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Ageing and Deterioration of Materials in the Environment – Application of Multivariate Data Analysis

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Additional information is available at the end of the chapter

1. Introduction

Ageing and deterioration of materials are key processes within the perpetual conversion of organic and inorganic matter. As far as natural cycles of organic substances are concerned a balance between syntheses, metabolic products, degradation and recycling can be expected. With respect to inorganic materials, weathering is the dominant natural process of ageing. It comprises transformation of chemical compounds and is caused by abiotic and biotic factors. The formation of new mineral phases closes the loop. Anthropogenic activities influence the well-balanced metabolism due to the increased consumption of resources and the inherent accelerated turnover rate. This development is paralleled by a relevant environmental impact caused by increasing concentrations of metabolic products. Especially greenhouse gases have become a crucial topic due to their global effect and the contribution to climate change. The fate of carbon, a key element in the global cycle, therefore attracts much attention [1-4]. Carbon sequestration and minimisation of gaseous emissions such as CO_2 and methane are promoted to decelerate the turnover. Deterioration and degradation are not only paralleled in many cases by the release of harmful substances but also by the loss of valuable resources. Prevention of negative environmental effects and careful use of resources therefore require a responsible management of products, substances and elements. Several elements such as nitrogen, phosphorus and sulphur that are released as different compounds during degradation of organic matter are in the focus of interest [5]. The ambivalence being both nutrient and pollutant has led to several techniques of resource recovery [6].

Ageing of materials or products implies changes of the original state, but it does not necessarily only comprise deterioration or degradation. Ageing can also mean formation of new substances and stabilisation. In some cases this effect is desirable. Ageing of

incineration ash and slag leads to carbonation [7, 8]. With respect to organic matter humic substances are built up resulting in a stable organic fraction with low turnover rates. These natural processes that come along with material ageing were adopted for technical applications, e.g. humification in the course of composting.

On the one hand natural processes serve as a model for anthropogenic activities with regard to the closed loop of material recycling, especially in the field of organic substances [9]. On the other hand every endeavour is made to prevent or retard the natural ageing, deterioration and degradation process of materials and to maintain a constant quality of products by adequate measures. There are several options to achieve this objective: modification of biogenic materials, treatment of the surface and application of chemical substances against microbial deterioration and ageing by abiotic factors. Although abiotic factors play a relevant role for ageing and deterioration of organic materials, biological processes dominate. Inorganic materials are primarily affected by chemical and physical attacks, but some specialised microbial communities are capable of promoting the ageing process of inorganic components. The environmental milieu plays a crucial role as it determines both biological and chemical reactions. Historical and archaeological finds owe their preservation to conditions that prevented or delayed deterioration.

This study reports on natural ageing and degradation processes of organic matter and ageing of inorganic materials over weeks, years, decades and centuries. The questions to be answered focus on two main aspects: the environmental impact by ageing and deterioration of organic and inorganic matter and the proof of resistance of organic materials against biological degradation which is a main concern in material sciences to maintain the quality of products [10-12]. Ageing and deterioration can be described by many parameters. They focus on chemical and physical changes of the material by which the process is paralleled. In some cases, especially for product control, a single parameter might be sufficient to verify the ageing of materials [13]. For an overall characterisation of the state of deterioration those analytical methods are advantageous that provide a "fingerprint" of the material. FT-IR spectroscopy and STA were applied to reveal material characteristics and their changes over time under different environmental conditions.

FT-IR spectroscopy is based on the interaction of infrared radiation with matter. Infrared radiation provides the energy for molecule vibrations that become visible as absorption bands. The plot of wavenumbers (energy) within a defined range vs. band intensities results in the spectrum. Infrared spectra describe materials by the unique pattern and provide information on material chemistry. Band intensities depend on the concentration of the compound and the molar decadic absorption coefficient that is reflected in the spectrum and on individual properties of the functional group. Most molecules are infrared active and represented by diverse bands due to different types of molecule vibrations. They are characterised by a typical energy level and are therefore found at defined wavenumbers. The molecule skeleton and other functional groups influence the band position and can cause a band shift. Whereas pure substances show distinct bands that can be attributed to functional groups, complex materials feature broad and overlapping bands that are often not assignable. However, the material shows a "fingerprint". The information of underlying

features can be extracted by multivariate data analysis. Spectroscopic methods are widely used due to many advantages, e.g. easy handling, robustness, complex information. Multivariate data analysis is an indispensable tool for data evaluation in practice.

The thermal behaviour of any substance depends on chemical and physical properties. Complex materials contribute with all components to a specific thermal pattern. STA comprises thermogravimetry (TG) and differential scanning calorimetry (DSC). Additionally the released gaseous compounds are recorded in the coupled mass spectrometer. With TG the mass loss of the material is measured during combustion. DSC measurements result in a heat flow curve indicating exothermic and endothermic reactions of the material during combustion. The enthalpy can be calculated by integration of the area below the heat flow profile and a baseline. The variation of combustion parameters regarding temperature range, heating rate, isothermal heating and gas flow, oxidative or pyrolytic conditions leads to different information about the sample. In material sciences thermal analysis is widely used for quality control. In general, distinct temperatures are in the focus of interest, e.g. melting and crystallisation temperature. The application of thermal analysis has been extended during the last decade. TG- and DSC-profiles also lead to comprehensive information as spectra do. Both FT-IR spectroscopy and STA have proven to be adequate tools for the characterisation and quality assessment of complex materials such as waste and soils [14-20]. The extensive use of these methods in this field is also a merit of multivariate data analysis. Based on this approach much information can be extracted from a huge data pool generated by FT-IR spectroscopy and STA.

2. Methods

2.1. FT-IR spectroscopy and simultaneous thermal analysis

FT-IR spectra of landfill samples were recorded by a Bruker Alpha® (Bruker, Germany) instrument in the mid infrared area (4000 cm^{-1} to 400 cm^{-1}) in the attenuated total reflection mode (ATR). For the milled lignocellulosic materials the ATR-FT-IR spectra were collected by a Bruker Vertex® with a Pike MIRacle™ ATR device in the wavenumber range from 4000 cm^{-1} to 600 cm^{-1}, at 4 cm^{-1} resolution averaging 32 scans. The milled sample was homogenised and directly applied on the ATR reflection module with a diamond crystal providing a measuring area of approximately 4 mm^2 and a pressure applicator. Twenty four scans per spectrum were collected at a resolution of 4 cm^{-1} and corrected against ambient air as background. The average of four spectra (maximum deviation of the four spectra from the average spectrum < 5%) was vector normalised prior to multivariate data analysis. Spectra treatment and data evaluation were carried out using the OPUS software.

Thermal analyses were carried out with a STA 409 CD Skimmer instrument (Netzsch GmbH) in an Al_2O_3 pan with the following combustion parameters: temperature range 30 – 950 °C, heating rate 10 °C·min^{-1}, gas flow 150 ml·min^{-1} (80% He and 20% O_2), sample amount 16.00 mg. The pyrolysis of wood powder was carried out at different temperatures (200, 300, 350, and 600 °C) under oxygen-free conditions (100% He) with a heating rate of 10 °C·min^{-1} and isothermal treatment for 20 min. After oxidative combustion of the pyrolysed wood

powder the enthalpy was calculated by integration of the area below the heat flow curve and a horizontal baseline from 30 to 650 °C, starting at 30 °C.

For data evaluation the heat flow profiles and the temperature resolved curve of the CO_2 ion current extracted from the mass spectrum were used. For data evaluation the integrated software PROTEUS was used.

The sample sets that were subjected to multivariate data analysis are mentioned in the text. Depending on the material and the question to be answered different multivariate evaluation methods were applied using The Unscrambler® 9.2 and 10.0 respectively (Camo®).

