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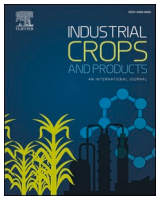

Dynamics of decomposition gases and release of volatile organic substances in long-term storage stockpiles of pine bark: Focus on mono- and sesquiterpenes

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ABSTRACT

Bark is one of the key sidestreams produced in sawmills and currently is typically used for energy generation. Storage of bark is required to ensure supply at times of high heating demand, i.e. in cold winter months. In addition to energy generation, mono-, sesqui-, and diterpenes are components of resin in coniferous trees that can be used in various applications. The main aim of the present work was to investigate emissions of mono- and sesquiterpenes and common greenhouse gases, their generation, and flux dynamics within stockpiles of Scots pine (Pinus sylvestris L.) bark occurring during long-term storage in outdoor conditions. The focus was therefore on conversions of organic matter by decomposition into various gaseous substances. The work adds to the understanding how the decomposition products and volatile organic compounds (VOCs) are emitted from a stockpile and their stockpile pore space gas dynamics. Furthermore, it demonstrates how ventilation of a stockpile can affect the dynamics of decomposition product release and timing of VOC emissions during the storage. The storage time lasted from mid-April until the end of September 2021, during which seven samplings were carried out. CO_2 was the main greenhouse gas liberated, with some emission of CH_4, CO, and methanol. The major content of monoterpenes was released in the first 11 days after the stockpile establishment, and approximately half the sesquiterpenes in a 50-day storage time. Ventilation showed an effect on the release in the analysed cases, as the compounds decreased more rapidly over time due to ventilation. While the main share of carbon (C) losses originated from the release through CO_2 in the non-ventilated stockpile, approximately 39 % more C was released in the ventilated stockpile. Gases other than CO_2 were responsible for about 1 % of the total gaseous C losses from the non-ventilated, and 2 % from the ventilated, stockpile.

1. Introduction

Forest-based biomass plays an important role in the Finnish bio-economy strategy, in which raw materials are efficiently used, and sidestreams are utilised for the highest possible degree of processing (Finnish Government, 2022). Supply chains of forest biomass have been established to work effectively to supply materials to end-using facilities (e.g. Väätäinen et al., 2021). The key sidestreams from the forest industry, and particularly from sawmills, include sawdust, bark, and wood shavings. These materials can be used for further processing or in energy generation when combusted. Bark is one of the key sidestreams produced by sawmills and is typically used for energy generation. The use of bark is especially common in large combustion plants, or when combustion is part of gasification, pyrolysis, or pelletising (Kons et al., 2022). In Finland, a total of 11.1 million cubic metres of by-products of the forest industry and wood residues were used for energy generation

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during 2022, and bark had the highest share, with the use of 6.7 million cubic metres (Natural Resources Institute Finland, 2023). The side-streams of the forest industry provide material throughout the year, whereas demand for such materials is fluctuating and more seasonal. Storage of bark is therefore required to enable the supply at times of high demand, typically in the cold winter months (e.g. Wihersaari, 2005; Alakoski et al., 2016; Väätäinen et al., 2017).

Biomass decomposition is a consequence of biological and chemical processes occurring within the storage stockpiles, predominantly caused by lignocellulolytic and thermotolerant microorganisms (Hakkila, 1989; Jirjis and Theander, 1990; Zöhrer et al., 2021); these cause dry matter losses, emissions, and consequently, economic losses (Routa et al., 2018). Carbon-cycle-related enzymatic activities and the abundance of various microbial communities cause biomass losses in given biomass storage conditions (Nagler et al., 2022). Hydrocarbon (e.g. terpenes; Rupar and Sanati, 2005) and greenhouse gas (Jylhä et al., 2017) emissions are also generated during biomass storage. In the storage of wood residues, emissions originating from storage may well be several times higher than emissions generated during production and the entire supply chain (Wihersaari, 2005). Furthermore, adding to these emissions, for example terpenes are abundant in the resin of coniferous trees and are released from living trees, as well as from the wood (Strömvall, 1992; Granström, 2007; Holopainen et al., 2013). Monoterpenes evaporate to the air easily due to the rather weak hydrophobic forces between molecules, their low molar weight, and high vapor pressure (Strömvall and Petersson, 2000). Sesquiterpenes are also naturally emitted into the air, and notably during wood drying (Granström, 2009). The terpenes and the photooxidants formed in reactions involving terpenes affect air quality, i.e. they are a source of primary and secondary pollutants (Granström, 2007; Holopainen et al., 2013). It has earlier been observed that c. 90 % of monoterpenes are released in the sawdust of Scots pine in the first ten days (Granström, 2010).

Bark is more easily decomposed than woodchips, probably due to its higher nutrient content and palatable organic matter (Jylhä et al., 2017). There is already some research on how the amounts of extractives decrease in bark during storage (Bianchi et al., 2016; Jyske et al., 2020; Routa et al., 2020, 2021; Halmemies et al., 2022). Studies on direct emissions from storage stockpiles of bark, particularly on different chemical compositions and conversions of organic matter by decomposition into various gaseous substances, are scarce, however. Hydrocarbon emissions have been investigated to resolve whether the quantity of emitted gases cause health problems for people living in nearby areas (Rupar and Sanati, 2005). Recently, Tagliaferri et al. (2022), (2024) presented results on odour emissions from woodchip storage, using a flux chamber system. Emissions caused by the storage of bark were investigated by Oksanen et al. (2022) for CO_2, CH_4, and N_2O, using a closed chamber method with subsequent gas chromatography analyses. However, previous studies have not separately investigated the emissions of valuable volatile organic compounds (VOCs) in the field, such as mono- and sesquiterpenes, their generation, and flux dynamics within stockpiles occurring during the storage of bark. Here, we have analysed the bark of Scots pine (Pinus sylvestris L.) during prolonged storage in stockpiles with and without ventilation and investigated decomposition of the organic matter. We have analysed mono- and sesquiterpenes, soluble carbohydrates and extractives in bark chips, measured several volatiles (selected mono- and sesquiterpenes, CO_2, CO, CH_4, N_2O, methanol) in the pore spaces of the stockpiles and those released to the atmosphere through the stockpile surface layer.

The study's main aim was to get a better understanding of the stockpile-internal decomposition dynamics with a particular focus on the release of mono- and sesquiterpenes. The objective was to analyse decomposition and gas emissions occurring in the stockpiles of bark chips of Scots pine during prolonged storage in outdoor conditions, and the effect of ventilation on this. Ventilation was performed applying wind-driven ventilators that provided additional exchange of gases between stockpiles and the ambient environment, whereas active cooling or drying using blowers (e.g. Lühr et al., 2021) or Dome Aeration Technology (e.g. Trois and Polster, 2007) were not applied. Changes in the chemical composition of the bark and liberation of various gases were analysed at selected timepoints during the summer.

The focus of this study was on the chemical composition of selected VOCs and their development over time, influenced by external and internal factors (e.g. temperature, moisture content (MC)):

- we hypothesised that mono- and sesquiterpenes were released from the bark, with a decrease in their amounts within the material over time, and that the release of selected mono- and sesquiterpene volatiles can be detected in the pore spaces of the stockpiles, as well as through the efflux measurements at the stockpile surface layer.
- we also hypothesised that the dynamics of carbon (C) losses could be evaluated with the aid of flux measurements of the carbon-containing gases at different heights on the stockpiles, and furthermore, that there was an effect of stockpile ventilation on these release processes.

2. Materials and Methods

2.1. Experimental design

The storage experiment was established in Uimaharju (62° 54' N, 30° 14' E) in eastern Finland at the unpaved storage site of Stora Enso's Uimaharju sawmill. The experiment was carried out between 15 April and 30 September 2021. The experiment consisted of two stockpiles of bark of Scots pine (Pinus sylvestris L.) originating directly from the debarking process of pine sawlogs at the sawmill. The exact harvesting time prior to the debarking of the sawlogs was unknown, but the bark was collected over a few days prior to the establishment of the stockpiles. A wheel loader formed the stockpiles, thereby mixing the fresh raw materials with those collected during the previous days. However, the mixing degree within the stockpiles remained unknown. The stockpiles' dimensions were 23.5 m × 8.1 m × 2.9–3.2 m and 19.3 m × 8.2 m × 3.2–3.35 m respectively. One of the stockpiles was ventilated using four metallic pipes with wind-driven ventilators (Fig. 1), similar to the ventilation setup presented by Jylhä et al. (2022).

The ventilator pipes consisted of a solid part that reached approximately 1–1.5 m above the stockpile level, a metal board at the stockpile surface to keep the ventilators in place, and a perforated part below, reaching approximately 1 m inside the stockpile. The stockpile volumes were determined using an iPad PRO 2020 LiDAR scanning function to create 3D scans of the stockpiles and to estimate their respective volumes (Fig. 2). The stockpiles had approximate volumes of 318 m^3 (pile 1, ventilated) and 276 m^3 (pile 2, non-ventilated). The average density of dry mass samples was 338 kg m^{-3} in the ventilated stockpile and 342 kg m^{-3} in the non-ventilated pile respectively. Consequently, carbon densities were estimated to 168 kg m^{-3} and 171 kg m^{-3}.

2.2. Sampling and analyses

Bark samples for chemical analyses were collected from the stockpiles a total of six times between 15 April and 3 September 2021. The samples were taken at a dedicated section at the western ends of both stockpiles (Fig. 2a) to avoid disturbance to the other stockpile sections. A crane was used to collect the samples at several spots, without interfering with the stockpiles themselves. The bark samples were collected at three height levels [bottom (1 m), middle (2 m), top (3 m)] at a depth of approximately 30–50 cm from the stockpile surface. At each spot, two samples were taken and placed into plastic bags with a volume of 2 L, after which the bags were closed tightly. A second bag was added on top of the first, and the samples were frozen at approximately −20 °C. For chemical analyses, the samples were transported to the laboratory in closed cooled transport bags and stored at −20 °C.

