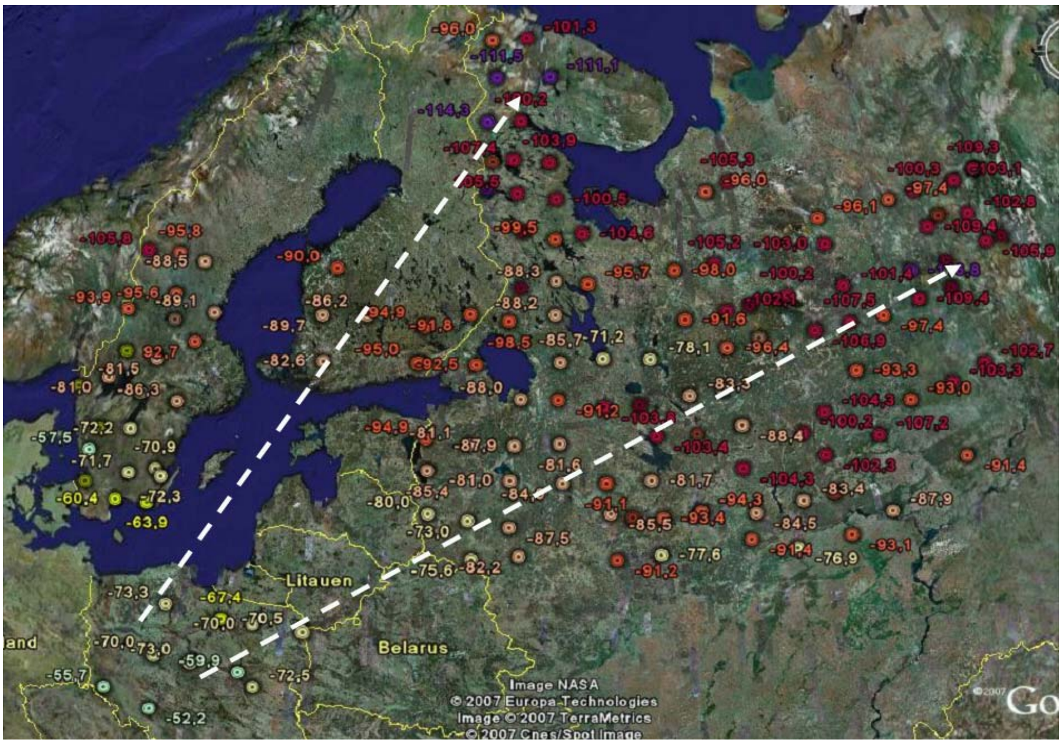

Figure 5:
Overview of theD/H data from North East Europe. The decrease of the value of the D/H ratio is symbolized by coloured points from white to dark purpleMap is generated by Google Earth®

From some locations samples of different species were collected. The number of samples is too small to make general conclusions, but the tendency fits well into the experiences with the isotopic fractionation of plants. The $^{18}O/^{16}O$ data of organically bound oxygen seem not to differ between the species (Figure 20a). The reason should be the use of atmospheric oxygen for some biosynthetic pathways. The D/H ratio originates from the tissue water itself and consequently a difference between coniferous and deciduous trees can be seen (Figure 20b).

Beside the general tendencies many exceptions will appear. But the combination of the D/H and the $^{18}O/^{16}O$ ratio is a successful tool to distinguish between different sources of timber. Combining the D/H and $^{18}O/^{16}O$ ratio of samples from different sources which may show the same value of one isotope, but differ in the corresponding other measurement (compare D/H and $^{18}O/^{16}O$ from Poland with Western Russia).

First observations of the influence of the species were possible if samples of different species were collected from the same site. Despite of the limited amount of data the differences of the water management between needle and deciduous trees can be seen. Both types of trees differ in the enrichment of D/H and $^{18}O/^{16}O$ and must be treated separately.

The physical and local conditions in North East Europe allow a clear differentiation between the various origins of samples collected or better cut in various regions. Both effects, the fall of temperature towards the north and the so-called continental effect, respectively, produce a pattern of the stable isotopes in the local precipitation and groundwater which finally is reflected by the biomass like wood. Local influences can be observed: Trees growing near a river from the high altitude of the Ural mountains show lower values.

Considering the biochemical details of the formation of biomass hydrogen isotopes shall be the most promising and independent parameter. No influence of the atmospheric oxygen pool have to be taken into account.