2.2. Multivariate data analysis

A large number of multivariate data analysis techniques are available. Depending on the questions to be answered the adequate method is applied. The methods presented here either belong to the group of "pattern recognition" or to the group of "multivariate calibration methods". The group of "pattern recognition" comprises exploratory data evaluation such as principal component analysis (PCA) and classification methods (SIMCA). The PCA visualises the inherent data structure in the scores matrix and thus reveals hidden phenomena. The influence of variables on the data structure is illustrated by the loadings plot. Classification aims at separation of groups of data. It is a prerequisite for classification that class characteristics have to be known prior to analysis. Therefore classification is called a "supervised method" compared to a non-supervised method by which groups of data are distinguished after the data analysis without previous knowledge. From supervised methods a model can be derived in order to discriminate between the groups [21]. Thus classification is a predictive method based on category variables, e.g. material types, age, degree of degradation. A library of spectra or thermograms provides the opportunity of data evaluation according to different aspects that are expressed by category variables and allows a multiple evaluation of spectra and thermograms. Soft independent modelling of class analogy (SIMCA) is a classification procedure based on PCA class modelling. ''Soft modelling'' that is often used in chemical pattern recognition means that two classes can overlap. Thus it is possible that samples have characteristics of both defined classes, or of neither of the defined classes. Samples are assigned to a defined class if they show similar characteristics. Similarity in this context means a particular class pattern. This approach allows the samples to have their individual properties besides common features of the class that are the decisive factor for the membership. In order to find out to which degree the class models really differ, the model (class) distance is determined by fitting members from two defined classes to their own model as well as to the other model. It is calculated on the basis of pooled residual standard deviations. The distance from a model to itself is 1. According to Esbensen [21] distances of more than 3 indicate a significant segregation between the defined classes. The results obtained can be visualised by the Coomans plot. The crossing horizontal and vertical lines that divide the area into four quadrants indicate the significance level. In two quadrants the defined classes are located. If samples feature properties of both classes they are assigned to the overlapping quadrant ("both"). New

samples outside the limits do not belong to the model. They are located in the quadrant "neither - nor". The 5% significance level means that 95% of the samples in the corresponding quadrants truly belong to the defined classes. New samples in these quadrants are therefore identified as members of the classes.

Partial Least Squares-Discriminant Analysis (PLS-DA) is based on PLS regression to model the differences between classes. For the separation of two classes the PLS algorithm is used with the dummy variable (e.g. -1/+1) to distinguish the two defined groups.

Methods of the "calibration" group allow models to be developed for parameter prediction if the parameter is adequately reflected by the collected data, in this study by the spectral and thermal patterns. Contrary to classification models by which class assignment according to defined properties is performed, the prediction model provides distinct values of the parameter in question. Prediction models focus on the determination of dependent Y-variables for new samples that were characterised by independent X-variables. Based on an established validated X-Y model the Y-variable can be derived from X-variables. Due to this relationship only X-measurements are necessary. This procedure can be advantageous if expensive and time-consuming methods for the determination of Y-variables are replaced by superior methods.

3. Application of multivariate data analysis

3.1. Deterioration of organic matter in dumps and landfills

Degradation of organic matter is a natural necessary process in the environment. On the one hand degradability is an inherent property of materials that depends on both chemistry and structure and on the other hand it is mainly influenced by environmental conditions that determine the velocity of this process. The balance between synthesis, transformation and degradation is a criterion of sustainability. Organic matter in mixed waste consists of native biomolecules, modified biomolecules or organic substances that are exclusively based on chemical syntheses. Modification means chemical and physical diversification. Modification of biomolecules, e.g. wood or cellulose is necessary to enhance the stability against microbial attacks. For biological degradation chemical or physical modification represents a barrier to some degree. Wood modification for instance such as acetylation and thermal treatment can increase the lifetime of a product, but pose a problem for degradation [22-24]. Microbial degradation of synthetics hardly takes place. Ageing by oxygen and UV exposure in the forefront can contribute to a certain bioavailability of molecule moieties. Due to the heterogeneity of materials and conditions in old landfills and dumps the turnover and the emissions are hardly predictable. This fact and the long aftercare phase led to the European "multi-barrier" concept that provides the pre-treatment of municipal solid waste prior to landfilling. This procedure ensures extensive degradation within a limited period of time under controlled aerobic conditions. Nevertheless, landfill sites from the past are still a current topic. Investigations of the solid waste focus on the assessment of the current stage, and the potential of future emissions can consequently be derived. Ageing of the landfill also comprises the attenuation of hazardous substances in the leachate that are released due

to degradation of organic matter via the liquid path. The duration of the emission process is mainly influenced by sorption and desorption processes of the landfill. Degradation has taken place in the past, but due to manifold interactions with the mineral matrix the release of mineralisation products is delayed and requires monitoring over a long period of time [25].

Within the scope of a landfill risk assessment regarding the remaining emission potential characterisation of an old landfill (AL) was carried out using FT-IR spectroscopy and thermal analyses besides bio-indication by vegetation, biological tests and conventional parameters. The objective of these investigations was to decide on additional measures for landfill restoration, e.g. *in situ* aeration, if natural attenuation had been insufficient. The landfill originated from the 1970s and 1980s. For the risk assessment 70 old landfill (AL) samples were classified. Additionally 15 samples from a reactor landfill, where municipal solid waste was deposited without pre-treatment until 2007, were integrated in the research programme for comparison and were classified as well. The SIMCA models [21] comprised 110 samples originating from different old landfills ("LF") with very low gas forming potential and 190 mechanically-biologically treated ("MBT") waste samples representing all stages of degradation and diverse reactivity. Besides samples from the old landfill (AL) to be assessed, 130 landfill samples (115 samples from old landfills + 15 reactor landfill samples) with low, middle and high gas forming potential were used for the total organic carbon (TOC) prediction model by means of PLS-R. Table 1 compiles the sample set used for SIMCA (section 3.1.1) and PLS-R (section 3.1.2).

Sample origin	Sample number (SIMCA)	Sample number (PLS-R)
Old landfill (AL)	70	70
Old landfills (LF)	110	115
Reactor landfill	15	15
MBT	190	-

Table 1. Origin and number of samples used for SIMCA and PLS-R

3.1.1. The degree of degradation - Assessment by classification

The degree of organic matter degradation is a key parameter for the verification of efficient waste pre-treatment and safe disposal. With respect to the assessment of old deposits it decides on additional measures for landfill sanitation, e.g. *in situ* aeration. Gaseous emissions such as methane and nitrous oxide should be minimised due to their contribution to global warming. The microbial activity and the gas forming potential of the solid waste are usually determined on the basis of time-consuming biological tests. Both FT-IR spectroscopy and STA are useful alternative methods. Different approaches are possible to evaluate spectral and thermal data to reveal the emission potential: prediction of reactivity parameters based on infrared spectra and PLS-R or classification (SIMCA) of unreactive and reactive samples according to their spectral pattern. Prediction of the required parameters "respiration activity" and "gas generation potential" by FT-IR spectroscopy replaces time-

consuming and expensive parameters if a model is available. This approach was realised for mechanically-biologically treated municipal solid waste and composts [26, 27]. For old landfill materials prediction did not lead to reliable results because chemical (spectral) characteristics do not adequately reflect the biological behaviour at low reactivity levels [4]. Mineral components affect the biological behaviour although biodegradable substances are still present and visible in the spectrum. Moreover, the biological tests are error-prone at low values. It should also be emphasised that the C-H vibrations of the aliphatic methylene group that are an essential indicator of decomposing biomolecules in fresh waste materials are rather assigned to plastics in old landfill materials which was confirmed by thermal analysis [4]. Due to these reasons classification by SIMCA was applied. It was based on mid-infrared spectra over the whole wavenumber range from 4000 cm^{-1} to 400 cm^{-1}. As mentioned above SIMCA does not lead to parameter values as PLS-R does, but provides information on specific properties of interest via classification. For the comparison with distinct limit values of the Landfill Ordinance [28] this might be a difficulty. However, the basis for the category variable can be distinct parameter values as illustrated in the following example. Two classes were defined: old landfills ("LF") with the reactivity level clearly below the limit values of the Austrian Landfill Ordinance [28] and biologically treated waste ("MBT") comprising all stages of degradation after mechanical pre-treatment. The limit values are defined for respiration activity to be 7 mg O_2 per gram dry matter over a 4-day-period and 20 NL (NL = norm litre) gas per kg dry matter over a 21-day-period. Samples used for the "LF" class cover a wide range of unreactive materials from different Austrian and German old landfills. Samples used for the "MBT" class originated from the sixteen Austrian treatment plants. Each class was modelled by a separate PCA. By means of SIMCA landfill (AL) and reactor landfill samples were classified. For the class "LF" very low reactivity is the common class property. The class "MBT" represents different degradation
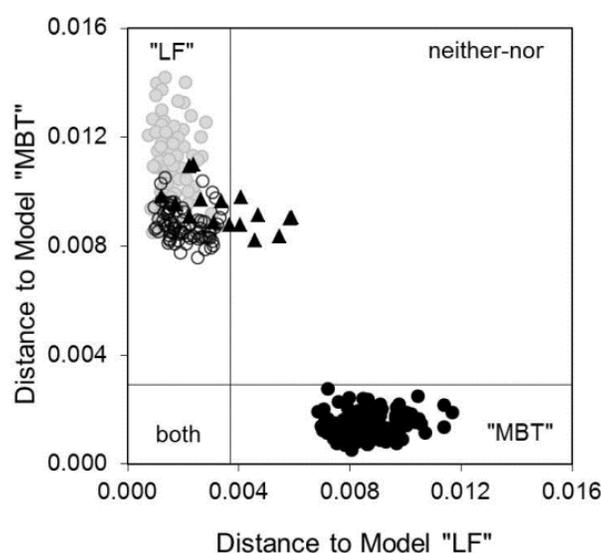

Figure 1. Classification of old landfill (AL) spectra (black circles) and reactor landfill spectra (black triangles) by means of the SIMCA model visualised by the Coomans plot; grey dots = "LF" class, black dots = "MBT" class

stages of municipal solid waste after the mechanical pre-treatment. The model distance was determined to be 42, which indicates a significant segregation between the class "LF" and the class "MBT". The results obtained were visualised by the Coomans plot (Figure 1). The assigned landfill (AL) samples (black circles) were identified as members of the "LF" class (grey dots). The chosen significance level of 5% indicates that 95% truly belong to unreactive landfills. The classification result of the investigated landfill samples reveals that ageing and degradation has taken place to a large degree and no risk is expected regarding the emission potential which is in accordance to the reactivity parameters that were determined for control. By contrast, the younger reactor landfill (black triangles) where degradation had progressed less, showed several reactive samples that are located in the quadrant "neither – nor" as they do not comply with the stability criteria that specify the "LF" class nor with characteristics of the MBT" class.