Fig. 1. A ventilated bark stockpile of Scots pine with efflux measurement collars in the central section of the stockpile and plastic hoses used for stockpile-internal gas measurements (a). Two collars were placed in the centre of each stockpile at three heights (bottom, middle, top) reaching the surface level, resulting in a total of 12 collars per stockpile (b) (Source: Luke/Prinz Robert).

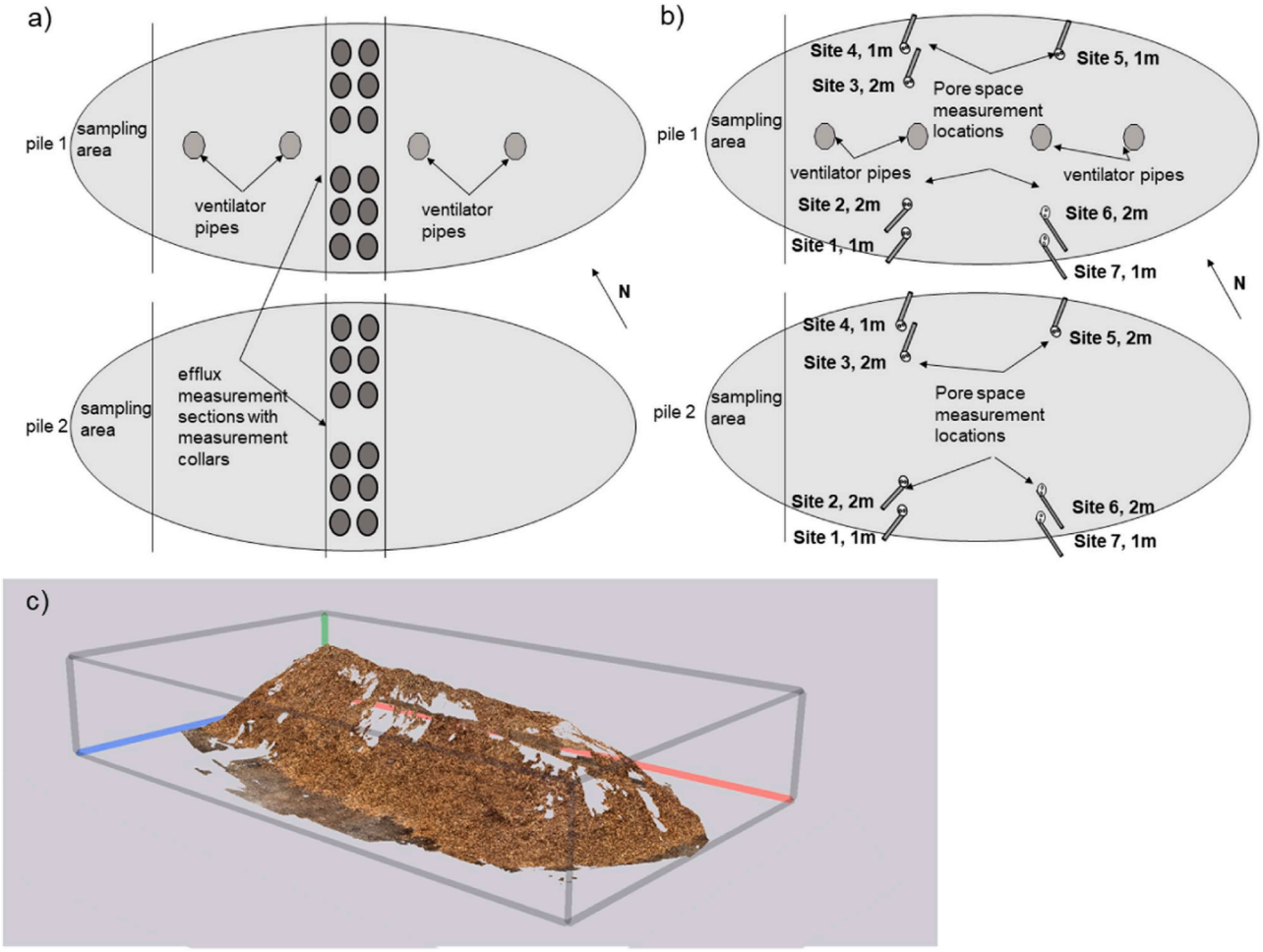

Fig. 2. Schematic top view of the study stockpiles with ventilators and gas flux collars indicated (a), with pore space measurement pipes indicated (b), and scanned 3D model of the non-ventilated stockpile generated using the iPad PRO 2020 LiDAR scanning application (c).

2.2.1. Determination of dry matter losses

Dry matter losses (DMLs) of the bark were studied using a net bag method in the same way as with woodchips in Jylhä et al. (2022). A total of 25 bark samples (c. 5 L) was collected from each stockpile from three height levels during the stockpile construction. These samples were divided into two subsamples of equal volumes. One subsample was packed in a plastic bag, stored at −20 °C, and used later to determine the bark properties in the laboratory. The other subsample was packed into a polyester balance bag (size 50 cm × 70 cm, material with 1 mm oval mesh). These bags were buried in both stockpiles so that ten bags were placed each at heights of 1 and 2 m, and five bags were placed at a height of 3 m. The balance bags were removed from the stockpiles at the end of the experiment after 168 days of incubation and stored at −20 °C until analysed.

The determination of the DML was based on changes in the mass and the MC (moisture mass fraction on wet basis, %) between the times of the stockpile construction and the end of the experiment. The MC was determined by applying the procedures in the valid standard method

(SFS-EN 14774–2, 2010).

2.2.2. Analyses of mono- and sesquiterpenes

Representative aliquots (10 g) of both freshly collected and stockpile-stored frozen bark samples were ground with a cooled mill (IKA A10, Germany), and the powders were stored at −20 °C in tightly closed vials. 2.0 mL dichloromethane supplemented with 1-chlorodecane (25 μg/mL) as an internal standard was added to 200 mg of the powder and was mixed vigorously by vortexing. The samples were then centrifuged (3000 rpm, 10 min, 21 °C) to collect all the material into the solvent and incubated for 15 min in an ultrasonic bath at 20 °C. The vortexing and centrifugation steps were repeated, and the samples were reincubated for 15 min in the ultrasonic bath. The samples were mixed by vortexing and centrifuged. One mL from the dichloromethane phase was pipetted into the gas chromatography (GC) vial.

Mono- and sesquiterpenes were analysed with a GC-MS instrument (Agilent 7980B) equipped with a ZB-5MSplus column (30 m × 0.25 mm, film thickness 0.25 μm). Humulene (10 and 20 μg/mL) was used as an external standard. Three bark samples collected from different height levels (1, 2, and 3 m) of the stockpile at each timepoint were analysed in duplicate. The protocol for the column oven was as follows: the starting temperature was 30 °C, hold time 0 min, temperature increase rate 10 °C / min, end-temperature 230 °C, hold time 5 min, temperature increase rate 40 °C / min, hold time 2 min. The injector temperature was 230 °C. Helium with a flowrate of 1.2 mL / min was used as a carrier gas. The GC instrument equipped with a mass selective detector (Agilent MSD 5977 A) was heated to 230 °C. The sample volume was 1 μL (splitless injection into the column). Aliquots of each bark sample were dried in an oven at 105 °C to determine the moisture content. The results were calculated per g dry weight of the bark.

2.2.3. ASE extractions

Bark powder (1.0 g fresh weight) was extracted with an accelerated solvent extractor (ASE-350, Thermo Scientific, Dionex, Sunnyvale, CA, US) with water at 100 °C, 3 times for 5 min cycles. The extracts were diluted in volumetric flasks with water to a constant volume (i.e. if the volume of the extract was less than 50 mL, the final volume was set as 50 mL). Aliquots (5 mL) of diluted water extracts were dried in the oven at 105 °C overnight, and the amounts of water-soluble extractives were measured gravimetrically. Oligosaccharides released by microbial degradation were analysed by methanolysis-GC (see below).

2.2.4. Methanolysis

The carbohydrates from the water extracts were analysed by acid methanolysis–GC with the flame ionisation detector (FID; GC-2010, Shimadzu, Japan) (Sundberg et al., 1996). For methanolysis, 0.5–4 mL of extract, depending on the concentration, was placed in a pressure-resistant pear-shaped flask. The samples were then frozen and freeze-dried. 2 mL 2 M solution of HCl in anhydrous MeOH was added to each sample, after which the samples were incubated at 100 °C for 5 h, with efficient mixing every hour. One mL of a calibration solution containing 0.1 mg / mL of arabinose (Ara), galactose (Gal), galacturonic acid (GalA), glucose (Glc), glucuronic acid (GlcA), mannose (Man), rhamnose (Rha), xylose (Xyl), and 4-O-methylglucuronic acid (4-O-MeGlcA) in a methanol–water mixture (9:1, v/v) was evaporated to dryness in a stream of N_2 at 60 °C and treated for 3 h in the same way as above. After cooling to room temperature, 200 μL of pyridine was added to neutralise the solutions, and the tubes were mixed thoroughly. Four mL of an internal standard containing 0.1 mg / mL sorbitol in 90 % methanol was added to the sample tubes (1 mL to the calibration tubes), followed by mixing. Aliquots (1.0 mL) of the clear solutions were evaporated to dryness under a N_2 stream at 60 °C, and further in a vacuum oven at 40 °C. The dried samples were dissolved in 100 μL pyridine, and silylated using a solution containing 150 μL hexamethyl disilazane (HMDS, Sigma-Aldrich, Missouri, US) and 70 μL TMCS. Silylation was conducted overnight at room temperature. The silylated samples were analysed by the GC–FID-system (Shimadzu GC-2010, Kyoto, Japan) with HP-1 Column (25 m x 0.2 mm I.d., film thickness 0.11 μm). The temperature profile was 100 °C -> 175 °C, 4 °C / min, 175 °C -> 290 °C, 12° C / min. The injector temperature was 260 °C, and the detector temperature was 290 °C. The following correction factors were used when calculating the results: Man, Glc, and Gal 0.9, Xyl and Ara 0.88, Rha 0.89, GlcA, GalA, and 4-O-Me-GlcA 0.91. All analyses were performed using three replicates.

