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Abstract: Oxidation products of α-pinene represent a fraction of organic matter in the environmental aerosol. α-pinene is one of most abundant monoterpenes released in the atmosphere by plants, located typically in boreal, temperate and tropical forests. This primary compound reacts with atmospheric oxidants, such as O_3, O_2, OH radicals and NO_x, through the major tropospheric degradation pathway for many monoterpenes under typical atmospheric condition. Although several studies identified a series of by-products deriving from the α-pinene photo-oxidation in the atmosphere, such as pinic and cis-pinonic acid, the knowledge of the mechanism of this process is partially still lacking. Thus, the investigation of the distribution of these acids in the different size aerosol particles provide additional information on this regard.
The aim of this study is twofold. First, we aim to improve the existing analytical methods for the determination of pinic and cis-pinonic acid in aerosol samples, especially in terms of analytical sensitivity and limits of detection (LOD) and quantification (LOQ). We even attempted to increase the knowledge of the α-pinene photo-oxidation processes by analysing, for the first time, the particle-size distribution up to nanoparticle level of pinic and cis-pinonic acid. The analysis of aerosol samples was carried out via high-performance liquid chromatography coupled to a triple quadrupole mass spectrometer. The instrumental LOD values of cis-pinonic and pinic acid are 1.6 and 1.2 ng L-1 while LOQ values are 5.4 and 4.1 ng L-1, respectively. Samples were collected by MOUDI IITM cascade impactor with twelve cut-sizes, from March to May 2016 in the urban area of Mestre-Venice (Italy).
The range concentrations in the aerosol samples were from 0.6 to 0.8 ng m-3 for cis-pinonic acid and from 0.1 to 0.8 ng m-3 for pinic acid.

Photo-oxidation products of α-pinene in coarse, fine and ultrafine aerosol: a new high sensitive HPLC-MS/MS method

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Dear Editor,

We have the pleasure to send you by electronic submission a copy of the work titled "Photo-oxidation products of α-pinene in coarse, fine and ultrafine aerosol: a new high sensitive HPLC-MS/MS method" by Matteo Feltracco ,Elena Barbaro, Daniele Contini, Roberta Zangrando, Giuseppa Toscano, Dario Battistel, Carlo Barbante,Andrea Gambaro to be consider for publication in Atmospheric Environment.

Best regards,

Matteo Feltracco

The purpose of this work is to present a high sensitive method to determine cis-pinonic and pinic acids in different particle size fractions including, for the first time, the nanoparticles. The quantitative performance of HPLC coupled to triple quadrupole API 4000 were carried out to

determine these acids in environmental samples at trace concentration levels. The article presents a theoretical section regarding analysis and there is a wide contribute to each phase of analytical operations. An important improvement of this work is to develop a higher sensitive analytical method than previous studies, suitable for an evaluation of the particle-size distribution of the target compounds in aerosols.

Supporting material (SM) include material directly relevant to the conclusion of a paper that cannot be included. SM provides figures and tables that enrich the data described in the paper.

This article has not yet been published and it is not under consideration by any other journal. All authors are aware of the manuscript and they accept responsibility for it.

1   **Photo-oxidation products of α-pinene in coarse, fine and ultrafine aerosol: a**

2   **new high sensitive HPLC-MS/MS method**

3

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21

22   **Abstract**

23   Oxidation products of α-pinene represent a fraction of organic matter in the environmental aerosol. α-

24   pinene is one of most abundant monoterpenes released in the atmosphere by plants, located typically in

25   boreal, temperate and tropical forests. This primary compound reacts with atmospheric oxidants, such

26   as O_3, O_2, OH radicals and NO_x, through the major tropospheric degradation pathway for many

27   monoterpenes under typical atmospheric condition. Although several studies identified a series of by-

28   products deriving from the α-pinene photo-oxidation in the atmosphere, such as pinic and cis-pinonic

29   acid, the knowledge of the mechanism of this process is partially still lacking. Thus, the investigation of

30   the distribution of these acids in the different size aerosol particles provides additional information on

31   this regard.

32   The aim of this study is twofold. First, we aim to improve the existing analytical methods for the

33   determination of pinic and cis-pinonic acid in aerosol samples, especially in terms of analytical

34   sensitivity and limits of detection (LOD) and quantification (LOQ). We even attempted to increase the

35   knowledge of the α-pinene photo-oxidation processes by analysing, for the first time, the particle-size

36   distribution up to nanoparticle level of pinic and cis-pinonic acid. The analysis of aerosol samples was

37   carried out via high-performance liquid chromatography coupled to a triple quadrupole mass

38   spectrometer. The instrumental LOD values of cis-pinonic and pinic acid are 1.6 and 1.2 ng L^{-1} while

39   LOQ values are 5.4 and 4.1 ng L^{-1}, respectively. Samples were collected by MOUDI II^{TM} cascade

40   impactor with twelve cut-sizes, from March to May 2016 in the urban area of Mestre-Venice (Italy).

41   The range concentrations in the aerosol samples were from 0.6 to 0.8 ng m^{-3} for cis-pinonic acid and

42   from 0.1 to 0.8 ng m^{-3} for pinic acid.

Introduction

The formation of secondary organic aerosols (SOA) in the rural atmosphere has attracted growing interest in recent years. The atmospheric formation of new particles and their chemical composition can have an important role for the determination of the global aerosol load and their effect on the climate change (Kulmala et al., 2004).

Monoterpenes are the most abundant biogenic hydrocarbons in troposphere and these compounds affect the oxidising capacity of the atmosphere (Kanakidou et al., 2000). In the last years, considerable studies (Lamb et al., 1987; Larsen et al., 1999; Librando and Tringali, 2005) have been carried out to determine the secondary organic aerosol (SOA) formation from the photo-oxidation of volatile organic compounds (VOCs). In particular, α-pinene is the most important monoterpene released by biogenic sources, particularly conifers. It has an emission rate projected at global scale of about 127 Tg y^{-1} (Guenther et al., 1995) and it has been shown to give high SOA rates in laboratory smog chamber research (Lamb et al., 1987; Larsen et al., 1999). The emission on global scale of total monoterpenes from the vegetation has been estimated between 120–480 Tg y^{-1} (Fehsenfeld et al., 1992), therefore the α-pinene fraction represent a large part of global monoterpenes, by considering its emission rate. α-pinene is a primary ingredient of pine resin and it is also found other conifers and non-coniferous plants. Nevertheless, the atmospheric degradation proceeds through a very complex mechanism that is still not totally identified, and this leads to form an abundance of reaction products (Glasius et al., 2000, 1999, Iinuma et al., 2016, 2004; Larsen et al., 1999; Librando and Tringali, 2005; Zhang et al., 1992).