The question why reactive samples are not assigned to the "MBT" class that covers all stages of degradation can be answered by the different composition and different metabolic products under aerobic and anaerobic conditions. The different composition mainly results from resource recovery and mechanical pre-treatment.

3.1.2. The degree of degradation - assessment by parameter prediction

The compliance with the limit values according to the Austrian Landfill Ordinance [28] is a prerequisite for landfilling of waste materials in Austria. The TOC is a key criterion for the assessment of organic matter as it is the source of potential emissions. Due to degradation of organic matter the TOC content decreases continuously to a low level. The remaining organic carbon can be assigned to recalcitrant components such as wood, waxes, cork, natural rubber, chitin, humified matter, modified biomolecules and synthetics. A low value therefore indicates extensive degradation of biodegradable substances. Apart from the special regulation for biologically treated municipal solid waste a limit value of 5% for the TOC was stipulated by the Austrian Landfill Ordinance [28]. Within the scope of the risk assessment of the old landfill (AL) the TOC contents of the 70 samples were determined together with different landfill materials (Table 1) using the carbon-nitrogen-sulphur (CNS) analyser. The thermal behaviour is strongly related to material composition and reflects physical and chemical properties. Biodegradation leads to substantial changes of material properties that can be revealed by thermal analysis. The content of organic carbon mainly influences the thermal behaviour. Therefore it can be expected that the TOC is adequately reflected by the thermal pattern of the material. Among different combustion parameters the heat flow profile, resulting from differential scanning calorimetry (DSC), was selected for the TOC prediction model by means of PLS-R. The TOC is the Y-variable being in demand and DSC data represent the X-variable. Figure 2A displays the heat flow profiles of two old landfill (AL) samples (A and B). Sample A contains a high portion of plastics that are revealed by sharp and distinct exothermic peaks in the heat flow profile. Figure 2B demonstrates the correlation between the predicted and the measured TOC values. Four PLS components were used to calculate the model.
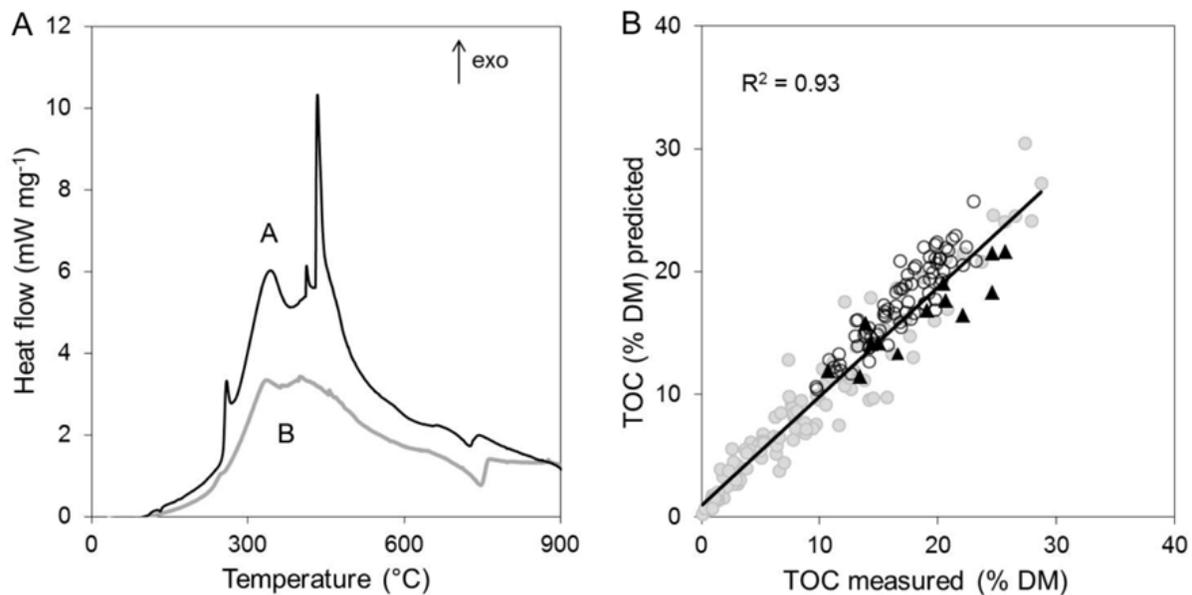
Figure 2. A-B: Heat flow profiles of two old landfill (AL) samples A and B (A); Correlation between the predicted and the measured TOC contents (B) based on heat flow profiles of old landfill samples (grey dots), old landfill (AL) samples (black circles), reactor landfill samples (black triangles) and PLS-R (n = 200, R^2 = 0.93, RMSECV = 1.95%); DM = dry matter

The root mean square error of cross validation (RMSECV) was found to be 1.95% and the coefficient of determination (R^2) 0.93. Despite the low reactivity the TOC values of the old landfill (AL) are relatively high and in the range of the reactor landfill. The TOC is a main parameter in the Austrian Landfill Ordinance [28] to describe the organic matter content. Landfilling criteria for all landfill types regarding organic matter contents are stipulated by the limit value of the TOC content. Only mechanically-biologically treated municipal solid waste of which landfilling criteria are defined by biological tests is an exception. The sum parameter does not differentiate organic substances that can considerably differ in the biological behaviour. This fact confirms the limited significance of the sum parameter, especially for the evaluation of old deposits where the high TOC is mainly caused by plastics and textiles that hardly contribute to emissions under anaerobic conditions.

3.2. Carbonation – ageing of incineration bottom ash deposits

Carbonates are relevant components in Austrian municipal solid waste (MSW). In the past construction waste was landfilled together with municipal solid waste which is still recognised by the high portion of carbonates in old deposits. The separation of construction waste has become a legal request in order to meet the target of material recycling, to improve the biological treatment of municipal solid waste and to comply with the limit values of the demolition waste landfill. Nevertheless, carbonates are always part of municipal solid waste. Residues of construction materials are the main source of carbonates. During waste combustion carbonate decay takes place at temperatures above 650 °C which is paralleled by CO_2 release and the formation of the corresponding oxides, e.g. CaO. The uptake of water leads to hydroxides and high pH-values between 12 and 13 of MSW

incineration bottom ash. During the natural ageing process of the deposited material CO_2 from air causes the inverse reaction in that carbonates are built up again. The velocity of the process in the environment depends on available surfaces where carbonation takes place. It can be accelerated by the increase of the surface and artificial CO_2 supply. Carbonation causes the pH-value to decrease which leads to the stabilisation of the system and immobilisation of heavy metals [29, 30].