The spatial variation especially of the $^{18}O/^{16}O$ ratio may at a first glance limit the application. At the other hand this effect allows a good separation of different batches of products. The D/H ratio can be used as a geographical guidance. The other isotopic pairs reflect the local situation and can confirm the general declaration of the geographic origin of a specimen, and will be included more detailed in future work.

3.3 South East Asian data

A spatial collection of samples in the tropics has two disadvantages: the systematic determination of species is difficult, additionally the next tree of the same species may be found only some kilometres distant. The number of species is very high compared to the Central European flora. Therefore the number of species was larger, and consequently more botanical families are included in this study. Figure 6 shows the percentage of the different families. The family of *Dipterocarpaceae* is the most frequent one of the botanically identified species and plays also an important role in timber trade from the tropics.

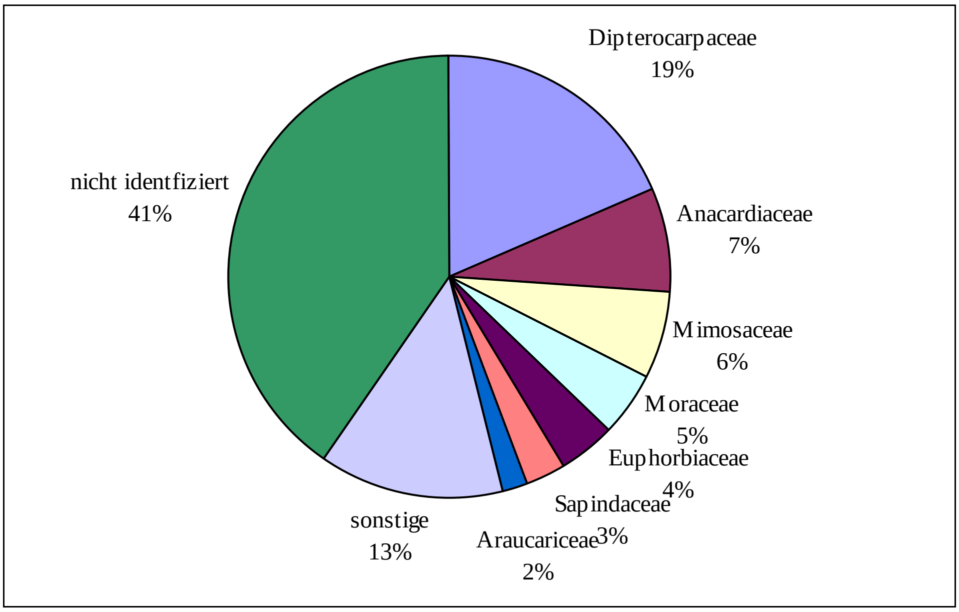

Figure 6:
Portion of the different botanically identified and not identified species assigned to its family

Cores from 4 collection sites in Vietnam, all from *Dipterocarpaceaea*, did not show significant differences between each other. The variations of the D/H ratios (between ± 4.5 and ± 8.2 ‰) and of the $^{18}O/^{16}O$ ratio (between ± 0.3 and ± 0.5 ‰) at one location are higher compared to the technical scattering of the method, but within the range which is usually observed for measurements under natural conditions. The largest standard deviation for the D/H ratios is generated by one extreme value only. The same general statement can be given for the $^{13}C/^{12}C$ ratios (between ± 0.4 and ± 0.7 ‰).

This consideration is a first screening only, for the number of samples is limited. The $^{18}O/^{16}O$ ratios of trees of different botanical classification at a certain location differ not more than ± 0.8 ‰. This means that the $^{18}O/^{16}O$ ratio seems not depend on the species. Half of the D/H ratio show a standard deviation of more than 0.8 ‰ and therefore seem to be more sensitive to systematic classifications, i.e. more depend on the physiological behaviour of the species. The standard deviations of the $^{13}C/^{12}C$ ratios are below ± 0.8 ‰ and not depend on the species, assuming that all samples are from C_3 plants only.

Table 3 summarizes the results and demonstrate the broad scattering. The data of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ seem to contain only limited information- More promising are the D/H and $^{34}S/^{32}S$ ratios.