The innovative purpose of this work is to present an evaluation of the distribution of the target compounds in aerosols as a function of particle size focusing on the ultrafine fractions. To our knowledge, the photo-oxidation products of α-pinene in the ultrafine fraction have never been investigated. The quantitative performance of HPLC coupled to triple quadrupole API 4000 were carried out to determine these acids in environmental samples at trace levels. Recently, photo-oxidation products of α-pinene have been investigated using GC-MS and HPLC-MS methods (Ding et al., 2008; Iinuma et al., 2007; Ion et al., 2005; Parshintsev et al., 2010; Pio et al., 2006; Reinnig et al., 2008; Sheesley and Kenski, 2004; Zhang et al., 2010). GC-MS is a widely used method for the separation, identification and quantification of individual organic compounds in aerosol samples, even though low-

71 volatile polar substances have to be derivatized prior to injection (Ion et al., 2005; Szmigielski et al.,

72 2007) and some compounds might decompose during analysis. HPLC/MS methods were used by some

73 authors to measure oxidation products from terpenes in atmospheric samples and with chamber

74 experiments (Anttila et al., 2005; Reinnig et al., 2008; Zhang et al., 2010). Anttila et al. (2005)

75 investigated the environmental aerosol matter with reversed phase chromatography applied to HPLC

76 system, coupled to an ion-trap mass spectrometer using an electro-spray ionisation (ESI) interface in

77 negative ionisation mode. Besides, Renning et al. (2008) carried out the ozonolysis of α-pinene in a

78 smog chamber and the samples were investigated using reversed phase chromatography coupled with

79 ion-trap mass spectrometer though an APCI source operating in positive mode. Zhang et al. (2010),

80 analysed aerosol samples using C18 column placed in a HPLC system coupled with a hybrid Qq-TOF

81 mass spectrometer. The benefit of HPLC is the suitability for polar and non-volatile compounds as well

82 as the conditions through the analysis, while mass spectrometer allows high sensitivity and selectivity.

83 The main objective of this work is to develop and quantify some of the main photo-oxidation products

84 of α-pinene, pinic and pinonic acids, in different particle size fractions of aerosol collected in the urban

85 area of Mestre-Venice (Italy). A sensitive improvement of analytical method is necessary due to the

86 high fractionation of aerosol in twelve different size ranges.

87 **Experimental section**

88 **Reagents and standard solutions**

89 Ultra-grade methanol (MeOH) and ultra-grade acetonitrile (ACN) were purchased from Romil® LTD

90 (Cambridge, UK), Ultrapure water (18.2 MΩ, 1 ppb TOC) was produced using a Purelab Ultra System

91 (Elga®, HighWycombe, UK), formic acid (≥98 %) eluent additive for HPLC system was obtained from

92 Fluka (Sigma Aldrich®, Buchs, Switzerland). Cis-pinonic acid (Sigma-Aldrich, Sant Louis, Missouri,

93 USA) and pinic acid (Santa Cruz Biotechnology®, Dallas, Texas, USA), were prepared by solid

94 standard (purity ≥98 %) and diluted in ultrapure water. Isotopically labelled vanillin^{13}C$_6$(VAH*)

95 wasobtained from Sigma Aldrich®.

96 Ultrapure water produced using a Purelab was furtherly purified to obtain higher water quality

97 necessary to reach lower limits of detection. The LC-Pak® (Merck KGaA, Darmstadt, Germany)

98 cartridge can be connected to the outlet of water system to produce water with a TOC level below 1 ppb

99   and deliver ultrapure water with minimum trace organic contamination. The LC-Pak® cartridge uses

100 the well-known reversed-phase silica purification media to remove traces of neutral organics.

101 **HPLC-ESI-MS/MS**

102 An Agilent 1100 Series HPLC Systems (Waldbronn, Germany) with a binary pump, vacuum degasser,

103 autosampler and thermostated column compartment) was coupled with an API 4000 Triple Quadrupole

104 Mass Spectrometer (Applied Biosystem/MSD SCIEX, Concord, Ontario, Canada) using a Turbo V

105 electrospray source (ESI) that operated in negative mode. The chromatographic separation used for the

106 sample determination of cis-pinonic acid and pinic acid was conducted using a Zorbax Extend-C18

107 column (Rapid Resolution, 4.6 -150 mm, 3.5 mm; Agilent Technologies). Elution was achieved by a

108 linear gradient using as mobile phase water with 0.01% of formic acid (eluent A) and MeOH/ACN

109 80:20 (eluent B). The binary elution program with flow rate of 0.5 mL min^{-1}was as follows: 0-1 min,

110 20% eluent B; 8-25 min, 100% eluent B; 25-35 min, equilibration with 20% eluent B; 100 μL of sample

111 was injected for analysis. The mass spectrometer's parameters were set as follows: temperature 650 °C,

112 ion spray voltage -4500 V, GS1 40 psi, GS2 60 psi, CUR 15 psi, CAD 8 psi and EP -8 V. Data were

113 collected with multiple reaction monitoring (MRM) mode. The first quadrupole (Q1) selected the

114 molecular ion, while the third quadrupole (Q3) selected the fragment. Both Q1 and Q3 were set at unit

115 resolution with peak width of 0.7±0.1 amu at 50% of maximum peak height. To improve the sensitivity,

116 declustering potential (DP), cell energy (CE) and cell exit potential (CXP) were set, using direct

117 infusions of 1 mg L^{-1} of each individual standard. The voltage of the orifice was controlled by the DP

118 parameter, the CE was the amount of energy that the precursor ions received as they were accelerated

119 into the collision cell, and the CXP was used to focus and accelerate the ions after leaving the collision

120 cell. The monitored transition and instrumental parameters for each compound are shown in Table S-1.