Fresh incineration bottom ash was compared to ashes aged under laboratory conditions. Laboratory conditions mean that the material is crushed < 20 mm and CO_2 is continuously supplied until saturation is reached and no additional CO_2 is adsorbed. Thermal analysis is an appropriate method for carbonate determination [31]. It was applied in combination with PLS-DA to find out whether artificially aged bottom ash could be clearly distinguished from fresh bottom ash. Additionally several samples of naturally aged incineration bottom ash that had been stored in a pile over decades and partially exposed to air were included to reveal the progress of carbonation under environmental conditions. The content of carbonates is reflected by both the mass loss (thermogravimetry) due to CO_2 release and by the peak intensity of the heat flow profile caused by the endothermic reaction of the carbonate decay above 650 °C. Moreover, the CO_2 ion current was recorded by the coupled mass spectrometer. It is evident (Figure 3A, curve A) that carbonates are also found in fresh bottom ash as the carbonation reaction starts immediately after contact of fresh bottom ash with air. Curve B displays a peak at around 450 °C. As the material does not contain organic compounds (TOC below the limit of determination) it can be assumed that CO_2 is adsorbed to a certain degree and is removed within this temperature range. The temperature resolved CO_2 ion current curves (Figure 3A) were used for data evaluation and subjected to PLS-DA. The dummy variable (-1) was assigned to fresh incineration bottom ash, the dummy variable (+1) to bottom ash with advanced carbonation. Figure 3B displays the result of the PLS-DA.
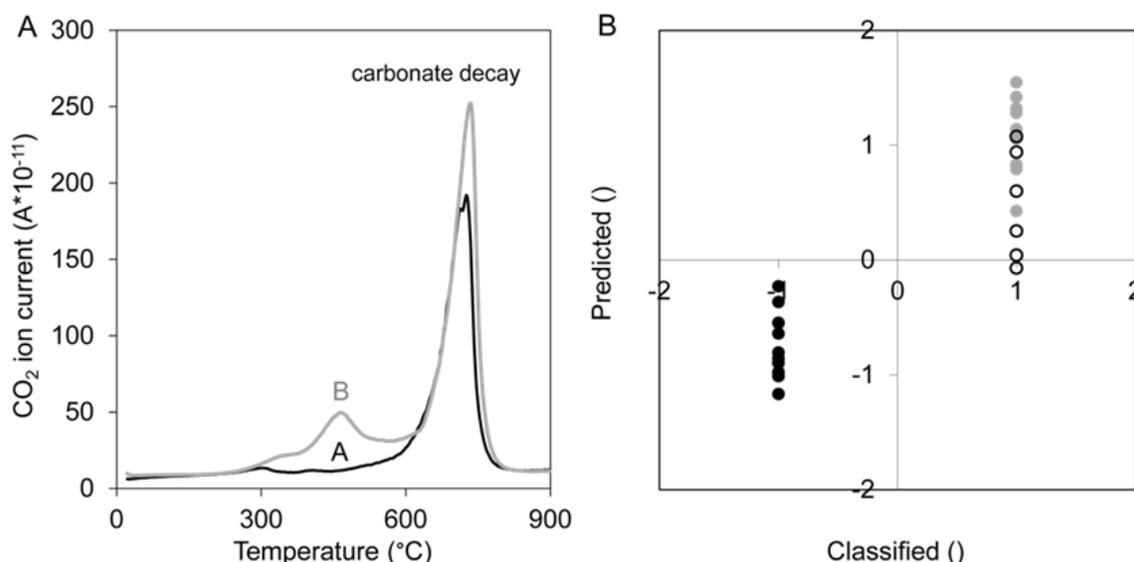

Figure 3. A-B: Temperature resolved CO_2 ion current (A) of fresh (black line A) and aged (grey line B) bottom ash; Discriminant analysis (PLS-DA) of the temperature resolved CO_2 ion current (B) of fresh (black dots) and aged bottom ash (artificial CO_2 supply = grey dots, natural ageing = black circles)

Despite the long lasting storage of incineration bottom ash in the environment carbonation was less efficient (black circles) and the discrimination from fresh ash is not as distinct which can be due to greater particle sizes and inhibited CO_2 supply in the pile. Minor carbonate contents are not the reason as more construction waste was usually deposited with municipal solid waste several decades ago.

3.3. Compost application on soils – Degradation and enrichment of organic matter

The loss of organic carbon in agricultural soils is caused by several factors. It is mainly influenced by tillage and application of mineral fertilisers. Climate change and increasing temperatures might support this development. The supply of organic matter is an indispensable measure to maintain relevant soil functions such as water and nutrient holding capacity and aggregate stability. Composting is one option to stabilise organic materials, especially by humification which corresponds to the natural process in soils. Although there are many questions to be answered how humification of composts can be improved, this procedure is a relevant contribution to carbon sequestration despite the benefits for soils. Composting is a process of degradation and stabilisation at once. Ageing does not only result in deterioration, but also in stable organic matter synthesis as it is the case for humic substances with a very low turnover rate. Depending on the input material the ageing process takes place in different ways. Some mixtures of organic materials are rather mineralised and deterioration dominates. A well-balanced mixture of organic residues containing a variety of biogenic materials with different biodegradability provides favourable conditions for humification and higher contents of humic substances are obtained. FT-IR spectra of different biogenic materials were recorded. They include several stages of decomposition and stabilisation from fresh to composted materials. The PCA result in Figure 4 shows the grouping of different biogenic materials. Group A (grey triangles = sewage sludge compost) comprises sewage sludge, paper sludge and bulk materials, group B (grey and black dots = biowaste composts from two composting plants) contains garden waste, kitchen waste and bulk materials. In order to track the humification process the relevant wavenumber regions (1745-1685 cm^{-1} and 1610-1567 cm^{-1}) according to Meissl et al. [27], where humic acids are reflected were selected for the PCA. The calculation was performed with four principal components (PC). The first PC explains 94% of the variance and the second PC 3%. Marginal humification took place in the sewage sludge mixture during composting [32]. Group B featured a relevant increase of humic acids to 40% of organic dry matter, as confirmed by chemical analyses.

Humic substances in composts are young compared to soil humic substances. It can be hypothesised that the process of ageing which includes further degradation, mineralisation and additional stabilisation of compost organic matter is continued after compost application to soils and influenced by many factors [33]. Several long-term experiments provide information on how soil parameters change and develop by fertiliser application and amelioration measures [34, 35]. Plaggen soils represent an example of anthropogenic soils generated by compost application over centuries which resulted in higher organic matter contents compared to the surrounding poor soils [36, 37]. The higher organic matter
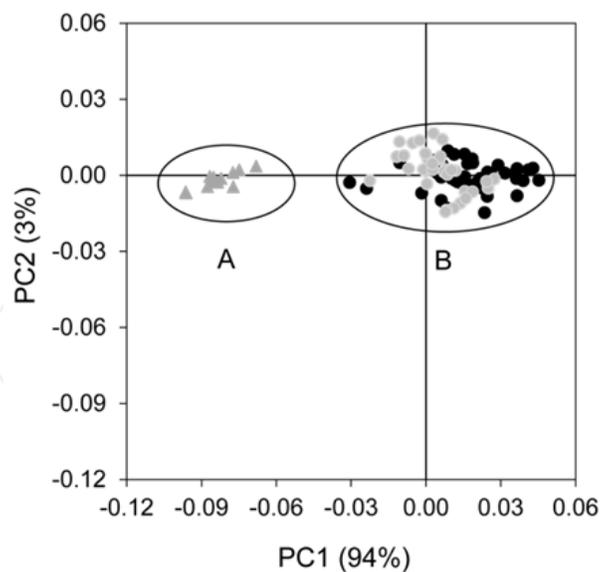
Figure 4. Scores plot of the PCA of hardly (A = grey triangles, sewage sludge compost) and well (B = grey and black dots, biowaste composts) humified composts based on the infrared spectral regions 1745-1685 cm^{-1} and 1610-1567 cm^{-1}

content is a typical feature of this soil type although it has considerably decreased if the level of the original compost serves as a rating scale. According to climate conditions the organic matter content develops towards the corresponding equilibrium over long periods of time. The interactions of compost organic matter with soil organic matter and mineral components under specific climatic conditions are hardly investigated, especially the influence of compost quality on dynamics of biodegradation [32]. Quality in this context focuses on the degree of organic matter stabilisation. Long-term monitoring systems will be necessary in the future to collect a comprehensive data set for statistical evaluation to find out which compost can efficiently compensate for organic matter losses. The multivariate approach enables identifying different factors that influence the ageing process, e.g. soil type, mineral matrix, degree of compost humification and climate.