Table 3:
Range of the results from the drill cores of East Asia

	$^{18}O/^{16}O$	D/H	$^{13}C/^{12}C$
Westmalaysia	17.9 / 20.7	-87.0 / -71.3	-29.7 / -27.1
Sumatra	17.1 / 20.3	-90.8 / -50.3	-30.9 / -25.3
Ostmalaysia	16.9 / 19.5	-82.8 / -58.7	-29.0 / -25.1
Kalimantan	15.4 / 18.9	-101.4 / -56.1	-30.0 / -26.6

In the tropical region the gradients shall not be as distinct as across the big northern continents. Generally, the local situation may play a dominating role. More details concerning the sampling should be available to interpret the data and to understand the reasons of these scattering (local climate, situation within the local ecosystem, etc.).

The situation in South East Asia differs from that of North East Europe. Water alone seems not to be the governing factor. This can be seen when the altitude effect is considered. Usually the content of the heavy stable isotopes of water decreases with increasing altitude above sea level. In the area of observation such effect could not be observed.

To differentiate between samples other isotopic pairs have to be added. This has been tested for Borneo where the political structure does not follow physical borders. Figure 7 shows that the sulphur results can be used to differ even between the regions of Borneo. Including these results sample can be distinguished beside the irregular shape of the political borderlines (Figure 8).

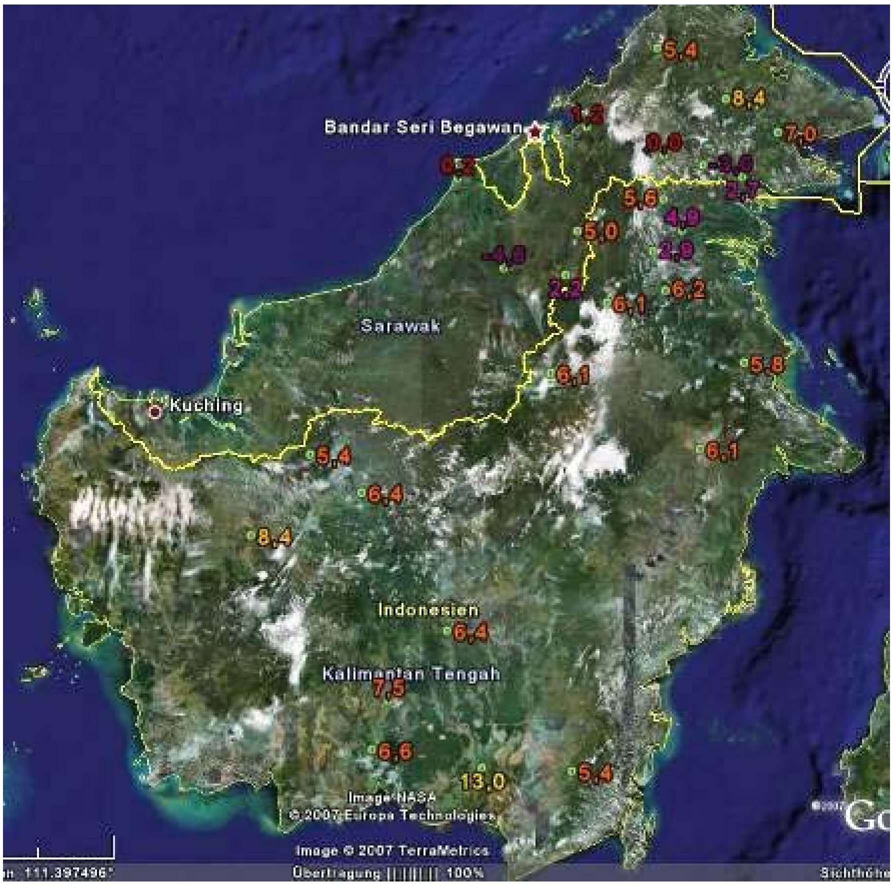

Figure 7:
$^{34}S/^{32}S$ ratios from Borneo (all political units included).Map is generated by Google Earth®