2.3. Setup for efflux measurements

After piling, at each of the two main side sections of the stockpiles (north and south) and at each height level, two solid metal collars were buried with their top located on the stockpile surface; a total of 12 collars was therefore placed on each stockpile (Fig. 2a). The collars had a length of 40 cm and a diameter of 31.5 cm. They remained open at both ends allowing gas flow. A rubber seal was added to the upper end to avoid losses of VOCs and other gases (Fig. 3a). This arrangement allowed us to place a gas exchange measurement chamber on top of the collars to create a closed chamber system in which the air circulated between the chamber and the external gas analysing device to determine the gas fluxes. The chamber had the same dimensions and was counterwise equipped with a rubber seal on the bottom end. The volume of the chamber was 27.8 L, and the volume of the headspace was used for flux measurements. The measurement chamber equipped with an electric fan and a thermometer was placed on top of the collars for measurements (Fig. 3b). The chamber was connected with silicon hoses to the gas analysing device, creating a loop for the air circulation between the chamber and the analyser. The mean temperature was also recorded during the measurement period. This measurement setup has typically been applied in soil respiration studies (see Alm et al., 2007) but has also been used in CO_2 efflux measurements in stockpiles of forest chips (Jylhä et al., 2017).

In addition to chambers, stockpile core pipes were placed at the bottom and middle levels close to the centre of each stockpile (Fig. 2b). The stockpile core pipes consisted of a total of seven plastic hoses equipped with a perforated plastic ball at their ends. The purpose was to measure gas components within the stockpiles and approximate the levels of specific gases.

2.3.1. Gas analyses

The efflux measurements were carried out between 22 April and 1 September 2021. The efflux measurements took place in the middle sections of both stockpiles (Fig. 2a) at three heights (1, 2, and 3 m). The gas mixing ratios of carbon dioxide (CO_2), methane (CH_4), dinitrogen oxide (nitrous oxide, N_2O), carbon monoxide (CO), nitrogen monoxide (NO), ethyl acetate ($C_4H_8O_2$), acetaldehyde (C_2H_4O), methanol (CH_4O), and the monoterpenes α-pinene, β-pinene, and 3-carene (all $C_{10}H_{16}$) were measured from both the pore spaces deep within the stockpiles as partial volumes (ppm) and at the stockpile surface-atmosphere boundary as flux rates (mg m^{-2} h^{-1}). A portable GASMET DX4015 FTIR analyser was used. The analyser recorded the partial volumes (ppm) of the gases, drawn by the device's own pump into the cuvette, every five seconds (GASMET), and the software interphase allowed online monitoring of the results. The detection ranges depended on the gas species, reaching from sub-ppm to percentage-level concentrations. Standard gases could not be applied as references, but GASMET was calibrated to zero using pure nitrogen every day prior to the measurements.

Prior to each measurement, the collar was ventilated, allowing the chamber fan to flush the headspace clean of previous gas residues. The attainment of the ambient baseline level was checked with the aid of the GASMET monitoring software. In all measurements, a crane was used to avoid contact with and disturbance of the stockpiles (Fig. 3b). In one exceptional case, when the crane was unavailable, a ladder placed on the side of the stockpiles was used. The attainment of a stabilised level of pore space concentration was checked in the field during the

Fig. 3. The collars for the chamber measurements were permanently buried in the bark stockpiles (a). A flux chamber was placed on top of the collars, with a closed circulation between the chamber and gas analyser during the measurement (b). The system was operated from a crane to avoid disturbance and compression (Photos: Luke/Alm Jukka).

measurement using the CO_2 and CH_4 graphs of the GASMET monitor software. Average ppm values were calculated from the data obtained within the stabilised concentration level.

2.3.2. Gas concentrations in the stockpile pore space

Gas samples from deep inside the stockpiles at heights of 1 and 2 m were collected from the pre-installed pipes, allowing pore space gas to be drawn directly into the analyser using its pump. After attaching the analyser to the pipe, the analysis was run for 2–4 min to stabilise to a concentration level that was assumed to represent an equilibrium of the average gas concentration in the pore space near the pipe's gas intake cavity. Any lower initial values originating in the pipe length were thus discarded.

2.3.3. Gas fluxes on stockpile surface

Gas flux rates on the stockpile surface were measured using a closed chamber method, in which a chamber (27.8 L) was closed airtightly on a pre-installed collar. The airtightness of the system was secured using a rubber casket on top of the collar and at the bottom of the chamber. The caskets were tightened using a clamp, or by adding a c. 1 kg weight on top of the chamber. The air in the chamber headspace was circulated between the chamber and the analyser, utilising the analyser's pump. The development of the chamber headspace gas mixing ratio was recorded over an approximately 5-min time span, or longer if disturbances were observed. The temperature of the chamber headspace was recorded during the chamber closure. The bark materials were compacted in the stockpiles over the study period. The average free space emerging over the compacted material was measured using a grid, and the volume was added to the chamber volume.

The disturbed parts of the measurement time series were removed so that only a linear increase or decrease of the gas concentration with a duration of at least 1–2 min was accepted and used for flux calculations. In flux calculations, all gases were assumed to perform ideally under ambient air pressure and temperature conditions. The changes in measured relative mixing ratios (ppm) during the chamber closure were therefore converted to mass units for each gas, using the ideal gas law ($pV = nRT$), where p is the air pressure (assumed static), V is the partial volume of the gas in the chamber, n is the molar fraction of the gas corresponding to its partial volume, R is the gas constant, and T is the temperature in the chamber (K°). A linear regression slope between the seconds of measurement and the respective time series of gas mixing ratio gives a positive or negative flux rate, converted to mass per area per time (gas mg m^{-2} s^{-1}). For convenience, the flux rates were converted to daily values and different mass units by multiplication.

2.3.4. Carbon gas losses during storage of stockpiles

Carbon losses (C losses) were determined with the aid of flux measurements of the carbon-containing gases at different heights on the stockpiles. The integration of the emissions was performed for both stockpile types by area weighing of each measurement level over a gas flux measurement period of 131 days. The simple stockpile sub-area model is shown in Fig. A1. For the most emitted gases (CO_2, methanol, and CO), the integration was based on fitting an inverted regression function to the daily flux rate averages for each measurement day, with the day number from the beginning of the experiment as the independent variable. For CH_4, the integration was conducted similarly, but using linear regression. The regression functions were evaluated for each day of the study period (number of days between the first and the last gas measurement = 131), and the estimates were summed. For other gases, an overall average was used, multiplied by the number of days.

2.4. Statistical analyses

Three distinct Bayesian modelling scenarios were developed, namely within i) the bark, ii) stockpile pore space, and iii) on the stockpile surface. Furthermore, several measurement locations were used: three different measurement heights for within the bark stockpile (1 m, 2 m, and 3 m), seven different measurement locations for the stockpile pore space (at heights of 1 m and 2 m in relation to the stockpile), and four different measurement locations for the stockpile surface at a height of 3 m. Bayesian statistics are a statistical approach that employs Bayes' theorem to update and refine our beliefs about uncertain events based on the new evidence. It provides a framework for combining prior knowledge or beliefs with the observed data to arrive at updated probability distributions. Bayesian statistics offer several benefits, including the ability to handle small sample sizes effectively, to quantify uncertainty through probability distributions, and to iteratively refine predictions as new data become available.

The response variables were: α-pinene, 3-carene, longifolene, and α-muurolene for within the bark (i); α-pinene, 3-carene, β-pinene, CO_2, CO, CH_4, and methanol for stockpile pore space (ii); and α-pinene, 3-carene, β-pinene, CO_2, CO, and CH_4 for the stockpile surface (iii). The predictor variables were: time (continuous), pile (ventilated and non-ventilated), and height (1 m, 2 m, and 3 m) for within the bark (i); time (continuous), pile (ventilated and non-ventilated; categorical), and site (site 1 – site 7; categorical) for stockpile pore space (ii); and time (continuous), pile (ventilated and non-ventilated; categorical), and site (site 1 – site 4; categorical) for the stockpile surface (iii).

First, the differences in the chemical content of the bark and gas emissions between ventilated and non-ventilated stockpiles were investigated visually. Based on the inspection, the focus was on investigating the difference between the time trends between the stockpiles via Bayesian modelling. Each response was modelled using a linear time trend model, except for β-pinene and methanol for the stockpile pore space, which were modelled using a second-order time polynomial.

A normal distribution was assumed for the response, where the mean was modelled either with a linear time trend model or a second-order time polynomial. An uninformative prior was assumed for the precision, namely a $Gamma(0.001,\ 0.001)$ distribution. Furthermore, uninformative priors were assumed for the time trend parameters, namely a $N(0,\ 10^5)$ distribution. Three separate chains were sampled, and their

convergence, autocorrelation, and Raftery-Lewis's diagnostics were studied. Based on these diagnostics, 70,000–200,000 iterations were drawn respectively for within the bark and both stockpile pore space and stockpile surface. Finally, convergence was achieved, and a sufficiently large effective sample size was used to achieve credible inference regarding the 95 % highest density interval (HDI) for each model parameter. Statistical analyses of slope differences for shown figures are presented in Fig. A2.

3. Results

Two stockpiles of bark chips of Scots pine were analysed during prolonged incubation during the summer to obtain a holistic view of the chemical changes occurring in the bark chips with emissions of various gases, with a special focus on mono- and sesquiterpenes. Soon after the stockpile establishment, the temperature in the stockpiles increased to 50–66 °C with a slightly higher temperature in the ventilated stockpile than in the non-ventilated stockpile (Fig. 4). The temperature remained constantly high in both stockpiles from April to the end of July, after which the temperature declined slightly.

Based on the samples taken within the stockpile during establishment, the average MC of the pine bark at the beginning of the experiment was 57 %, from which it decreased to 42 % in the ventilated stockpile and to 47 % in the non-ventilated stockpile by the end of the experiment. Drying was strongest closest to the soil at a height of one metre. In the ventilated stockpile, the MC at the lowest measuring height (1 m) decreased by an average of 27 percentage units, and in the non-ventilated, by 21 percentage units. In both stockpiles, MC increased near the surface of the stockpile, and in the non-ventilated stockpile, slightly more than in the ventilated one.