A long-term project was started in 2010 to find out the development of organic matter contents in agricultural soils by application of well humified compost. The data represent the first two years of the long-term monitoring programme. Compost was applied on three different test plots (10 m x 10 m) in an agricultural region in Eastern Styria, Austria. A plot of the corresponding agricultural soil (10 m x 10 m) without compost application served as a reference. The composition of the soils differed in the clay content. Samples originating from the trial fields with compost application and samples from the reference plot were collected after the first and the second year of compost application and characterised by means of thermal analysis. All plots were represented by 4 composite samples, each one consisting of 10 individual samples. The material was taken from a depth up to 30 cm. Particles of organic matter (roots, leaves, stalks, vegetable residues etc.) were carefully separated in order to analyse only degraded organic matter. Thermal analysis is an appropriate method to describe complex matrices. Water in interface layers of clay minerals in soils can pretend higher organic matter contents if this parameter is determined via the mass loss caused by
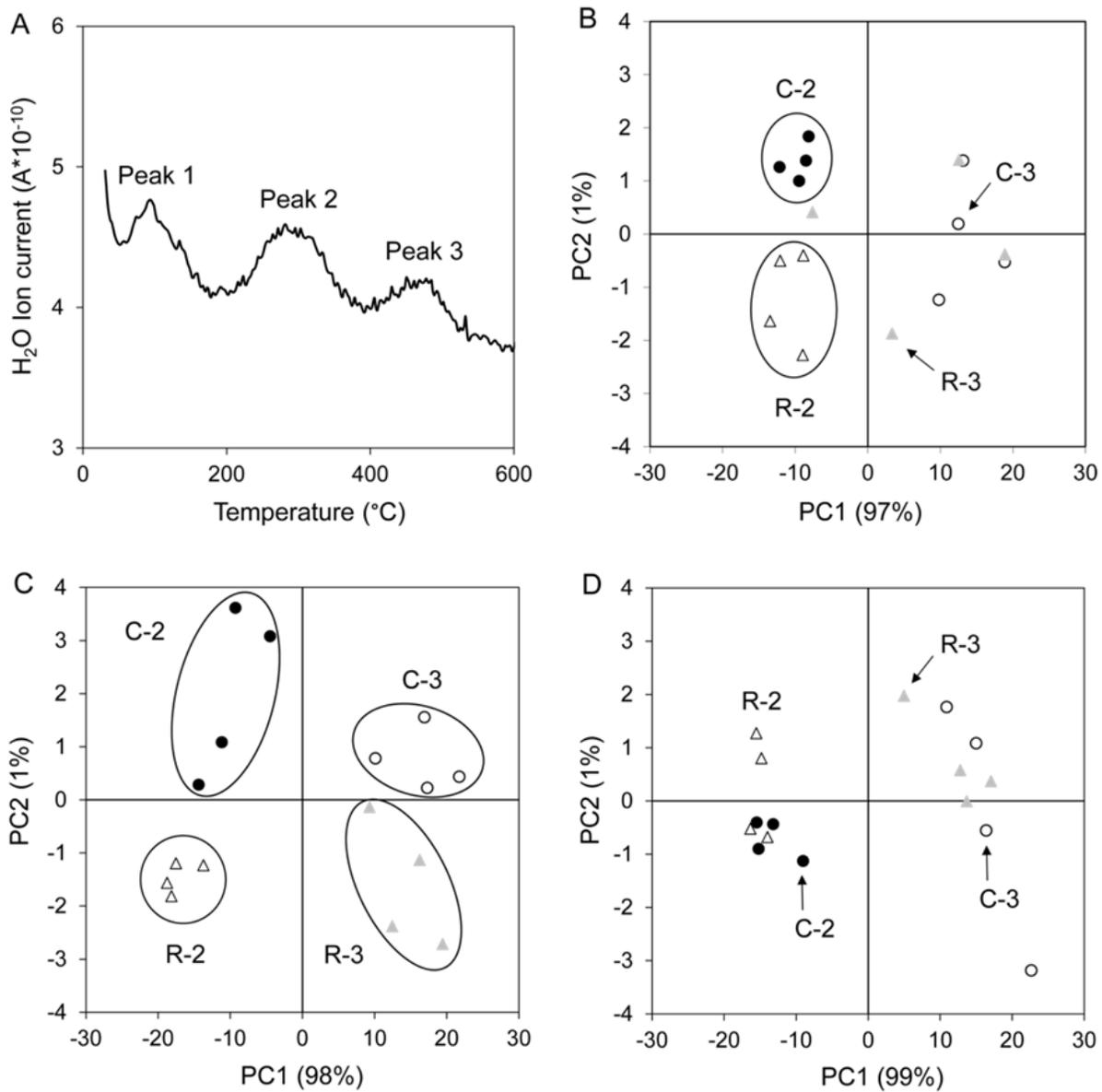
Figure 5. A-D: Temperature resolved H₂O ion current of combustion gases (A); Scores plots of the PCA based on the DSC profiles of samples from the three (B-D) test plots; sampling after one and two years with (C-2, C-3) and without (R-2, R-3) compost application

combustion in the muffle furnace. Figure 5A confirms this assumption by the temperature resolved ion current of water (m/z = 18) extracted from the mass spectrum of combustion gases. Peak 1 is assigned to residual water of the air-dried sample, peak 2 results from the oxidative combustion of organic matter and peak 3 can be attributed to water from interface layers of clay minerals. The PCAs were based on the heat flow (DSC) profiles. The heat flow pattern reflects the exothermic reaction of organic matter combustion and is therefore an adequate method to evaluate the development of organic matter in soils. Figures 5B-D display the scores plots of the PCAs calculated for the three test plots with compost (C) and the corresponding reference plots (R) after one (C-2, R-2) and two years (C-3, R-3). The different sampling times can be clearly distinguished (left and right areas in the scores plot

of the PCA). Apart from the test plot shown in Figure 5C the influence of compost application on soil organic matter is not detectable after 2 years. Differences between the two sampling times are caused by other effects. It is evident that the process of organic matter deterioration is also affected by the soil matrix and local conditions. The interference by other effects implies long-term observations in order to unambiguously verify an increase of organic matter, especially if carbon sequestration is assessed and CO_2 balances are derived.

3.4. Ageing of charcoal

Carbonaceous residues from combustion processes in the environment have become a field of increasing interest. Incomplete combustion of organic materials under oxygen-free or -poor conditions is a common feature of carbonaceous materials. Depending on the material and the pyrolysis process several terms are in use for the resulting products: biochar, charcoal, chars, and soot carbon. All types of these products are subsumed under the terms "black, charred or pyrogenic carbon". Charcoals are ubiquitous in terrestrial and aquatic environments. They are found in many areas due to forest fires and in urban soils where anthropogenic activities or fire disasters have left their marks. Charcoal production has a long tradition in the context of early technical processes where heat and energy were needed. Residues of charcoal are found at historical sites of charcoal burning in connection with ore mining and metallurgical processes, glass production and lime kilns. The traditional production of charcoal has been abandoned in most cases. It is only found in a few areas on a diminished scale nowadays as cultural heritage. Charcoal is currently produced in closed systems, not least because of organic pollutants generated during pyrolysis.

Carbonaceous residues rank among the fraction of recalcitrant organic matter in soils. In the context of climate change its relevance in the carbon cycle and the contribution to carbon sequestration has become a crucial topic during the last decades [38, 39]. With the emerging scientific interest in "Terra preta" soils where charcoal is thought to play an important role in the amelioration of physical and chemical properties of tropical soils [40-42], additional benefits are attributed to pyrolysis products. The particular capillary structure of charcoals leads to enhanced water und nutrient retention and might explain their favourable impact to soils.

Due to its recalcitrance charcoal is a witness of anthropogenic activities in the past as revealed by excavations at archaeological sites [43, 44]. Besides historical, cultural and technological aspects, questions about the long-term behaviour of charcoals in the environment, carbon release, effects on soil and vegetation arise. Historical charcoals enable us to track the ageing process of a recalcitrant carbon fraction, to discover chemical and physical changes and to identify the significance of their environmental impact. Historical charcoals that trace back to the Middle Ages and the Modern period were investigated using thermal analysis and compared to recent charcoals that were produced according to the ancient technology in rectangular charcoal mounds. The historical charcoals were produced

in rectangular mounds, but also in charcoal pits or charcoal platforms. Depending on the region and the availability different kinds of wood were used. The sample set used for these investigations was dominated by the following species *Picea abies*, *Pinus sylvestris* and *Fagus sylvatica*.

Thermal analysis is an appropriate method to characterise these materials [45]. The influence of pyrolysis temperature and wood species on the thermal behaviour was investigated in several experiments in order to support data interpretation. Figure 6A (left side) displays the enthalpy of charcoal that was produced from wood powder at different pyrolysis temperatures (200, 300, 350, and 600 °C) under laboratory conditions. The grey bars indicate the enthalpy referring to dry matter (DM) and the black bars the enthalpy referring to organic dry matter (oDM). It is evident that increasing pyrolysis temperatures result in higher enthalpies of the charcoal. Figure 6A (right side) additionally shows the enthalpy of charcoals (left pair of bars) produced at 350 °C from different wood species (Pa = *Picea abies*, Ps = *Pinus sylvestris*, Fs = *Fagus sylvatica*) under laboratory conditions and the enthalpy of the corresponding untreated wood (right pair of bars). The enthalpy of wood is low compared to its pyrolysis product. According to preliminary results the pyrolysis temperature has a stronger effect on enthalpies than the wood species. Further analyses will be performed to reveal more details about the impact of wood species, pyrolysis time and applied historical technologies. For multivariate data evaluation every influencing factor requires an adequate number of samples.