121 Analyst Software version 1.5.2 (Applied Biosystems MDS SCIEX Instruments) was used for the

122 identification and quantification of the target compounds.

Sample collection

The aerosol samples were collected at Scientific Campus of Ca' Foscari University (45°28'47"N, 12°15'12"E, Mestre-Venice, Italy) during spring 2016, using the rotating model 120 MOUDI-II™ cascade impactor. The particle size distribution was obtained for aerodynamic diameter (D) ranging from greater of 18 μm to below 0.056 μm. The configuration of sampler consists to eleven stages with cut sizes at 18, 10, 5.6, 3.2,1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and 0.056 μm, plus a final back-up filter used to collect particles with D<0.056 μm. The impaction plates, 25 nm thick aluminium substrate having a diameter of 47 mm, were prepared in the laboratory and inserted into the impactor at the time of use. The substrates were made using aluminium foils cut with a hollow cutter. Finally, the collection of ultrafine atmospheric particles in the last stage was carried out with a quartz fibre filters (SKC Inc., Eighty-Four, To-13 model).

The duration of the sampling was about 160 h for most of the samples, with an average flow rate of 30 ± 1 L min^{-1}. The air flow at the inlet was measured with a flowmeter before and after each sampling. The sampling period was chosen to obtain enough matter even for weighting. In fact, one of the most important feature of MOUDI II^{TM} is the possibility of the weighing of each aluminium substrate, thanks to their restrained diameter. After conclusion of sampling, the substrates were stored separately at -20 °C until chemical analysis. The sampler was placed on the roof of a building at a height of 20 meters, to avoid direct human contaminations and to prevent winds modification or alteration.

The weather information was provided by station FISTEC-Mestre (IUAV, Venice - Environmental engineering physics laboratory, website: fistec.iuav.it). Precipitation has a great variability especially in spring due to the high humidity, in fact there were a significant precipitation events from 9th to 12th of March (22.8 mm) and a minor from 13th to 15th of April (4.2 mm) and from 11th to 13th of May (3.2 mm). The range humidity was included between 22% (4th May) and 98.5% (most of the data). Moreover, the sampling period was conditioned by the medium-high temperature ranging (from 4 °C to 25 °C) and the prevailing winds were from NW and SW with wind speed between 1 and 7 m s^{-1} (Figure S-1 and S-2, supporting material).

The impactor with the rotation of the nozzle and impaction plates at 1 rpm, formed a near-uniform particle deposit on each substrate.

Sample treatment

To determine and quantify cis-pinonic acid and pinic acid, airborne aerosol was collected on aluminium plates pre-cleaned with MeOH, and on quartz fiber filter, decontaminated with a pre-combustion (4 h at 400 °C in a muffle furnace). Before the closing inside in a clean aluminium foil, the aluminium plates were weighted to allow the calculation of the collected aerosol.

Aluminium plates and filters were removed from the storage package in a laminar flow hood, broken up into small pieces and placed in a 15 mL vial (previously cleaned with ultra-pure water by sonication at 25 °C) with steel tweezers. 50 µL of isotopically labelled vanillin$^{13}C_6$ (78 ng absolute weight) and 4.95 mL of ultrapure water was added to the substrate before cold-ultrasonically extracting at 10 °C to avoid the volatilization of the analytes. The extract has been filtrated through a 0.45 mm PTFE filter (Minisart® Sartorius SRP25, Goettingen, Germany) to remove particulate and filter traces before instrumental analysis.

During the sampling periods, field blanks were taken at the beginning, during and end of the sampling period. The blank samples were collected by loading, carrying and installing the filter holder in the instrument with the air pump turned off.

Result and discussion

Chromatographic separation

The LC–MS/MS conditions were set in terms of eluent composition, eluent pH, gradient conditions and ionisation conditions using standards pinic acid and cis-pinonic acid. Previous studies demonstrated an efficient separation of target acids using conventional reversed phase HPLC columns (Anttila et al., 2005; Parshintsev et al., 2010; Reinnig et al., 2008; Zhang et al., 2010) and GC capillary columns (Ding et al., 2008; Ion et al., 2005; Pio et al., 2006; Sheesley and Kenski, 2004). The coupling with mass spectrometer was always preferred to guarantee sensitivity and selectivity.

In the present study Zorbax Extend-C18 column 4.6x150 mm (Agilent Technologies,Santa Clara, California, USA) was chosen for the chromatophic separation and its performance was evaluated by considering retention time (t_R), peak width (W), number (N) and height (HEPT) of teoretical plates, asymmetry (A_S) for each compound. Resolution (R_S) and selectivity (α) were evaluated between cis-pinonic and pinic acid in order to avoid interferences in the transition of each compound.

179   Three different eluent B composition were investigated to improve the chromatographic performance:

180   pure MeOH (method 1), 80:20 MeOH/ACN (method 2) and 50:50 MeOH/ACN (method 3). MeOH is

181   the best solvent for the ESI source but the addition of ACN in eluent B can improve the peak symmetry

182   (Kostiainen and Kauppila, 2009). The composition of eluent A was always ultrapure water with 0.01%

183   formic acid to improve the peak resolution.

184   Figure 1 shows the chromatographic separations of cis-pinonic and pinic acid and $^{13}C_6$ vanillin (internal

185   standard) using the three different eluition program (method 1, 2 and 3).

186   Higher percentage of ACN allowed a more rapid elution of both analytes with method 3 (50:50

187   ACN:MEOH) respect to pure MeOH used as eluent B (method 1), due to high eluent power of ACN.

188   Moreover, MeOH used as eluent B (method 1) carried out to higher value of peak width for cis-pinonic

189   acid, while this value decreased by adding ACN in the eluent B (method 2 and 3) (Table S-2). Peak

190   broadening is typically described as plate number (N) or as height equivalent to a theoretical plate

191   (HETP). This notion is equivalent to a plates-series model reflecting the number of equilibrium steps

192   represented by the column. Table S-1 shows that the method 2 has the higher value of N (and the

193   smallest HETP value) for cis-pinonic acid, while the method 1 has the higher value of N for pinic acid,

194   although the N value of method 2 is relatively close. Futhermore, another parameter that points out the

195   good chormatographics conditions is the peak asymmetry. The most important reasons for the presence

196   of asymmetry are slow mass transfer, column overload, the heterogeneity of the stationary phase surface

197   and the heterogeneity of the column packing (Pápai and Pap, 2002). The method 2 shows an

198   asymmestry closer to 1, approximating in a better way the gaussian form (A_S >1: tailing; <1: fronting).