DMLs from sampling during the 5.5-month experiment were on average 16.3 % in the ventilated, and 18.5 % in the non-ventilated, stockpile. In the ventilated stockpile, the largest loss was measured at the lowest measuring height (1 m), and in the non-ventilated stockpile, at the highest measuring height (3 m). The MC at the beginning and at the end of the experiment as well as the DMLs are shown in Table A1.

The amounts of total soluble carbohydrates (mono-, oligo, and polysaccharides) in water extracts of bark chips decreased during prolonged storage (Fig. 6a). The total amount of monoterpenes also decreased rapidly in the bark in both stockpiles after pile establishment, with the most prominent loss occurring in the first 11 days (Fig. 6b). A decrease in the concentrations of α- and β-pinene, as well as of 3-carene, was also detected in the gas measurements in the pore space (see below). Similarly, the amount of sesquiterpenes in the bark chips decreased, but more slowly than those of monoterpenes, with the total amount halving

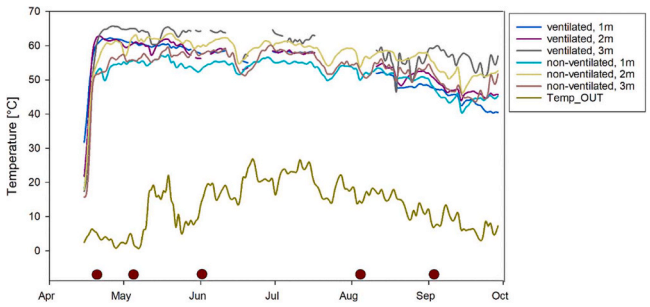

Fig. 4. Temperature conditions during the bark stockpile experiment from April to September 2021 in Uimaharju, Finland. Daily (24 h) average temperatures measured outside the stockpile (Temp_OUT) and within both stockpiles (ventilated and non-ventilated) at three heights (1, 2, and 3 m) in relation to the stockpile height. Missing measurement points in some of the presented graphs are due to temporary technical problems at some sensors in the data collection unit for the periods indicated by data gaps. The timing of the measurement and sampling is indicated with circles along the timeline.

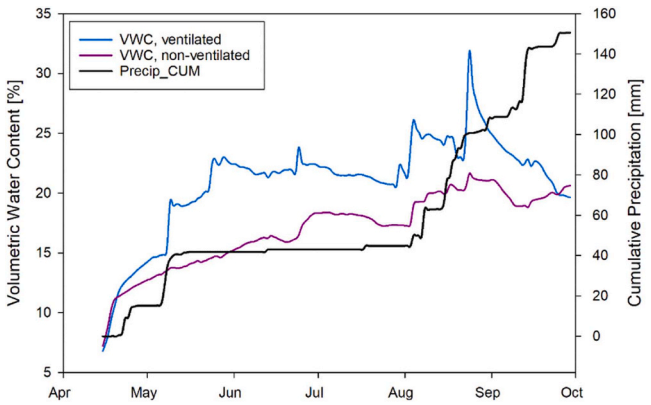

Fig. 5. Weather conditions during the bark stockpile experiment from April to September 2021 in Uimaharju, Finland. Cumulative precipitation (Precip_CUM) and average daily (24 h) volumetric water content (VWC) within both stockpiles (ventilated and non-ventilated) measured at three heights (1, 2, and 3 m) in relation to the stockpile height and presented as average values.

in c. 50 days (Fig. 6c). The carbohydrates (determined as monosaccharides in the acid methanolysis–GC) and mono- and sesquiterpenes detected are presented in Tables A2–A3.

Ventilated and non-ventilated stockpiles were compared (Fig. 7) and modelled (Fig. 8). Cases where either the slopes or the second-order polynomial terms differed significantly are shown in Figs. 9–11. The significance was determined as the posterior distribution of the model coefficient term difference differing significantly from zero with over 95 % probability. A Bayesian R^2 value (Gelman et al., 2014) was calculated for Figs. 9–10 to assess the goodness-of-fit. The fitted models were not assumed to fully describe the underlying phenomenon, but rather serve as useful tools for comparing the main differences between the stockpiles.

All the methods used (chemical analysis of the bark and both types of gas measurements) showed that the total amount of monoterpenes decreased in both stockpiles rapidly after stockpile establishment (Fig. 7). The decrease in the concentrations of α- and β-pinene, as well as of 3-carene, was also detected in the gas measurements in the pore space, although the significance of the models varied (Fig. 8).

Similarly, the amount of sesquiterpenes in the bark chips decreased, but more slowly (Fig. 9a,b). There are linear downward sloping time trends for the longifolene and α-muurolene measured in the bark. For both cases, the slope for the ventilated stockpile is steeper, meaning that the compounds decreased more rapidly over time due to ventilation.

Second-order polynomial trends were identified for β-pinene for pore space (Fig. 10). For the non-ventilated stockpile, the values seem to first increase and then decrease, whereas for the ventilated stockpile, the values first decrease and then increase. It is not strictly assumed that the second-order polynomial is the exact mechanism for the stockpile data. However, the second-order polynomial is a suitable approach for comparing the stockpiles, and it is clear that there is a difference. The bayesian R^2 values for both ventilated and non-ventilated stockpiles were 0.42. Thus, the models show some merit, but most of the variance remains unexplained. However, as we mentioned, the model is far from a comprehensive description of the underlying phenomenon.

Linear trends were identified for CH_4 for pore space (Fig. 11a). For the non-ventilated stockpile, the trend slopes downwards, whereas for the ventilated stockpile, the slope is practically flat. The difference between the slopes is driven primarily because of the sole extreme observation at the very beginning for the non-ventilated stockpile. CH_4 flux values for the ventilated and non-ventilated stockpiles for the stockpile surfaces with both slopes show an upwards trend (Fig. 11b). However, the slope for the non-ventilated stockpile is much steeper, driven solely by an extreme value at the end of the timeline. The R^2 values for the ventilated and non-ventilated stockpiles for Fig. 10a were 0.30 and 0.38,

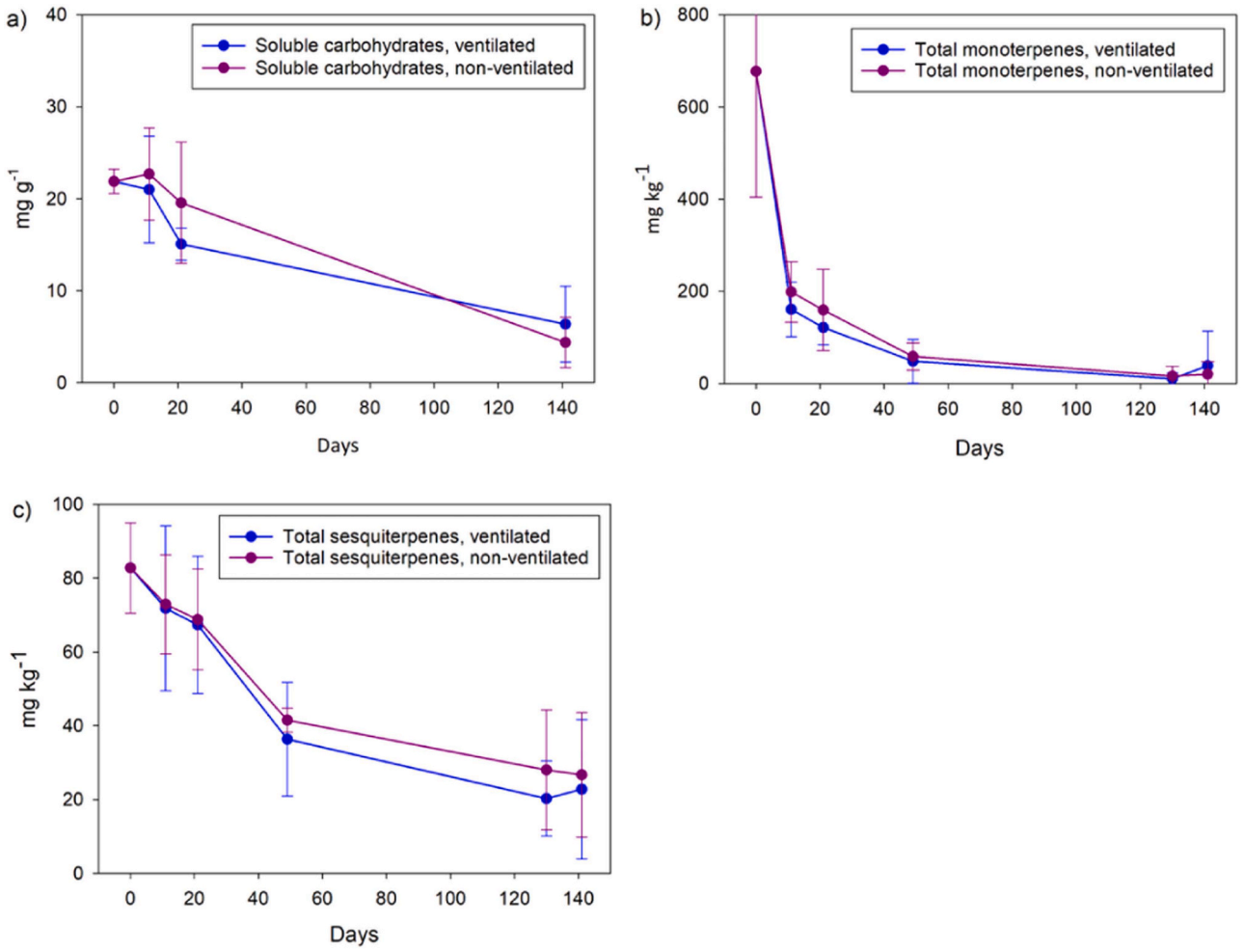

Fig. 6. Amounts of soluble carbohydrates (mono-, oligo-, and polysaccharides) in the bark of Scots pine during storage in stockpiles during the summer (average ± stdev of values of all sampling heights, n=3, except n=2 for the first and n=6 for the last timepoint respectively) (a). Soluble carbohydrates were extracted from the bark with water and analysed by acid methanolysis–GC as described in Materials and Methods. The total amount was obtained by summing the amounts of all monosaccharides determined separately. The amounts of total monoterpenes (b) and sesquiterpenes (c) in the bark of Scots pine during storage in stockpiles during the summer (average ± stdev of values of all sampling heights; n=6, except n=3 for the timepoint 0). Terpenes were extracted and analysed by GC–MS as described in Materials and Methods. The total amount was obtained by summing the amounts of all mono-/sesquiterpenes determined separately.

respectively. For Fig. 10b the R^2 values for ventilated and non-ventilated stockpiles were 0.27 and 0.56, respectively. Therefore, there is some merit in the models in sense of explaining the variance in the data. However, most of the variance is unexplained, except for the non-ventilated data for Fig. 10b.