Due to the long exposure time in the environment historical charcoals are contaminated by different substances. In order to minimise the portion of adhesive mineral components from the surrounding soil, only charcoal particles were collected at historical sites. The surface of
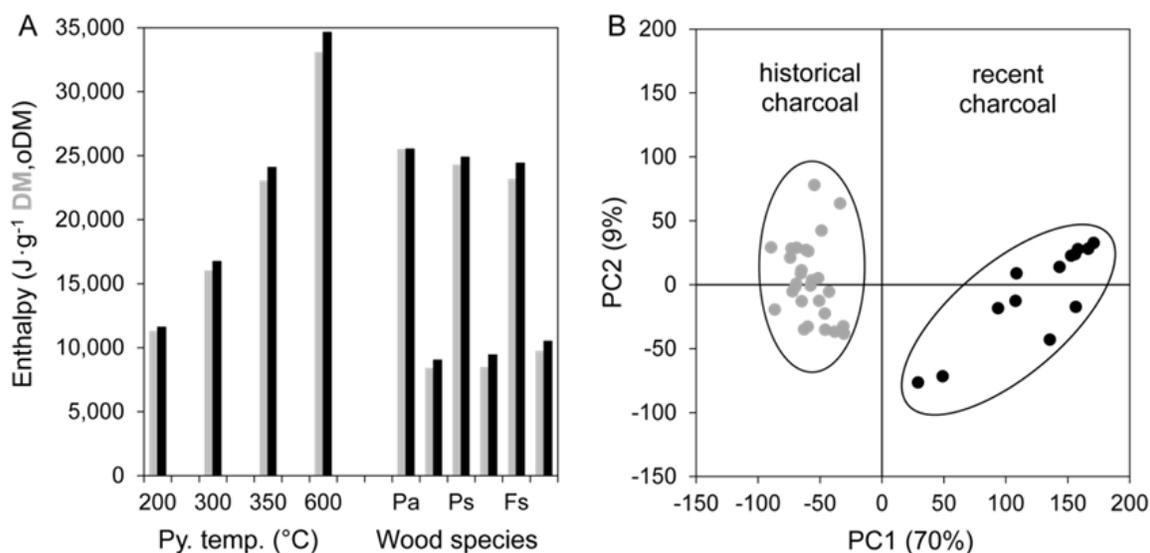

Figure 6. A-B: Left side (A): Enthalpies of charcoals from wood powder (pyrolysis temperatures 200, 300, 350, and 600 °C), right side (A): enthalpies of charcoals (pyrolysis temperature 350 °C) from different wood species and corresponding non treated wood (Pa = *Picea abies*, Ps = *Pinus sylvestris*, Fs = *Fagus sylvatica*, grey bars referring to DM, black bars referring to oDM); PCA based on DSC profiles of historical and recent charcoals (B).

the particle was removed and the core was used for sample preparation. However, mineral particles were also found in the capillaries of historical charcoals. Their presence was confirmed by the higher percentage of inorganic matter. It can be assumed that other unknown chemical compounds were adsorbed at the surfaces of charcoal capillaries. The inclusion of non-charcoal compounds was considered as an intrinsic factor of the ageing process and therefore the whole sample was taken as "historical" charcoal. Figure 6B displays a PCA result based on DSC profiles of historical and recent charcoals. Historical and recent charcoals are clearly segregated. The first PC explains 70% of the variance.

3.5. Lignocellulosic materials

Wood or lignocellulosic materials in general are ubiquitous in the environment and are therefore involved in many degradation processes of material mixtures such as municipal solid waste, landfill materials or soils. In the previous sections lignocellulosic material was often part of waste organic matter and evaluated together with other components. Although the degradation behaviour of the mixture can be or is different from those of single constituents, the knowledge of their composition, of differences and physico-chemical properties are useful for a better understanding of the behaviour of lignocellulosic material. The main structural wood polymers - cellulose, hemicelluloses, and lignin - are the most abundant biopolymers of the Earth's carbon cycle. These polymers form the lignocellulose complex in all woody tissues. The highly ordered structure of cellulose microfibril aggregates embedded in a matrix of hemicelluloses and lignin provides the basis for its mechanical strength [46] and for the resistance to microbial attack [47], to which also low molecular mass extractives contribute [48].

3.5.1. Wood types / species and their composition

The two wood types - hardwood and softwood – can be identified by FT-IR due to their different chemical composition. A PCA based on the fingerprint region (1800 cm^{-1} to 700 cm^{-1}) of ATR-FT-IR spectra of different wood species belonging to hardwood (Poplar - *Populus × canadensis*, Beech - *Fagus sylvatica*, Birch - *Betula pendula*) or softwood (Pine - *Pinus sylvestris*, Spruce - *Picea abies*) shows their separation in the scores plot along PC1 (Figure 7A), which accounts for 77% of the spectral variation. The loadings plot of the first principal component (PC1) (Figure 7C) shows the variables (wavenumbers) that are responsible for the separation, describing the differences due to different contents or numbers of functional groups representing chemical compounds. A positive loading means that the samples with positive values in the scores plot have a higher number of the functional group represented by this wavenumber, e.g. hardwoods have a higher number of acetyl groups (C=O stretching vibration of the acetyl group at 1735 cm^{-1}) than softwoods (Figure 7C) or vice versa softwoods have a lower number of acetyl groups. The acetyl groups derive from the acetic acid esters attached to the hemicelluloses. Comprehensive lists for the assignment of bands found in the infrared spectra of wood and acetylated wood can be found elsewhere [49-51]. The band at 1235 cm^{-1} corresponds to the C-O vibration of this acetyl ester. Three further remarkable bands at 1593 cm^{-1}, 1510 cm^{-1}, and 1268 cm^{-1} represent lignin. The lignin

content and composition of hardwoods and softwoods are different. Softwood has higher lignin contents than hardwood which is represented in PC1 by the negative loading of the band at 1510 cm^{-1}. Softwood lignin consists mainly of G-lignin (guaiacyl units) and hardwood lignin mainly of S-lignin (syringyl units). Besides small differences of the wavenumber at which the maxima of the bands appear the latter has a stronger band at 1593 cm^{-1}. Therefore the loading of this band is positive (Figure 7C, PC1).
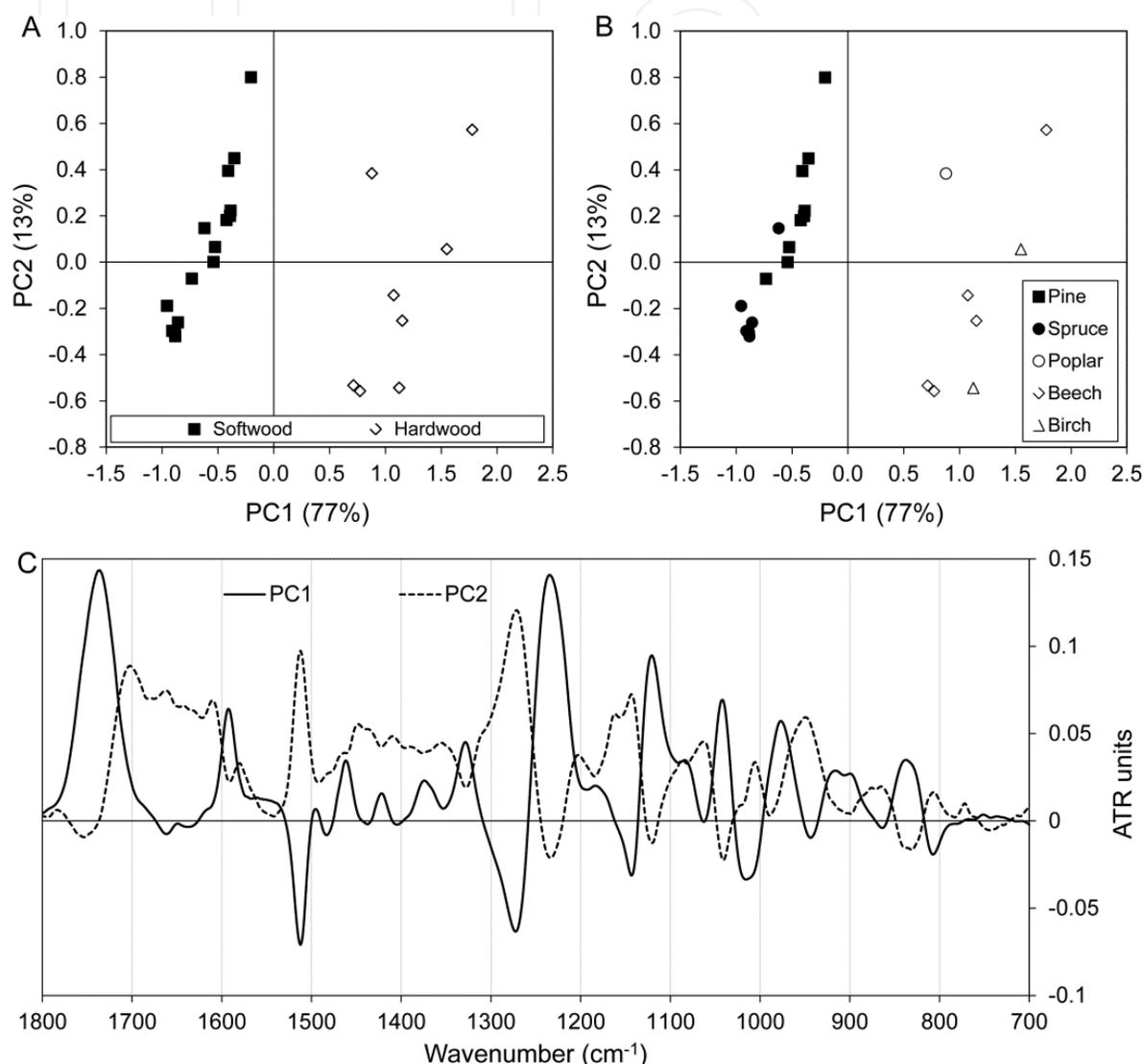