199   Probably, this means that the composition of the mobile phases of the method 2 provided a better mass

200   transfer. We investigate moreover the selectivity (α) and the resolution factor (R_F). High α values

201   indicate good separating power and a good ability of the chromatographic system to distinguish

202   between sample components, and the best values are provided by the method 2 (α = 1.12) and 3 (α =

203   1.20), while the method 1 gave a α = 1.07. The resolution values are always plenty above 1.5. This

204   ensure that the samples are well separated to a degree at which the area can be accurately measured.

205   The study of the whole parameters permitted to choose the operative conditions shown in the "HPLC-

206   ESI-MS/MS" section.

207   The chromatographic method is different if compared to some previously published LC–ESI–MS/MS

208   methods (Anttila et al., 2005; Glasius et al., 1999) in which was used acidic conditions using acetic acid

209   as buffer and a gradient starting with fully aqueous conditions with methanolic gradient.

210

211   **Quantitative performance**

212   The analytical procedure was validated through linear range, instrumental limit of detection (LOD),

213   instrumental limit of quantification (LOQ), procedural blank, method detection limit (MDL), method

214   quantification limit (MQL), trueness, repeatability, and extraction yield. The internal standard method

215   by isotope dilution was used to quantify cis-pinonic and pinic acids and labelled $^{13}C_6$ vanillin was

216   chosen as internal standard because it demonstrated similar instrumental and pre-analytical behaviour.

217   The linearity of the calibration curves for of cis-pinonic acid and pinic acid with labelled $^{13}C_6$ vanillin

218   as internal standard was evaluated using a series of standard solutions prepared in ultrapure water at

219   average concentrations from 0.01 to 50 µg L^{-1} and a constant concentration of labelled $^{13}C_6$ vanillin

220   (15.5 µg L^{-1}). By considering the ratio between concentration of target acids and internal standard and

221   the ratio between the relative peak areas, linearity was evaluated obtaining $R^2 \geq 0.9997$. LOD and LOQ

222   values are calculated as three and ten times the signal-to-noise ratio of the known absolute amounts of

223   the analysed target compound in a standard solution (Bliesner, 2006). The LOD values of cis-pinonic

224   and pinic acid are 1.6 and 1.2 ng L^{-1} while LOQ values are 5.4 and 4.1 ng L^{-1}, respectively. Parshintsev

225   et al. (Parshintsev et al., 2010) obtained a LOD value of 27 and 12 µg L^{-1}, while Zhang et al. (Zhang et

226   al., 2010) obtained 3.3 and 0.35 µg L^{-1}, respectively for cis-pinonic acid and pinic acid. In both of cases

227   the studies were carried out via HPLC-MS systems and the LOD values of this study are considerable

228   lower than reported literature. Furthermore, to our knowledge, the method has the lowest LOD values

229   compared to previous studies. The instrumental precision was evaluated and CV% value (reported as a

230   percentage and calculated from the average and standard deviation, calculated as (SD/A)×100) was

231   below of 10%. Due to the lack of certified reference materials for cis-pinonic and pinic acid in the

232   aerosol or dust, we estimated trueness, precision and recovery by analyzing five spiked cleaned

233   aluminium plate and QFF with 63 ng of cis-pinonic acid, 45 ng of pinic acid and 78 ng of $^{13}C_6$ vanillin.

234   The quantification was carried out using a response factor in order to avoid the instrumental signal

235   fluctuations.

236   Trueness is an important parameter to evaluate during method validation. It refers to the degree of

237   closeness of the determined value to the known "true" value. It is expressed as a percent error,

238   calculated as (Q−T)/T×100 where Q is the determined value and T is the "true value". The error for cis-

239   pinonic acid and pinic acid was calculated performing the same pre-analytical procedure achieved with

240   the environmental samples. For the evaluation of the extraction yield to estimate the procedural

241   extraction efficiency the isotopically labelled $^{13}C_6$ vanillin was added after the PTFE filtration. Table 1

242   shows the validation values just described for cis-pinonic acid and pinic acid. The internal standard

243   method provided an error percentage and CV% $<\pm 10$ % for each compound. The recovery of the

244   analytical procedure for the investigated acids ranged between 66±7 and 85±5 %; Parshintsev et al.

245   (Parshintsev et al., 2010) reached extraction levels from 77±9 to 96±4%: the values are close with the

246   extraction levels of QFF, but they are higher than aluminium plates. This means that the quartz fiber

247   filter is a better substrate for extraction. In Table 1 is reported the mean absolute blank amount which

248   was subtracted from the analytical results. The MDL and The MQL were evaluated through 5

249   procedural blanks, i.e. 5 aluminium substrates and 5 quartz substrates in which it has been added only

250   the $^{13}C_6$ vanillin after the extraction. The MDL and the MQL were evaluated as 3 and 10 times the

251   standard deviation of these field blanks. Even though the fiber filter has a higher MDL compared to the

252   aluminium plate due its porosity, the values are quite similar to the procedural blanks, demonstrating a

253   minimal contamination during the operation before and after the sampling.