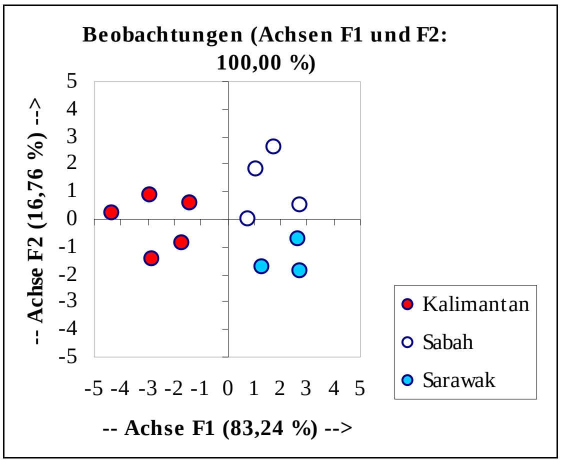

Figure 8:
Discrimination analysis including the $^{34}S/^{32}S$ ratios

4 Final discussion and conclusions

The pilot study of the stable isotopic composition of wood compares two important regions of timber trade. The isotopic composition is one of the best criteria to trace back the origin of a product. The origin and the declaration respectively can be controlled. No paperwork is needed, for water is fractionated within the global hydrological cycle. Therefore the isotopic ratios of hydrogen D/H and oxygen $^{18}O/^{16}O$, in liquid or in organically bound form respectively, are useful tracers. Two effects govern the isotopic composition at a certain location: the temperature and the distance from the sea. As a third effect the altitude above sea level is the important parameter, but may be not important in the tropics.

To obtain a useful spatial pattern of the isotope ratios of hydrogen and oxygen a gradient of one of the both parameters is necessary. This is the case for Northern Europe. The isotopic composition of water has a distinct pattern, a decrease of the heavier isotopes of hydrogen and oxygen from south to north and simultaneously from west to east. The incomplete local balance of precipitation and evapotranspiration results in a clear continental effect. Neglecting some local exceptions this general tendency has been observed for the D/H ratio of wood. The pattern of the $^{18}O/^{16}O$ ratios does not show a similar distinct pattern, probably caused by different biochemical pathways of the synthesis of biomass (Schmidt et al. 2001).

The $^{18}O/^{16}O$ ratio of cellulose is assumed to result mainly from an equilibrium between water and the carbonyl groups which happens during biosynthesis (Sternberg 1989, Sternberg and DeNiro 1990). The proportion of cellulose to lignin may determine finally the $^{18}O/^{16}O$ ratio of the wood (Gray and Thompson 1977, Keppler et al. 2007). Nevertheless the $^{18}O/^{16}O$ ratio is a tool to discriminate between timber of different origin.

In South East Asia the situation is different from that of North East Europe. The land is divided in a group of islands and peninsulas. The distances of locations at land are not far from the sea. Surprisingly the altitude above sea level seems to have no influence on the isotopic ratios of hydrogen and oxygen, even up to altitudes higher than 1500 m. The region under observation is situated around the equator, the zone of intensive hydrological turnover and the border of northern and southern atmospheric circulation. There the local water turnover seems to be intensive enough to minimize geographical tendencies. Additionally the ecological situation of each tree is not known. The tropical forest is divided into subsequent layers from the top to the bottom. Only a part of the species has been identified.

The first observations from North East Europe point to a difference between needle and deciduous trees. In the tropic forest the deciduous trees are the overwhelming portion of species, but differ in the physiological behaviour. Nevertheless a first comparison between species collected at the same location does not show too many differences within one botanical family, except for the D/H ratios. If the isotopic ratios would not depend on the kind of species this will be an important simplification for the practical use of the stable isotope fingerprinting.

The method is improved by adding other isotopic pairs like $^{14}N/^{15}N$ and $^{34}S/^{32}S$. The content of both elements in wood is low. Specific methods have to be developed. The $^{87}Sr/^{86}Sr$ ratio can also be included. This parameter is the result of long-time radioactive mother-daughter decay. The equilibrium of this decay is disturbed by geological turnover processes and depends on the local geological situation only. No isotopic fractionation is expected because of the high atomic weight of strontium and the small difference between both isotopes.

The practical work has also demonstrated that the collection of reference material should always include the mapping by a geographically based location system which makes the orientation much easier and in some cases allows a repeated collection of material of the same site or even tree.

The study has tested whether untreated wood, beside a Soxhlet extraction before the measurements, shows a sufficient variation of the stable isotopic composition across large areas. At least for North East Europe the assumption of a clear gradient has been confirmed for D/H ratios. Further studies should test whether the separation of the different pure materials from the wood as well as the addition of other isotopic pairs can improve the method. First measurements of the $^{34}S/^{32}S$ ratio of some samples from Borneo support this assumption.

5 Acknowledgement

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Figures 2,4,5 and 7 are based on Google Earth® and are applied in this scientific study.

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