Figure 7. A-C: PCA based on the fingerprint region (1800 cm^{-1} to 700 cm^{-1}) of the baseline-corrected and minimum-maximum normalised ATR-FT-IR spectra of different wood species (Pine - *Pinus sylvestris*, Spruce - *Picea abies*, Poplar - *Populus × canadensis*, Beech - *Fagus sylvatica*, Birch - *Betula pendula*); Scores plots of the first two principal components labelled according to wood type (A) and species (B) and their loading spectra (C)

The band at 1268 cm^{-1} typical for G-lignin shows negative loadings and scores, because more G-lignin is found in softwoods. The separation along PC2 (13%) is mainly due to different lignin contents of the different species. For further interpretation of the differences the reader is pointed to additional literature [49-52].

Lignin content and lignin composition are important wood parameters. Their fast and reliable determination is therefore of interest and was studied with infrared spectroscopic methods using both ranges the near infrared (NIR) [53-59] and the mid infrared (MIR) [56, 60] leading to many PLS-R models. Simple linear regressions between the ratio of bands heights (H_{1510} / H_{897}) [60] and the lignin content (Figure 8A) result in prediction models with similar precision as those obtained form PLS-R models for MIR (Figure 8B) and NIR [58, 59].
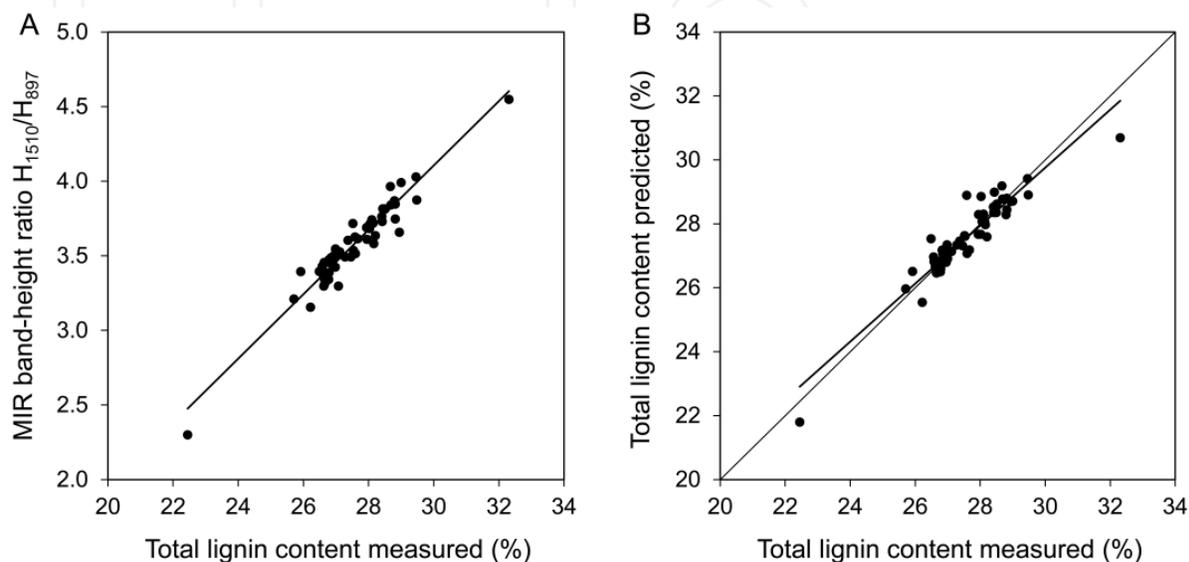

Figure 8. A-B: Calibration with a good correlation (r = 0.965) between band-heights ratios H_{1510} / H_{897} from MIR spectra and lignin contents (A); Cross-validation result of the PLS-R model for the total lignin content determination (B) using the minimum - maximum normalised MIR spectra in the wavenumber range from 1745 cm^{-1} to 790 cm^{-1} with 4 PLS components, R^2 = 0.89, and a RMSECV of 0.43%

3.5.2. Degradation of wood

Ageing and deterioration of wood is caused by light [61], temperature [62], moisture, microorganism [10], fungi [47, 63], and others, which influence physical and chemical properties.

Wood is a remarkably durable material. In nature, only higher fungi have developed biochemical systems to degrade the lignocellulose complex and perform the conversion and mineralisation of wood to carbon dioxide and water. Most of these fungi belong to basidiomycetes. Although they are phylogenetically closely related [64] their strategies of degrading wood are diverse: While brown-rot fungi degrade primarily the wood polysaccharides and leave behind a polymeric but highly modified lignin, simultaneous white-rot fungi degrade all polymeric wood constituents at similar rates. Selective white-rot fungi, which lack the ability to degrade cellulose efficiently, cause extensive delignification of wood. Ascomycetes and Deuteromycetes may cause soft-rot decay that leads to softening of wet wood. Cavity formations in wood cell walls are most characteristic for this decay type. Extensive reviews on decay pattern, chemistry, and biochemistry of microbial wood degradation are available [47, 63, 65].

NIR [60, 66-72] and MIR [73, 74] spectroscopy have been used since about three decades to follow the chemical changes due to fungal decay. How less invasive spectroscopic and microspectroscopic methods contribute to understand fungal wood decay has been reviewed recently [75].

The result of fungal decay of wood which has been exposed for a longer period can normally be seen at once. From the practical point of view when e.g. construction wood in service has to be evaluated the early degradation stages which cannot be seen are of special interest because the mechanical properties of wood are strongly influenced. Therefore spruce wood (*Picea abies* L. (Karst.)) was incubated with three strains of the selective white-rot fungi *Ceriporiopsis subvermispora* (namely FPL 90.031, FPL 105.752 and CBS 347.63) for 14 days (details in [60]). The PC1 – PC2 scores plot (Figure 9A) of a PCA, based on the second derivatives of the MIR spectra from 1800 cm^{-1} to 1490 cm^{-1}, shows that the time course can be followed along PC1. From the loadings spectra (not shown here but in [60]) it is known that the lignin content decreases with increasing incubation time. Along PC3 (Figure 9B) a kind of clustering of the three strains was obtained. This means that the PCA also allowed separation of the three strains and as a consequence from the loading spectra (cp. Figure 2e in [60]) information about the different behaviour of the three strains can be gained. Besides small differences in oxidation products and water adsorption properties the number of acetyl ester groups is different, which points to slightly different decay pattern of hemicelluloses. A better separation of the three strains was obtained using NIR spectra [60].
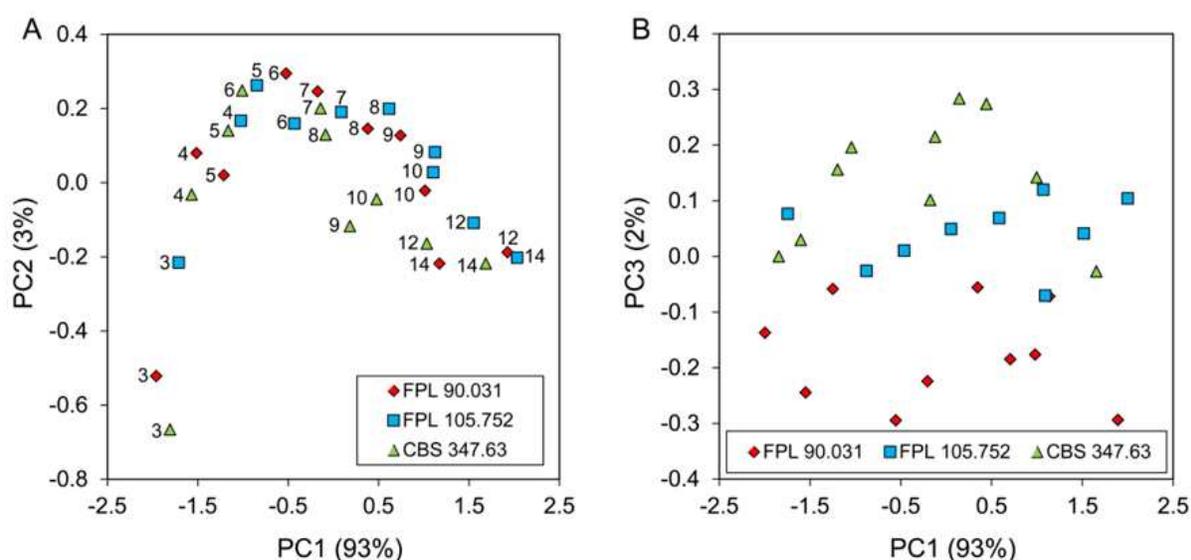

Figure 9. A-B: PCA results of the second derivatives of the MIR spectra from 1800 cm^{-1} to 1490 cm^{-1}: (A) scores plot PC1 – PC2; (B) scores plot PC1 – PC3; Adapted from [60] with the permission from IM Publications

The degradation of wood exposed for a longer period, was investigated using three types of pine wood (*Pinus sylvestris*) samples: a) recent, b) strongly degraded in a forest, and c) subfossil wood. The latter one, which was found in the sediment of a lake in Finland, was dated dendrochronologically to be 4000 – 5000 years-old [76].