254
255   **Cis-pinonic and pinic acid in the urban atmospheric aerosol**

256   Cis pinonic and pinic acids were determined in the atmospheric aerosol collected in the urban area of

257   Mestre-Venice (Italy) from 14 March to 13 May 2017. The total concentration of each acid, calculated

258   as the sum of their size distributions in all aerosol samples, has an average value of 0.3 ng m^{-3}. Cis-

259   pinonic acid was usually found in the ultrafine fraction (<0.056 nm), and its concentrations ranged from

260   below MDL to 0.8 ng m^{-3}. Instead pinic acid concentrations ranged from below MDL to 0.6 ng m^{-3}. The

261   concentration values found in this study are lower of an order of magnitude than the investigation

262   reported in literature (Fu et al., 2009; Kavouras et al., 1998; Kavouras and Stephanou, 2002; Sheesley

263   and Kenski, 2004; Yu et al., 1999; Zhang et al., 2010) (Table 2). These authors collected the samples

264   very close to conifers and deciduous areas, while in the present study the sampling site was just near a

265   restrict area of deciduous trees. To ensure that is so, Lamb et al. (Lamb et al., 1987) demonstrated how

266   monoterpenes are mostly formed near coniferous and deciduous trees, although the formation of the

267   photo-oxidation products follows a partially unknown mechanism, forming an abundance of SOA

268   compounds with a wide range particles diameter. Consequently, fine and ultra-fine particles can be

269   transferred for long distances, according to the atmospheric conditions. The location of aerosol site

270   collection certainly influences the concentrations of photo-oxidation products of α-pinene, although

271   other parameters can have an important role. The sampling site provide even the chemical atmospheric

272   evolution of the two terpenoic acids. In fact, the features of the urban area, considering even the huge

273   distance from coniferous sources, is such as to give information about the atmospheric transformations.

274   In literature it is demonstrated that the highest concentrations for cis-pinonic acid and pinic acid are

275   measured in spring and summer months (Sheesley and Kenski, 2004; Zhang et al., 2010). The results of

276   this study agree with these observations (Figure 2) for cis-pinonic acid, because it increased its

277   concentrations form March to May, while pinic acid has a different behaviour. The major

278   concentrations of cis-pinonic acid have been found in the three samples of April 26-29 and May 3-6 and

279   May 10-13, while pinic acid is most concentrated in the collecting periods of March 14-18, 18-22 and

280   May 3-6.

281   It is known how cis-pinonic acid is a high/semi-volatile compound (Zhang et al., 2010) and it was

282   detected in the gas and particulate phase in forests atmosphere (Kavouras et al., 1999, 1998; Kavouras

283   and Stephanou, 2002; Pio et al., 2001). Figure 2 and the box-plot diagram of Figure 3 show that cis-

284   pinonic acid was only found in the ultrafine particles (mostly distributed below 0.056 nm diameter) and

285   this suggests that it is a typical first-generation reaction product (Jimenez et al., 2009) with a gas-to-

286   particle process (Anttila et al., 2005; Pio et al., 2006), due to its abundant presence in the gas phase.

287   Several studies explained that pinic acid derives from pinonic acid thought photo-oxidation processes

288   (Lamb et al., 1987; Larsen et al., 1999; Librando and Tringali, 2005; Noziere et al., 1999). The

289   scientific literature describes pinic acid as low/semi-volatile compounds that is mainly present in the

290   submicrometer fraction of ambient aerosols (Alves et al., 2000; Pio et al., 2006). However, considering

291 that SOAs from monoterpene photo-oxidation constitute good CCN (cloud condensation nuclei) in the

292 atmosphere (Huff Hartz et al., 2005; O'Dowd et al., 2002), cis-pinonic acid can undergo the photo-

293 oxidation in particulate phase creating pinic acid that, being also a good CCN, grows forming fine

294 aerosol with a greater diameter, up to 1 μm (Spurny, 2000). Coarse particles (diameter > 1 μm) are

295 mostly emitted to the atmosphere during mechanical processes from both natural and anthropogenic

296 sources. A further explanation of the presence of pinic acid in coarse particles might be the result of

297 condensation of pinic acid, produced by the gas-phase photo-oxidation of cis-pinonic acid, onto larger

298 existing aerosol particles or of particle coagulation, especially during long-range transport (Herckes et

299 al., 2006; Wang et al., 2009; Zangrando et al., 2016, 2013). Very often the equilibrium-phase

300 partitioning depends strongly on temperature, because of the variation of vapour pressures of the

301 condensing compounds with temperature (Seinfeld and Pankow, 2003). Figure 3 show that the trend

302 concentration, fractions distribution and the formation processes of pinic acid tends to distribute in all

303 the fractions. It can be explained with a tri-modal view: nucleation (Aitken) mode (particle diameter <

304 0.1 μm), accumulation mode (particle diameter: 0.1 μm > d > 1 μm) and coarse mode (particle diameter

305 > 1 μm).

306 In this study cis-pinonic acid and pinic acid don't have a clear correlation with temperature (Figure S-

307 3), probably due to the different atmospheric conditions undergo by the particles during the transport

308 processes. Moreover, there is not a clear relationship among the trend concentrations of the acids and

309 precipitations, relative humidity and wind directions and intensity (relative humidity, precipitation and

310 wind rose are shown in the supporting material, Figure S-2 and S-3). Pio et al. (Pio et al., 2006) has

311 shown, using a cascade impactor, how pinonic and pinic acids appeared mainly in fine particles (<0.69

312 μm diameter): the distribution differences with this study is due to the distance from the sources. To our

313 knowledge this is the first study in which we can observe the behaviour of cis pinonic acid and pinic

314 acid in aged aerosol in an urban environment.

Conclusions

In this study a method for the quantification in particulate matter of two terpenoic acid, cis-pinonic acid and pinic acid, using a HPLC-ESI(-)-MS/MS system was developed. We obtained a sensitive method with instrumental detection limits of 1.6 and 1.2 ngL^{-1}, respectively. To our knowledge, this is the most sensitive method to quantify these target acids. The analytical procedure was validated to accurately quantify these compounds in the aerosol samples though the estimation of trueness, repeatability, and recovery.

The HPLC-MS/MS method developed in this study was applied to the atmospheric samples collected in Mestre-Venice, to characterise particle size distribution of cis-pinonic acid and pinic acid. The sampling was conducted using a MOUDI II cascade impactor to discriminate the particle size from 18 μm to < 0.056 nm. This is the first study about the characterization of the pinic and cis-pinonic in the ultrafine particles. During the spring 2017 fourteen different samples demonstrated that cis-pinonic acid is mostly distributed in the ultra-fine fraction (below 0.056 nm diameter) while pinic acid show a steady distribution among the 12 fractions. Both acids seem don't have a clear correlation with temperature.