CO_2 levels in the pore spaces were higher in the non-ventilated stockpile than in the ventilated stockpile; the values in both stockpiles decreased with time. The CO_2 flux rates, on the other hand, were higher in the ventilated stockpile than in the non-ventilated stockpile; the flux rates decreased in both stockpiles during the summer. The flux rates measured at a height of 3 m, especially in the ventilated stockpile, were higher than those measured lower in the stockpile.

To evaluate the gas measurement results of C losses, the amount of C loss was also calculated based on the measured DMLs of the stockpiles. The gaseous C loss during the 131-day gas exchange measurement period in the non-ventilated and ventilated stockpiles was c. 1.3 t C from the ventilated and 1.1 t C from the non-ventilated stockpile respectively (Table 1). The calculated gaseous C loss results were thus lower than those derived from the DML measurements (2.4 for the ventilated and 2.4 t C for the non-ventilated stockpile respectively) (Table 1). Note that the gas measurement period, for which the estimation of C loss was made using the flux data, was only 131 days compared to the period of the DML C loss method, which covered the whole storage period of 168 days. The main share of the gas-flux-derived C losses originates in the gases released through the decomposition of the biomass in the stockpiles.

C losses through CH_4, methanol, and CO emissions were very low compared to those of CO_2 (Table 1). However, more CH_4-C was released from the ventilated than from the non-ventilated stockpile. The C losses caused by the release of CO-C was highest at the beginning of the follow-up period (Fig. 12). In all, the total C loss as CH_4, methanol, and CO gases during the 131-day gas exchange measurement period was about 7.2 kg C from the ventilated and about 4.1 kg C from the non-ventilated stockpile. The losses of carbon as larger molecular mass gases such as acetaldehyde, ethyl-acetate, and the monoterpenes α- and β-pinene and 3-carene followed a similar pattern, with more C released from the ventilated than the non-ventilated stockpile (Table 1). The gases other than CO_2 were thus responsible for only about 2 % of the total gaseous C losses from the ventilated stockpile, and about 1 % from the non-ventilated stockpile. Overall, using the average C density (0.5 * dry mass density) and the approximate stockpile volumes of 318 m^3 and 276 m^3 in the ventilated and non-ventilated stockpiles respectively, the DML-derived C losses per unit volume corresponded to c. 7.5 kg m^{-3} and 8.6 kg m^{-3}. The corresponding estimates, calculated per cubic metre using the gas flux data showed losses only about half that much, 3.5 kg and 4.7 kg respectively.

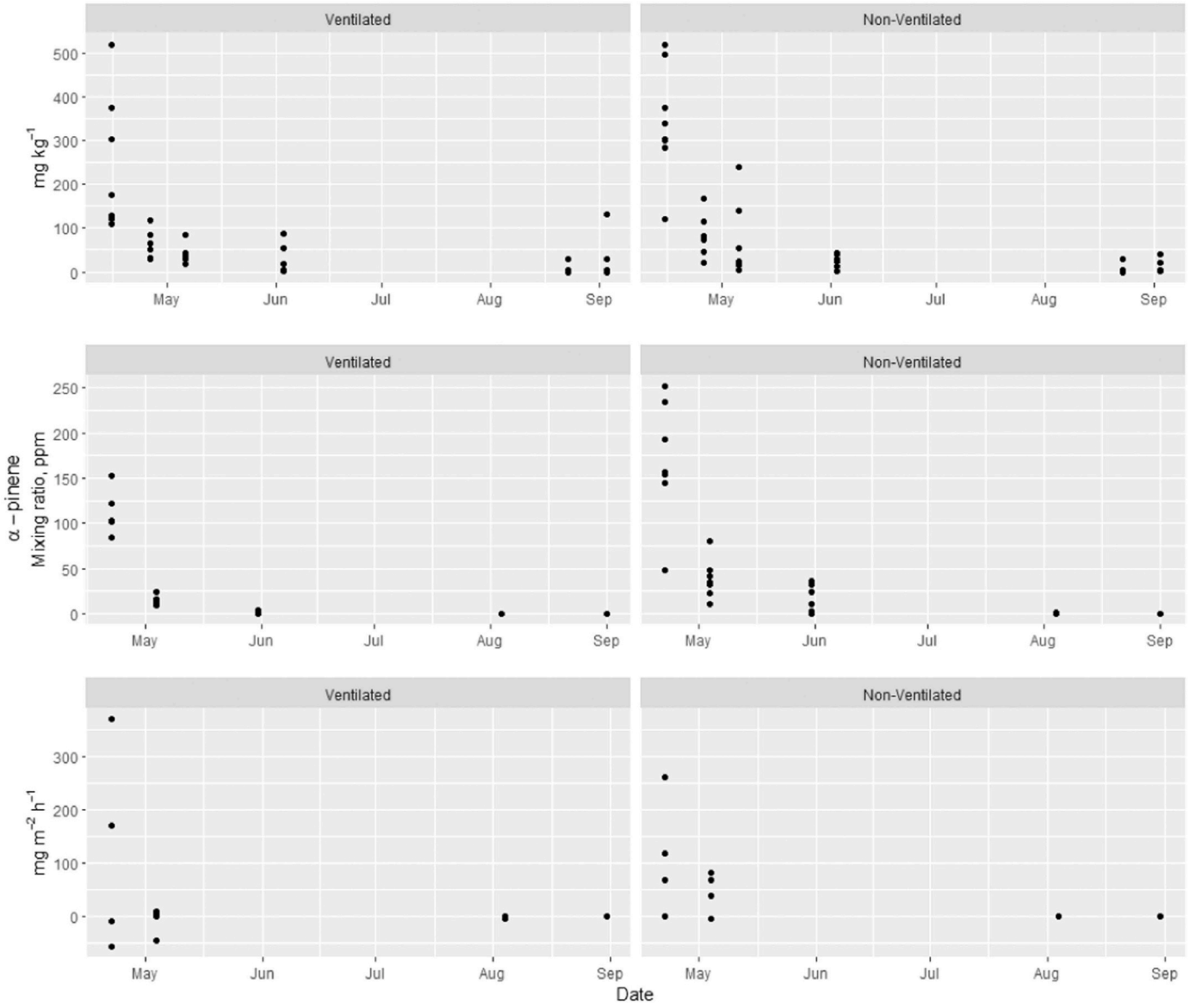

Fig. 7. Values of α-pinene with respect to stockpiles (columns) and measurement locations (rows). Y-axis units are mg kg^{-1} for within the material (Bark), the relative gas mixing ratio in the stockpile pore space as part per million (ppm) (Pore space), and mg m^{-2} h^{-1} for the gas flux rate through the stockpile surface to the atmosphere (Surface) respectively. The X-axis denotes the sampling dates.

4. Discussion

4.1. Effects of ventilation on biomass decomposition and VOC release

The study aimed to investigate the release of mono- and sesquiterpenes and common greenhouse gases, their generation, and flux dynamics within non-ventilated and ventilated stockpiles of Scots pine bark occurring during long-term storage during the summer in outdoor conditions in Eastern Finland. The storage conditions were typical for this kind of raw material (Fig. 5), with temperatures rising to approximately 60 °C within a few days after the stockpile establishment, and a slow decrease in temperature until the end of the study period (Fig. 4). Soluble carbohydrates (mono-, oligo-, and polysaccharides) decreased in the bark of Scots pine during storage (Fig. 6a). The total amount of monoterpenes decreased rapidly in both stockpiles after stockpile establishment (Fig. 6b), and that of sesquiterpenes also decreased, but more slowly (Figs. 6c, 9a,b). Based on chemical measurements in the bark samples, as well as gaseous flux measurements, the release of major monoterpene content occurred within the first 11 days of stockpile establishment. CO_2 was the main greenhouse gas liberated, with some emissions of CH_4 (Fig. 11), CO and methanol (Fig. 12). While the main share of carbon (C) losses originated in the release through CO_2 in the non-ventilated stockpile, approximately 39 % more C was released in the ventilated stockpile (Table 1). Ventilation showed an effect on the release in the analysed cases, and the compounds showed a more rapid decrease over time due to ventilation, although the significance of the models varied (Fig. 8).