The results of a PCA based on the fingerprint region (1800 cm^{-1} to 700 cm^{-1}) of the ATR-FT-IR spectra of pine wood (*Pinus sylvestris*) of varying degradation stages are shown in Figure 10. The scores plot of the first two principal components (Figure 10A) reveals that the two strongly degraded samples are far from the other ones along both axes. The loadings plot of PC2 (Figure 10C – PC2 A) shows that mainly polysaccharides, preferably hemicelluloses have been degraded. This conclusion is confirmed by the loss of the acetyl-ester band at 1735 cm^{-1}.

The loading spectrum of PC1 (Figure 10C – PC1 A) shows that the strongly degraded sample consists almost exclusively of lignin. A comparison of this spectrum with a milled wood lignin spectrum confirmed this (not shown). Therefore it can be concluded that this
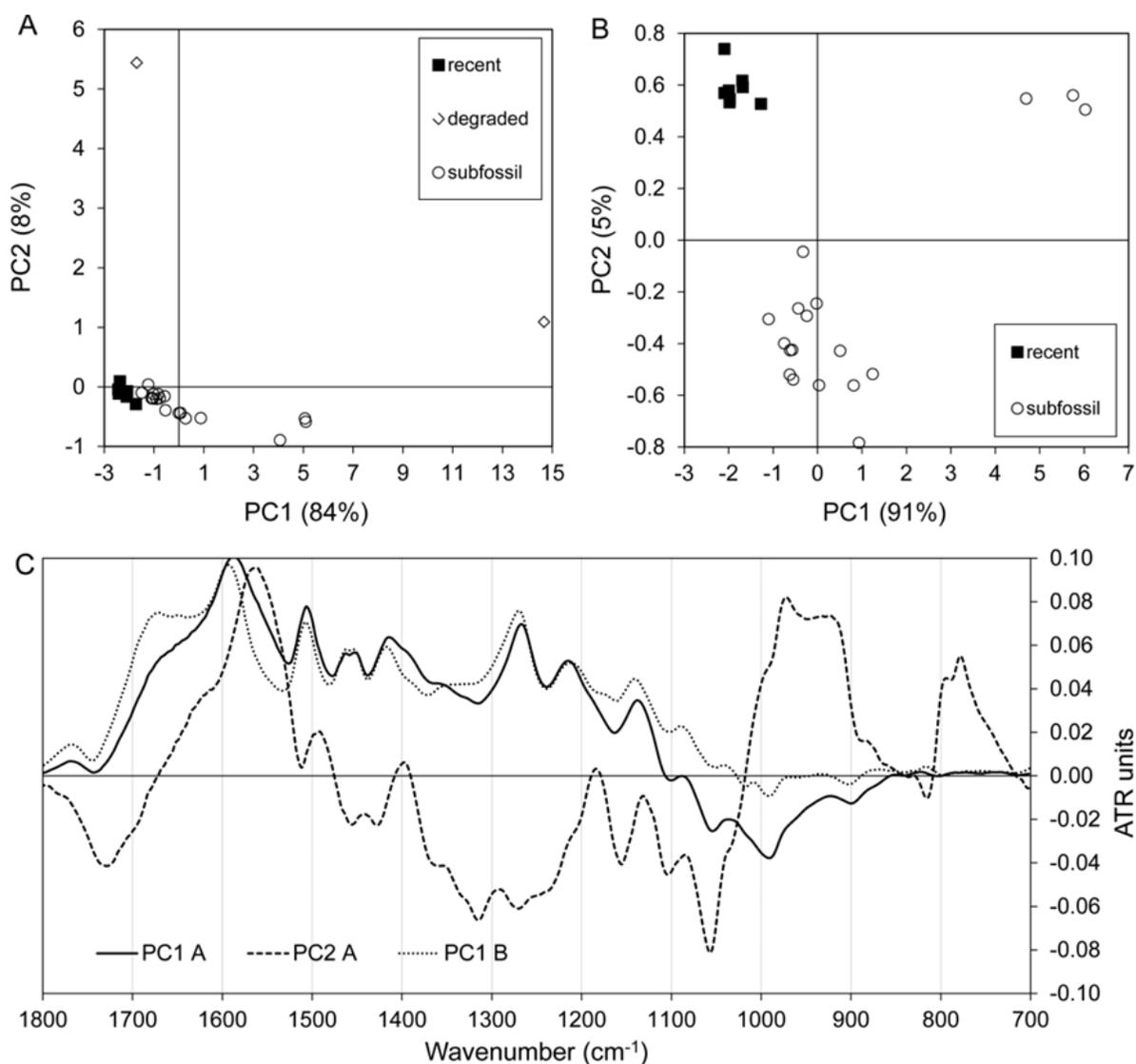
Figure 10. A-C: PCA based on the fingerprint region (1800 cm^{-1} to 700 cm^{-1}) of the baseline-corrected and minimum - maximum normalised ATR-FT-IR spectra of pine wood (*Pinus sylvestris* L.) of varying degradation stages; Scores plots of the first two principal components labelled according to degradation stage with (A) and without the samples labelled "degraded" (B) and their loading spectra (C), whereas A refers to the PCA in (A) and B to the PCA shown in (B)

sample was degraded by brown-rot fungi. The loading spectrum of PC1 (PC1 B) of the PCA shown in Figure 10B shows similarity with the previous one. This means that the difference between the recent samples and the subfossil samples is an increase in the lignin content. In his thesis Stich [76] reviewed possible degradation types and mechanisms including the preservation of organic matter in subfossil and fossil samples [77]. Based on his spectroscopic and chemical results he concluded that a slow *in situ* hydrolysis had taken place in these subfossil samples.

3.5.3. Natural durability of wood - Preventing wood from degradation

The service life of wood for outdoor use such as for windows, doors, balcony, roofs, bridges, and other applications should be as high as possible. Wood is a remarkably naturally durable material. This natural durability in terms of decay resistance against fungi, varies in a wide range between species and even within species [78-80] and can also be predicted by infrared spectroscopy [78, 81, 82]. The natural durability of wood mainly depends on the extractives composition [79, 83] but also on the extractives content [79] and is in general higher in hardwoods than in softwoods. Besides the natural durability and biological control of wood decay against fungal infection [84] thermal treatment of wood has shown to improve the service life [62, 85, 86] as well as chemical modification of wood such as acetylation [86-91], butyrylation [92] or furfurylation [93]. Traditional wood protection methods employ chemicals [94-99] that are considered toxic and can adversely affect human health and the environment [100]. Serious efforts are made globally to develop alternative protection methods based on natural products with little or no toxicity. The implementation of these technologies progresses slowly because of certain limitations, including discrepancies between laboratory and field performance of natural products, variability in their efficacy related to exposure/environmental conditions, and legislation difficulties due to disagreements on setting standards defining the quality of their performance and use. However, information on those natural compounds that have shown promise for wood protection is available under defined interactive categories [100].

4. Conclusions

Ageing and deterioration of different complex materials in the environment were characterised using FT-IR spectroscopy and thermal analysis. Due to large data pools generated by these analyses multivariate statistical methods were applied for data evaluation. Several examples of practical application and basic research were selected. Several samples originate from current investigations (section 3.3 and 3.4). The sample sets will be extended to elucidate the processes of ageing and deterioration. For compost application on soils the question of remaining organic matter in the long-term under the given climatic and soil conditions will be relevant. The contribution of different environmental factors should be revealed by multivariate data analysis. With regard to charcoals more historical samples from different regions are necessary to find out the contribution of pyrolysis temperature and time, wood species, applied technology and environmental conditions. Based on the collected data sets evaluation can be performed under diverse aspects by means of adequate multivariate methods.

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Acknowledgement

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