Table 1

Compound	Error %	Recovery %	CV%	Blank (ng)	MDL (ng)	MQL (ng)
Aluminium						
Cis-pinonic acid	5.9	77±1	2	2.3±0.2	0.7	2.5
Pinic acid	-9.2	66±7	10	3.1±0.4	1.2	4.1
Quartz QFF						
Cis-pinonic acid	2.3	80±2	2	3.0±0.8	2.3	7.5
Pinic acid	0.9	85±5	6	2.7±0.6	1.9	6.2

Table 1. Average errors (%), recovery (%), CV%, blank (ng), MDL and MQL (ng)

Table 2

Compound	Average conc. ng m^{-3}	Location, time
Cis-pinonic acid	0.3 ± 0.3	Mestre-Venice, Italy, March-May 2016 (this study)
	1.22 ± 1.33	Mainz, Germany, May 2006–June 2007 (Zhang et al., 2010)
	0.069 ± 0.023	Canadian Arctic, February–June 1991 (Fu et al., 2009)
	18 ± 31	SMEARII station, Finland, August 2007 (Parshintsev et al., 2010)
	40.5 ± 67.5	Alabama, USA, May 2004-April 2005 (Sheesley and Kenski, 2004)
	9.7 ± 11	Pertouli, Greece, August 1998 (Kavouras and Stephanou, 2002)
Pinic acid	0.3 ± 0.2	Mestre-Venice, Italy, March-May 2016 (this study)
	2.32 ± 2.72	Mainz, Germany, May 2006–June 2007 (Zhang et al., 2010)
	0.51 ± 0.40	Canadian Arctic, February–June 1991 (Fu et al., 2009)
	1 ± 9	SMEARII station, Finland, August 2007 (Parshintsev et al., 2010)
	0.54 ± n.d.	Nova Scotia, Canada, July 1996 (Yu et al., 1999)
	0.5 ± n.d.	San Bernadino, Canada, September 1998 (Yu et al., 1999)
	2.4 ± 1.5	Pertouli, Greece, August 1998 (Kavouras and Stephanou, 2002)

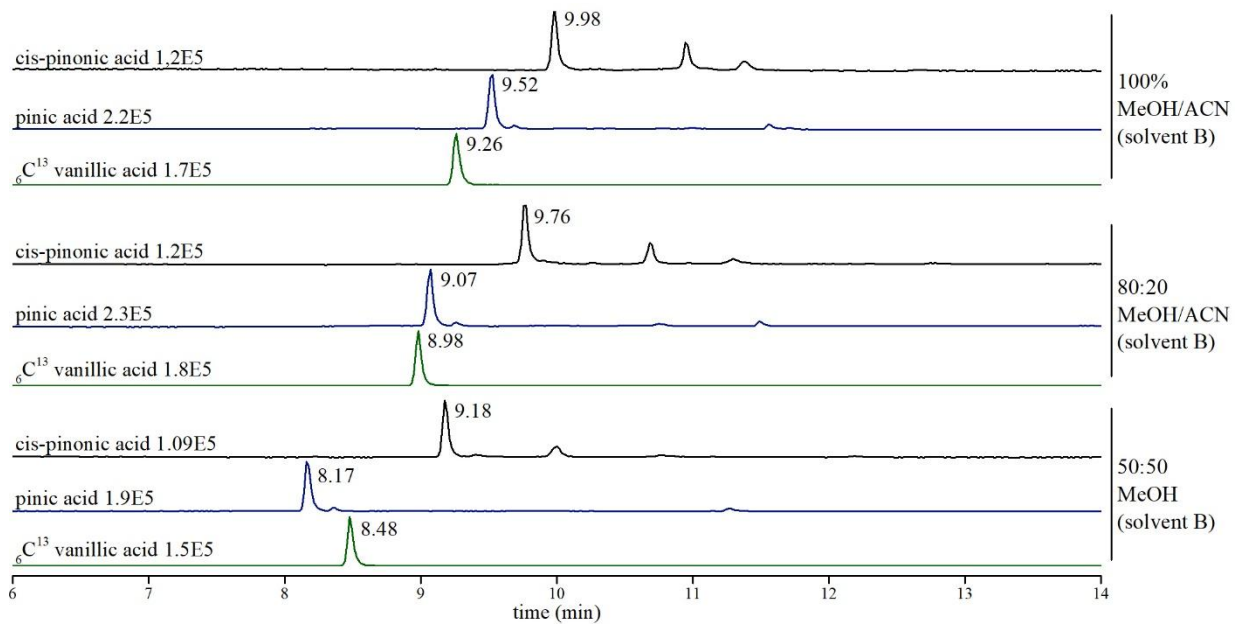Table 2. Average TSP concentration comparison with other studies of investigated organic compounds.

351   **Figure 1**

352

353   Figure 1. Chromatograms of the target acid and their internal standard tested with 3 different mobile

354   phases from 6 to 14 minutes. Each ion chromatogram is related to most intense ions of MRM method

355   for a standard solution of the acids with an average concentration of 50 μg L^{-1} (cis-pinonic acid