Physical (e.g. stockpile ventilation, size, density) and chemical factors affect the release of VOCs from the stockpiles of pine bark. Decomposition also changes the physical and chemical environment of the bark chips. This decomposition involves the conversion of solid substances into gaseous decomposition products (e.g. CO_2, CH_4, CO, methanol). The complex relationships of such numerous factors are reflected by the array of methods involved in the present study. However, our study could only cover a portion of the actual dynamics related to the gaseous emissions from the stockpiles of pine bark. Similarly, identified trends (e.g. linear, second-order polynomial) were presented for selected compounds, despite the fact that it was not strictly assumed

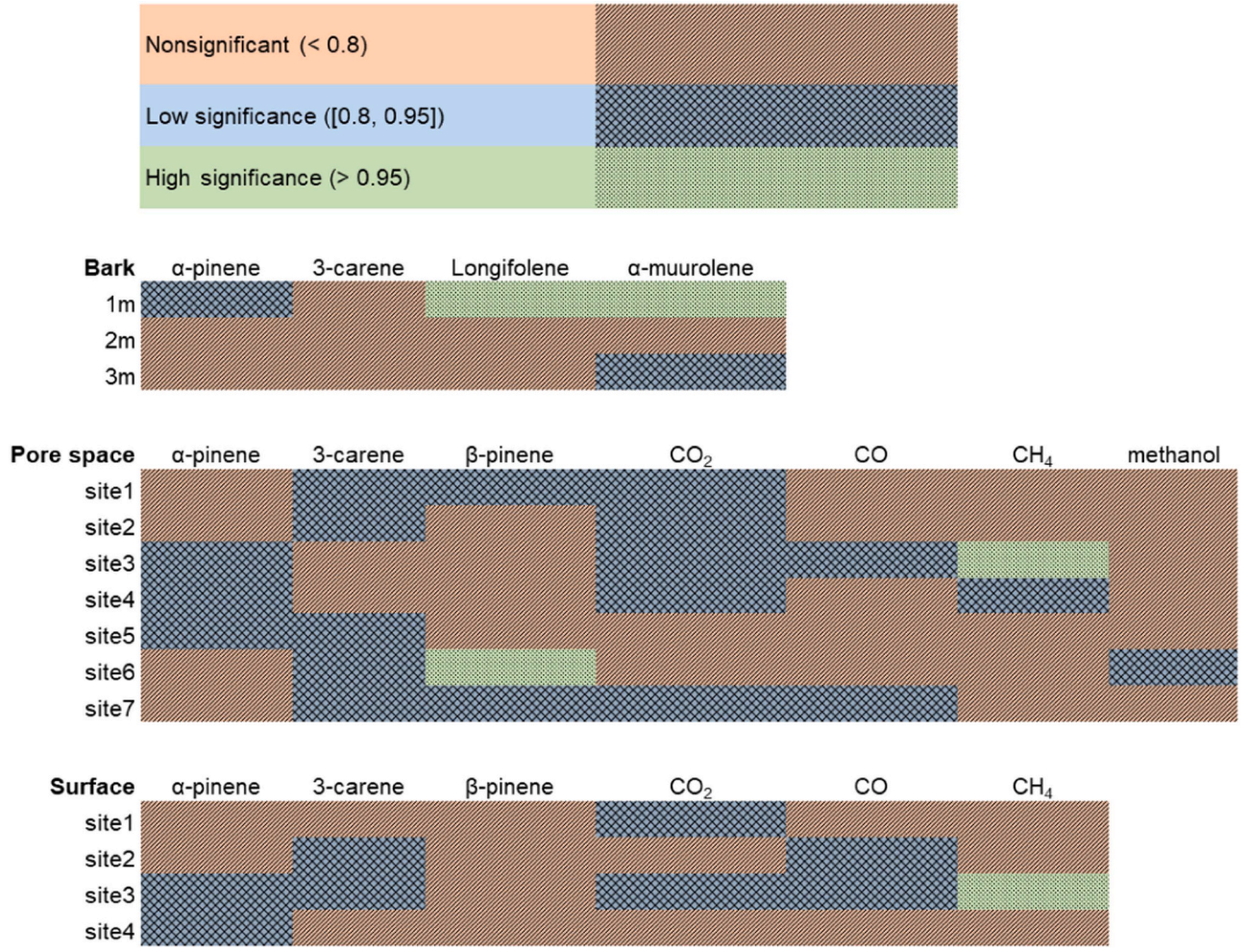

Fig. 8. Significance chart for the models. The colour and pattern codes – red with diagonal stripes, blue with diagonal crosshatch, and green with dots – correspond to nonsignificant (probability less than 0.80), low significance (probability range from 0.80 to 0.95), and high significance (probability higher than 0.95), respectively. The site number refers to the specific measurement location within the respective stockpile (see Fig. 2a,b).

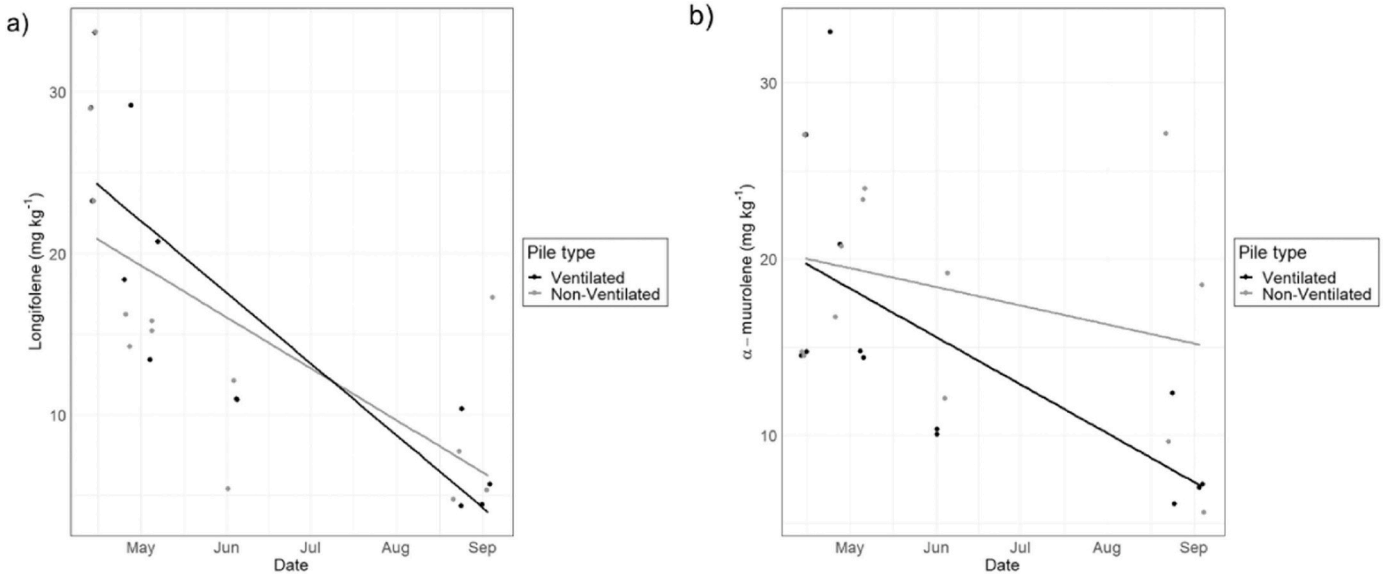

Fig. 9. Longifolene (mg kg^{-1}) values and regression lines as a function of time for bark (1 m above the soil) (a). α-muurolene (mg kg^{-1}) values and regression lines as a function of time for bark (1 m above the soil) (b). The black and grey colours correspond to ventilated and non-ventilated stockpiles respectively.

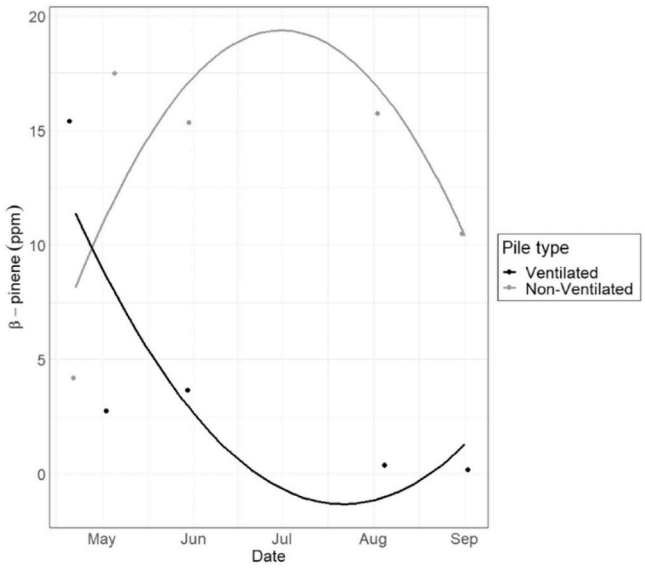

Fig. 10. β-pinene (ppm) values and regression lines as a function of time for pore space (site 6, top of the pile). The black and grey colours correspond to ventilated and non-ventilated stockpiles respectively.

that these statistical tendencies also represented exactly the mechanism for the stockpile data, as process rates seemed to change over the storage time. Nevertheless, the results provide an indication of the released amounts of the studied compounds, as well as their stockpile ventilation status and specific measurement location within them (e.g. heights of 1, 2, and 3 m). Finally, we studied the extent to which decomposition and the resulting emissions were responsible for the storage loss of organic matter in the stockpiles by using balance bags. It has already been shown that gas emissions and DMLs are positively correlated (He et al., 2014). Compared to the DML in the bark samples, the C losses originating from gas fluxes gave lower estimates, probably because the stockpile–air interface was disturbed by strong winds, temperature gradients, and heavy rain, which disturb the gas gradient by depleting the gases from the pore spaces close to the surface. The fluxes measured by the chamber in weather-disturbed conditions may thus become underestimates. Furthermore, we measured the gas fluxes approximately once a month. There is a risk that the gas mixing ratios within the stockpile's topmost layers may not have been balanced, resulting in an underestimation of the flux rate, and therefore underestimated the emissions integrated throughout the period. Nevertheless, our results show the emission dynamics and should support the decision making of practitioners in the field, regarding the effect of VOC release on storage stockpile management (e.g. storage duration, release of VOCs over time).

4.2. Dynamics of decomposition

As previously reported (e.g. Jirjis and Theander, 1990; Wihersaari, 2005, Routa et al., 2021), the temperature inside the bark stockpiles increased in a few days after piling (Fig. 4). This is due to the activity of microorganisms producing heat in their metabolic activity (MacGregor et al., 1981). Three key mechanisms, i.e. cell respiration, biological degradation, and thermo-chemical oxidative reactions, are reported to involve mass to energy conversion, contributing to self-heating and DML (Krigstin and Wetzel, 2016). Initially, the growth of mesophilic organisms is stimulated, but the temperature soon approaches self-limiting conditions. A further temperature increase induces a succession towards thermotolerant and thermophilic fungi and bacteria, enabling the efficient degradation of the biomass especially at temperatures of 52–60 °C (MacGregor et al., 1981; Nagler et al., 2022). Our logger outcomes

Table 1
Carbon losses (in kg of C) for non-ventilated and ventilated stockpile calculated as DML through samples and as a gaseous C release respectively.

		non-ventilated stockpile (kg carbon)	ventilated stockpile (kg carbon)
DML based on bark samples		2380	2400
Gaseous C release	as CO_2	1071	1298
	as CH_4	1.2	1.0
	as CO	0.9	2.4
	as methanol	1.9	3.8
	as acetaldehyde, ethyl-acetate, and monoterpenes α- and β-pinene and 3-carene	11.9	25.9
	gaseous C release total	1087	1331

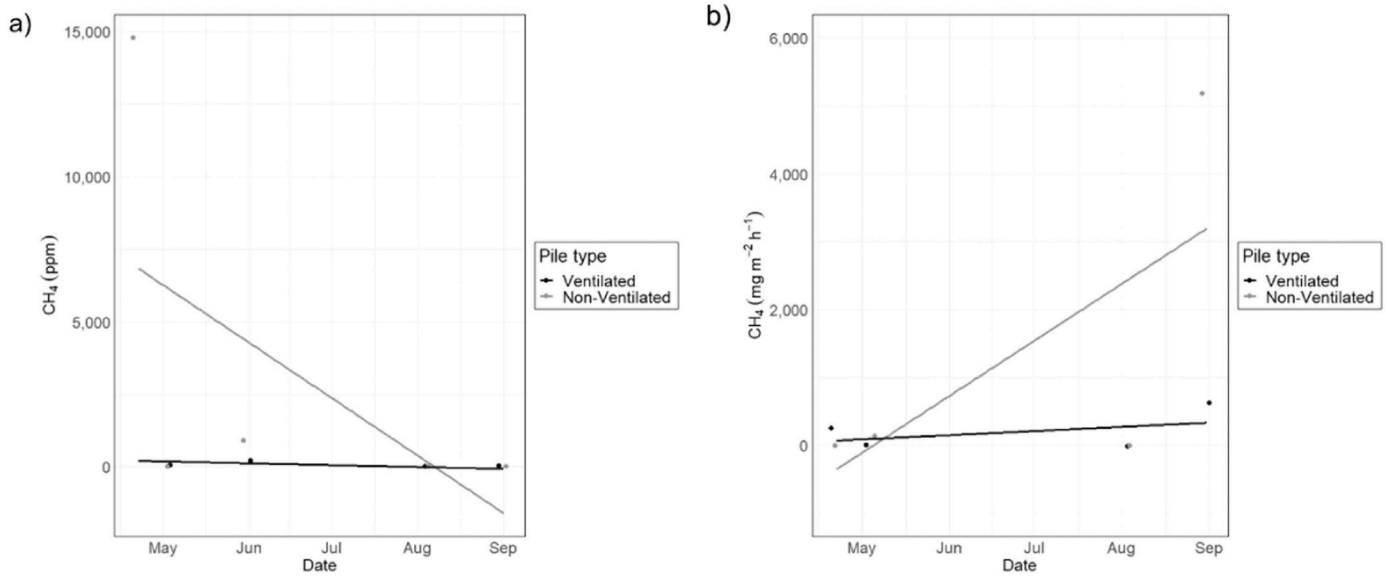

Fig. 11. CH_4 flux values (ppm) and regression lines as a function of time for pore space (site 3, high top of the pile, at least 3 m above the soil) (a). CH_4 flux values (mg m^{-2} h^{-1}) and regression lines as a function of time for the surface (site 3, high top of the pile) (b). The black and grey colours correspond to ventilated and non-ventilated stockpiles respectively.

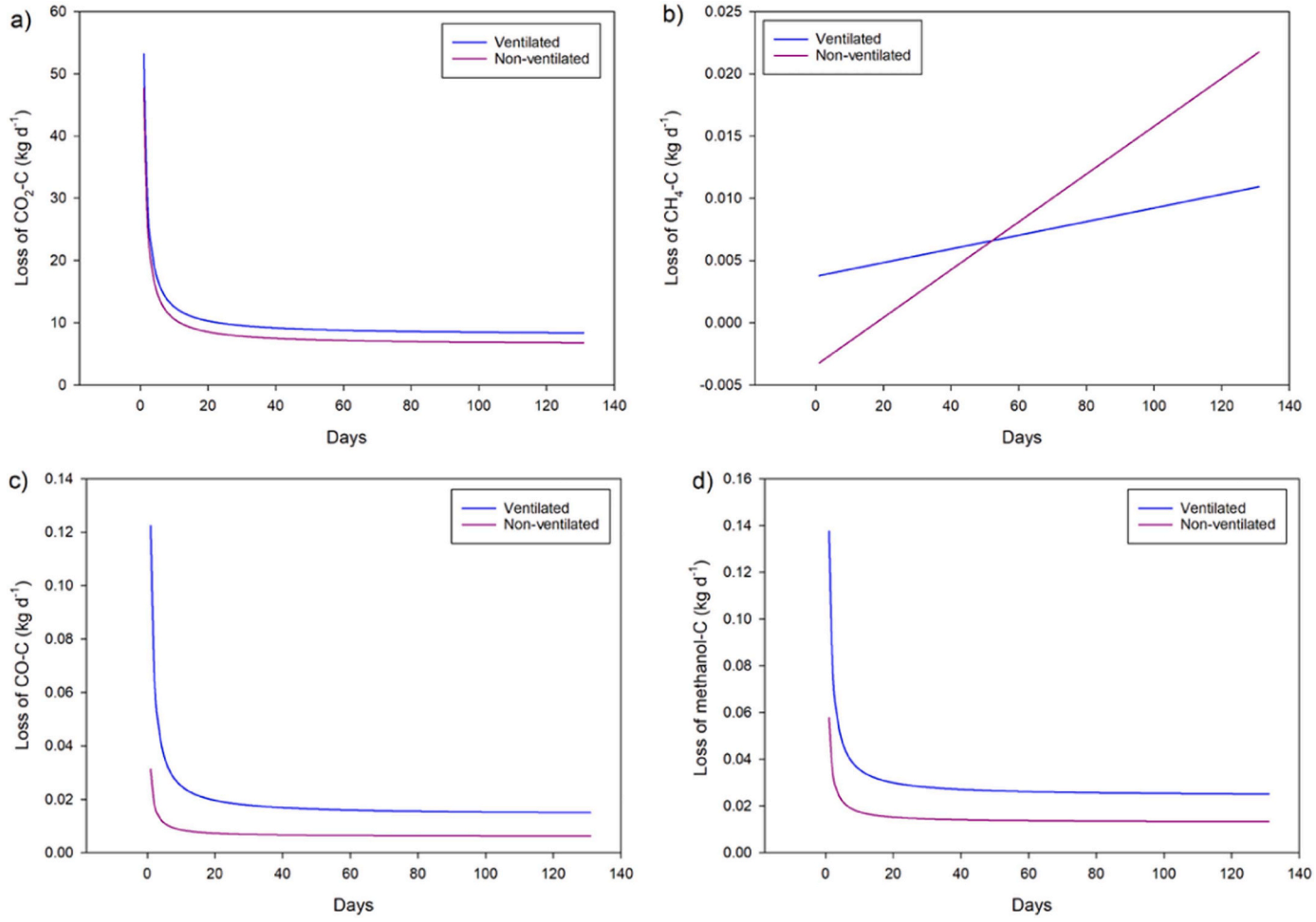

Fig. 12. Total daily carbon (C) loss (kg d^{-1}) as CO_2 (a), CH_4 (b), CO (c), and methanol (d) from the stockpiles of pine bark. The blue and purple colours correspond to ventilated and non-ventilated stockpiles respectively.

are in line with the results of Krigstin et al. (2019), who reported that bark stockpiles, unlike the woodchip stockpiles, heat up gradually while retaining more heat over time; the peak temperatures were also reached approximately within a similar time range after establishment. In line with this, clear decreases in the content of water-extractable carbohydrates were observed concomitantly with the CO_2 release (Fig. 12a). This is probably due to the availability of nutrients in the bark tissues at the beginning of incubation.

CO_2 is generated during biodegradation of organic material in both aerobic and anaerobic conditions, as well as in thermal oxidation (Alakoski et al., 2016). He et al. (2014) reported higher emissions of CO_2 and non-methane VOCs in aerobic conditions. CO levels in the stockpile pore space were strictly correlated with those of CO_2, an observation which may indicate a true relationship or may result from an artefact of the analyser due to the very high gas and water vapour concentrations within the stockpile. CO is generated in limited O_2 concentrations, and indeed, the CO levels in the stockpile pore spaces were higher in the non-ventilated stockpile 1.5 months after stockpile establishment, whereas in the ventilated stockpile, the levels decreased regularly. However, on the surface of the stockpiles, CO flux rates were highest soon after the stockpile establishment (Fig. 12c), especially in the ventilated stockpile at a height of 3 m, after which they decreased in both stockpiles.

CH_4 emissions were also detected in both stockpiles (Fig. 12b). CH_4 is produced in strictly anaerobic decomposition conditions (e.g. Beck-Friis et al., 2000; Wihersaari, 2005; Cayuela et al., 2012). In storage stockpiles that generate heat by oxic decay, lower oxygen solubility in water at higher temperatures may create anoxic microenvironments, enabling the growth of methane-generating archaea (Buan, 2018). Some CH_4 can be oxidised to CO_2 by methanotrophs during the transfer from inside the stockpile to the surface (Wihersaari, 2005; Cayuela et al., 2012). In both stockpile types, the CH_4 emissions seemed to increase towards the end of the storage. This may have been related to increased moisture content (Fig. 5) and anoxia. In the present study, the flux rates of CH_4 emissions on the surface of the non-ventilated stockpile were much higher at the last timepoint in September than in the ventilated stockpile (Fig. 12b), especially when measurement was conducted at a height of 3 m. However, in the pore space the levels of CH_4 were relatively low (Fig. 11a), with high mixing ratios detected only in the non-ventilated stockpile during the first measurement round. However, the temperatures within the non-ventilated stockpile were slightly lower than in the ventilated one (Fig. 4), indicating that the conditions for microorganisms were somewhat different. It is likely that the CH_4 oxidation rates were high in both stockpiles, but as the gases were probably largely conducted through macropores between the bark chips, local preferential pathways may have bypassed our fixed flux measurement collars. Furthermore, the conditions within the stockpile evolve over time, and the processes may occur at different rates in different positions within the stockpile. This is in line with results by Ahmadinia et al. (2022), who showed that moisture redistribution took place within storage piles of woodchips, leading to different drying rates in different sections of the pile, and are thus affected by the stockpile's size and porosity. It is unlikely that the measured high surface flux value (Fig. 11b) is an analysis artefact because on the surface, the gas mixing ratios were relatively low and

within the detection limits of the analyser.