356   183.2/139.0; pinic acid 185.2/140.9; $_6C^{13}$ vanillic acid 156.9/141.8).
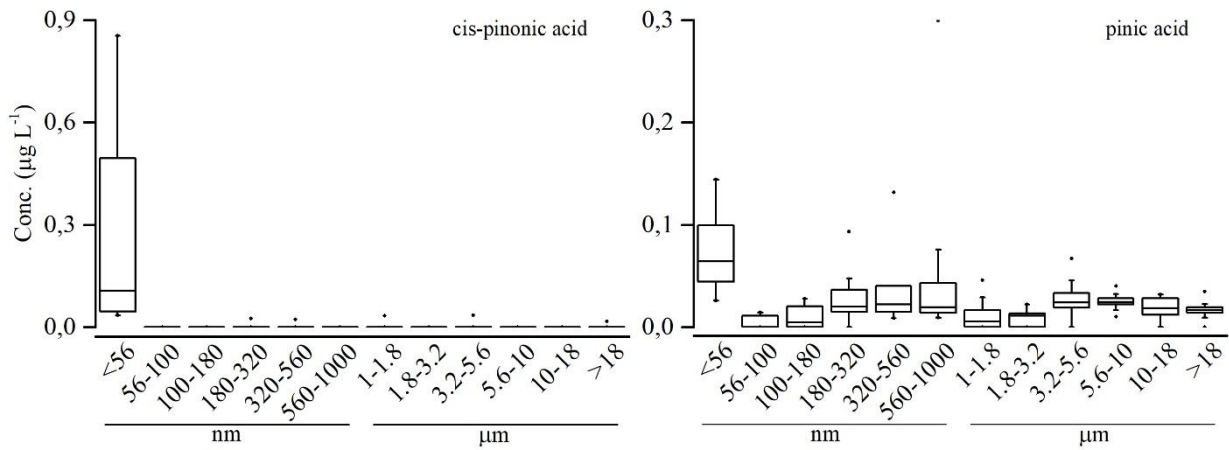
357   **Figure 2**
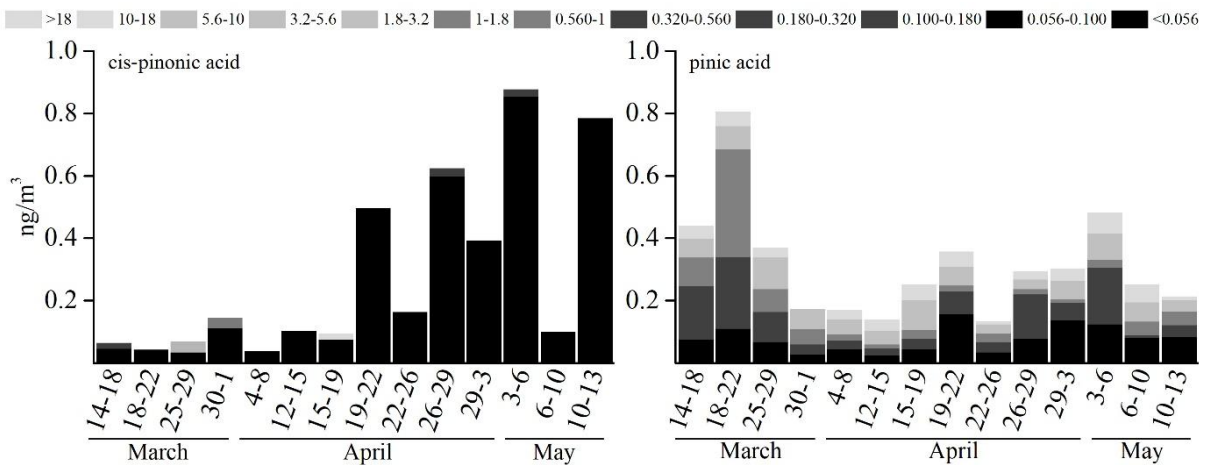
358

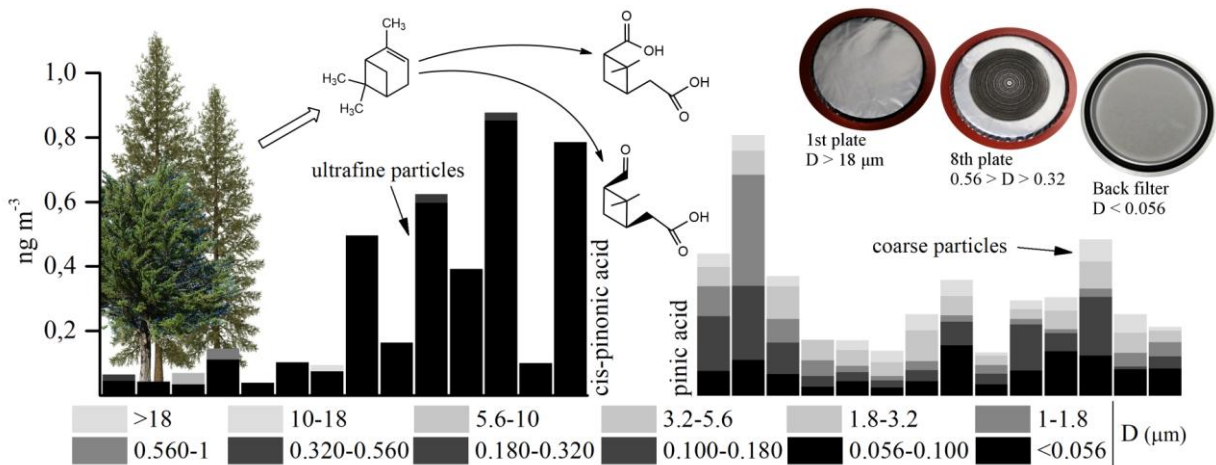359   Figure 2. Monthly variations and fractions distribution of target acids (ng m^{-3}).

360

361

362

363

Figure 3

Figure 3. Box-plot diagram of cis-pinonic acid and pinic acid according to the particles diameter. The

line inside the box is referred to the median.

FOR TOC ONLY

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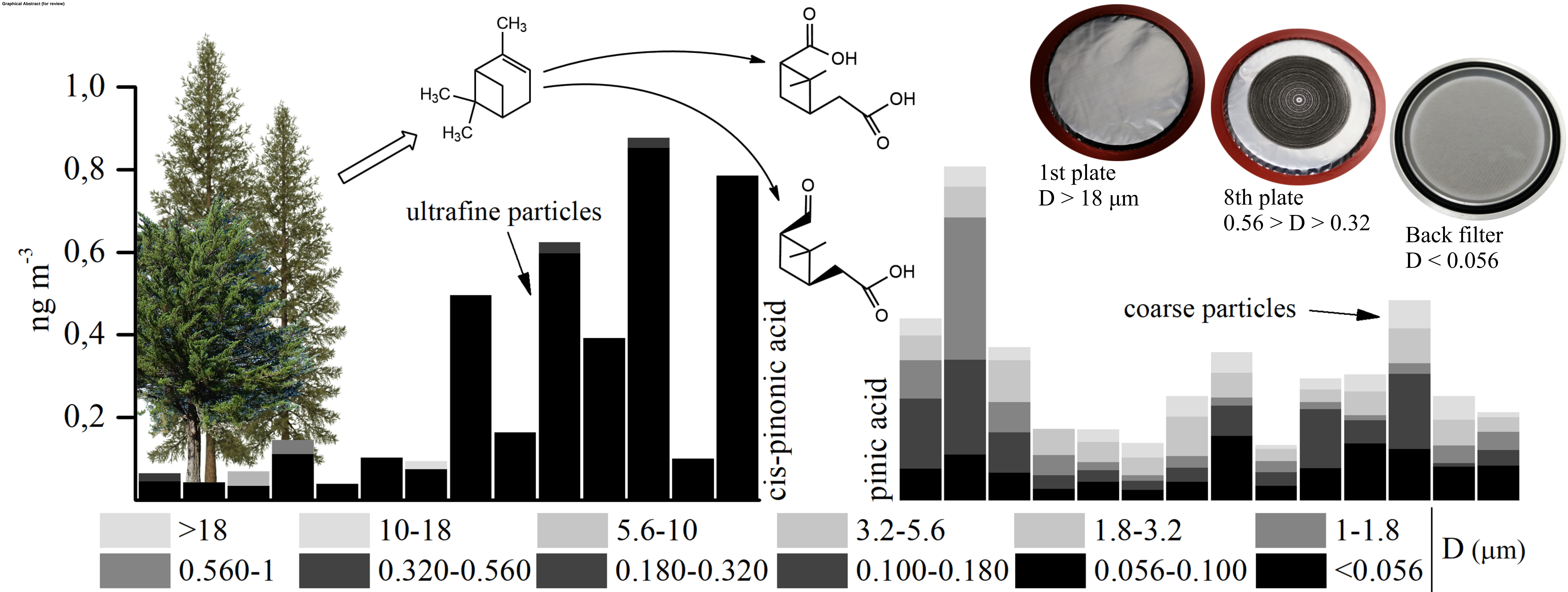489   544, 606–616. doi:10.1016/j.scitotenv.2015.11.166