Another greenhouse gas, N_2O, is generated in composts by nitrification and denitrification (Beck-Friis et al., 2000; Cayuela et al., 2012; Jämsén et al., 2015). In the present experiment with bark stockpiles, ambient to low N_2O levels (ca. 0.3–1 ppm) were detected in the pore spaces of both stockpiles (data not shown). Negligible N_2O emissions have also been detected in an earlier storage experiment, where pulp and paper mill sludge was mixed with the wood bark (Oksanen et al., 2022). The low levels of N_2O detected in the present study are probably accounted for by the high C/N ratio (52: 0.3) present in the Scots pine bark (Rasi et al., 2019) and the high temperature inside the stockpiles, as nitrifying bacteria do not tolerate temperatures above +40 °C (Wihersaari, 2005). Furthermore, it should be noted that there was contact between the stockpiles and the soil below, which may have led to N_2O and CH_4 emissions (Jämsén et al., 2015).

Starting from c. 2.5 weeks from the stockpile establishment, methanol concentrations in the stockpile pore space were about two times higher in the non-ventilated stockpile than in the ventilated stockpile. On the stockpile surface of the ventilated stockpile, on the other hand, methanol flux rates were highest soon after piling and decreased thereafter, with some emissions still in August, especially at a height of 3 m; the values were lower in the non-ventilated stockpile (Fig. 12d). The differences within the same stockpile may have been related to local effects and places within stockpiles where gaseous releases are channelised (a chimney effect), similar to the phenomenon described by Tagliaferri et al. (2024) as “dry regions” and “smoking regions”. Enhanced liberation of gases from the higher elevation measuring points may have been due to the higher exposure of these sites to outside factors (e.g. UV light, wind, rain), as well as to internal stockpile activities (e.g. steam generated by the self-heating of the stockpile) compared with lower measuring sites (Halmemies et al., 2022). The release of methanol from bark chips is probably due to the action of pectin methyl esterases. These enzymes are present in plants and in certain fungi and bacteria, and release methyl ester groups from pectin as methanol (Kohli et al., 2015). Pectin is abundant in the cell walls of bark tissues (Kim and Daniel, 2017; Halmemies et al., 2022).

4.3. Release of VOCs

Our interest was in investigating the release of mono- and diterpenes, and how ventilation affected this process. Terpenes are abundant in conifer resin (Strömvall, 1992; Holopainen et al., 2013). Anthropogenic terpene emissions occur during wood harvesting, storage, and processing and contribute with biogenic emissions to the formation of atmospheric aerosols, and in the presence of light and nitrogen oxides of photo-oxidants; these have an impact on climate change and on plant and human health respectively (Strömvall, 1992; Strömvall and Petersson, 1993; Granström, 2007). Additionally, many sesquiterpenes are used by insects in chemical communication, and conifer trees react to insect attacks with a terpene-rich resin flow (Ghimire et al., 2016). In the present study, the data obtained from the chemical analyses of bark showed that the amount of total monoterpenes decreased rapidly in the bark after piling (Fig. 6, Fig. 10). This change was also observed in the gas measurements in the stockpile pore space: monoterpenes α- and β-pinene and 3-carene were abundant in the first measuring day (one week after piling) but more than halved in the following 12 days, and then with a slower velocity. Similarly, in undried sawdust of Scots pine, 90 % of the monoterpenes were released in the initial 10 days at room temperature (Granström, 2010). The decrease in the amount of sesquiterpenes (e.g. α-muurolene; longifolene) from the bark chips was less rapid than for monoterpenes, but their concentration decreased more slowly during the summer (Fig. 6c, Fig. 9a,b). Nevertheless, reconstruction of the emissions between the observed instances contain uncertainty and may not show the absolute differences quantitatively. Rather they provide an additional, relative aspect of the spectrum of emissions generated. Yet, our results are in line with recent findings presented by Tagliaferri et al. (2024), who reported that the release of terpenes was highest on particular sites in “smoking areas”, supporting our findings that higher concentrations of released terpenes occurred locally (chimney effect). The reason for the monotonous release of terpenes into the atmosphere is considered a physical release mechanism (Strömvall and Petersson, 2000; Tagliaferri et al., 2024). As temperature conditions are due to exothermic reactions in the decay process, the surface flux kinetics may be related to convective pore gas transfer, and the aeration there could play a physically significant role. Indeed, the terpene emissions were accelerated due to ventilation, as observed in the measurements in the stockpile pore space (Fig. 10). Furthermore, the total concentration of VOCs seems to be connected with the temperature (He et al., 2015).

Many of the gaseous substances are released as a result of organic matter decomposition, but some may simply be released due to the difference in concentration between the chip and the pore space. A correlation has also been found between precipitation and terpene emission levels in the air (Rupar and Sanati, 2005). A stimulatory effect of rehydration on the release of monoterpenes was also observed in softwood timber after one year of storage (Muilu-Mäkelä et al., 2021). A small particle size and greater porosity of material increase the evaporation of volatile terpenes.

When considering the potential to exploit the compounds found in bark stockpile, there is a rapidly growing global market for terpenes, with an estimated value of USD 885.1 million in 2022 (Market.US, 2023). For example, monoterpenes and sesquiterpenes can be used for pharmacological, flavour, fragrance, medicinal, and cosmetic purposes (Hohmann et al., 2016; Tetali, 2019; Zielińska-Błajet and Feder-Kubis, 2020), as well as within the fine chemicals and biofuel industries (Schwab et al., 2013; Tetali, 2019), and condensed tannins from pine bark may also be used for wood surface modification (Filgueira et al., 2017).

Based on the rapidly occurring release of mono- and sesquiterpenes in the bark stockpile, they should be extracted immediately after debarking. If bark would be exploited in a cascading process, in the first stage, bark can be pre-steamed to heat the material, and volatile terpenes can be obtained from the condensate (Bertaud et al., 2017). Pre-steamed material can be further extracted with hot water to acquire tannins (Kilpeläinen et al., 2023). Furthermore, the use of the forest industry’s bark sidestreams promotes sustainability and the transformation into a bioeconomy, as shown for the use of natural antibacterial and antioxidative agents obtained from Norway spruce bark (Välimaa et al., 2020). However, the upscaling of laboratory knowledge for value-added uses of extractives for commercial utilisation still requires detailed opportunity analyses (Verkasalo et al., 2021).

5. Conclusions

In outdoor storage conditions from April to September, the stockpiles of Scots pine bark released gaseous substances as a result of the decomposition of the organic matter and a release of VOCs, which were present in the bark. The ventilation of the stockpile by means of wind-propelled chimneys had an effect on the gas emissions, and probably also on the conditions in the depths of the stockpile, where most of the gas release originated. Decomposition products such as CO_2, CO, and methanol were released in relatively higher quantities from the ventilated than from the non-ventilated stockpile, similarly to the gravimetrically measured dry matter loss. Compared with the non-ventilated stockpile, the ventilated one showed approximately 39 % higher C losses through the release of CO_2. Moreover, with gases other than CO_2, twice the amount of C losses occurred in the ventilated stockpile. Consequently, we confirmed the hypothesis that the dynamics of C losses could be evaluated with the aid of flux measurements of the carbon-containing gases at different heights on the stockpiles, and moreover, there was an effect of stockpile ventilation on these release processes.

Furthermore, ventilation seemed to accentuate the emission of the

terpenes, with the highest release rates in the early stages of storage. The amount of mono- and sesquiterpenes decreased in samples retrieved from inside the bark piles, confirming our hypothesis of their exhaustion and release to the stockpile pore space. The most prominent losses for monoterpenes occurred rapidly in the first 11 days. The depletion rate of sesquiterpenes was lower than monoterpenes, taking place more quickly in the ventilated pile. In consequence, we confirmed the hypothesis that mono- and sesquiterpenes were released from the bark, with a decrease in their amounts within the material over time, and that the release of selected mono- and sesquiterpene volatiles can be detected in the pore spaces of the stockpiles, as well as through the efflux measurements at the stockpile surface layer.

In conclusion, our results contribute to the practical biomass management by providing evidence that future pine bark storage management strategies need to take the storage time carefully into account if the release of valuable gaseous compounds such as mono- and sesquiterpenes, as well as storage C losses, is to be reduced. The ventilation had no major effect on the overall release of VOCs but the release was accelerated in ventilated compared to the non-ventilated stockpile, leading to the conclusion that stockpile ventilation is not preferable if one wants to retain the VOCs within the material for a slightly longer period when storing the pine bark.

CRediT authorship contribution statement

Robert Prinz: Writing – original draft, Writing – review & editing, Methodology, Data curation, Funding acquisition, Project administration, Investigation, Conceptualization, Visualization. **Anna Kärkönen:** Writing – original draft, Writing – review & editing, Methodology, Investigation, Conceptualization, Validation, Visualization. **Jukka Alm:** Writing – original draft, Writing – review & editing, Methodology, Data curation, Investigation, Conceptualization, Validation, Visualization. **Eero Liski:** Writing – original draft, Writing – review & editing, Methodology, Investigation, Validation, Visualization. **Jenni Tienaho:** Writing – original draft, Writing – review & editing, Methodology, Investigation, Validation, Visualization. **Petri Kilpeläinen:** Writing – original draft, Writing – review & editing, Methodology, Investigation, Conceptualization, Validation. **Hanna Brännström:** Writing – review & editing, Methodology, Conceptualization. **Lauri Sikanen:** Methodology, Data curation, Investigation, Conceptualization, Supervision, Visualization. **Johanna Routa:** Writing – original draft, Writing – review & editing, Methodology, Data curation, Funding acquisition, Project administration, Investigation, Conceptualization, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.119457.

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