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499

ultrafine particles

cis-pinonic acid

pinic acid

coarse particles

1st plate
D > 18 μm

8th plate
0.56 > D > 0.32

Back filter
D < 0.056

| | >18 | | 10-18 | | 5.6-10 | | 3.2-5.6 | | 1.8-3.2 | | 1-1.8 | D (μm) |
| | 0.560-1 | | 0.320-0.560 | | 0.180-0.320 | | 0.100-0.180 | | 0.056-0.100 | | <0.056 | |

ng m^{-3}

1,0

0,8

0,6

0,4

0,2

CH_3

H_3C

H_3C

Highlights

A sensitive HPLC-MS/MS method was developed to quantify cis-pinonic and pinic acids.

Aerosol particle size distribution of cis-pinonic and pinic acids was evaluated.

For the first time cis-pinonic and pinic acids were found in the nanoparticles.
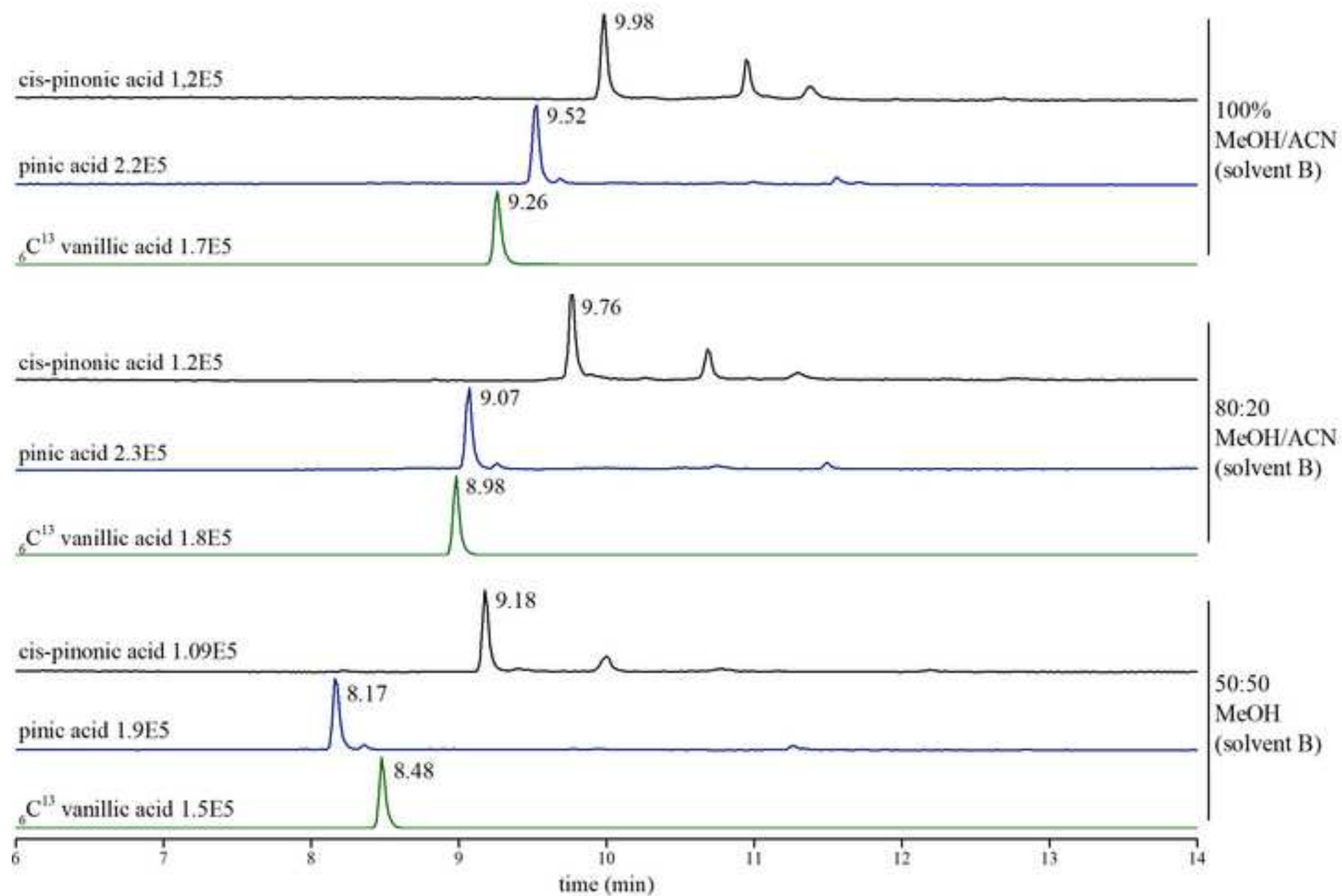
Figure 1
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Figure 2
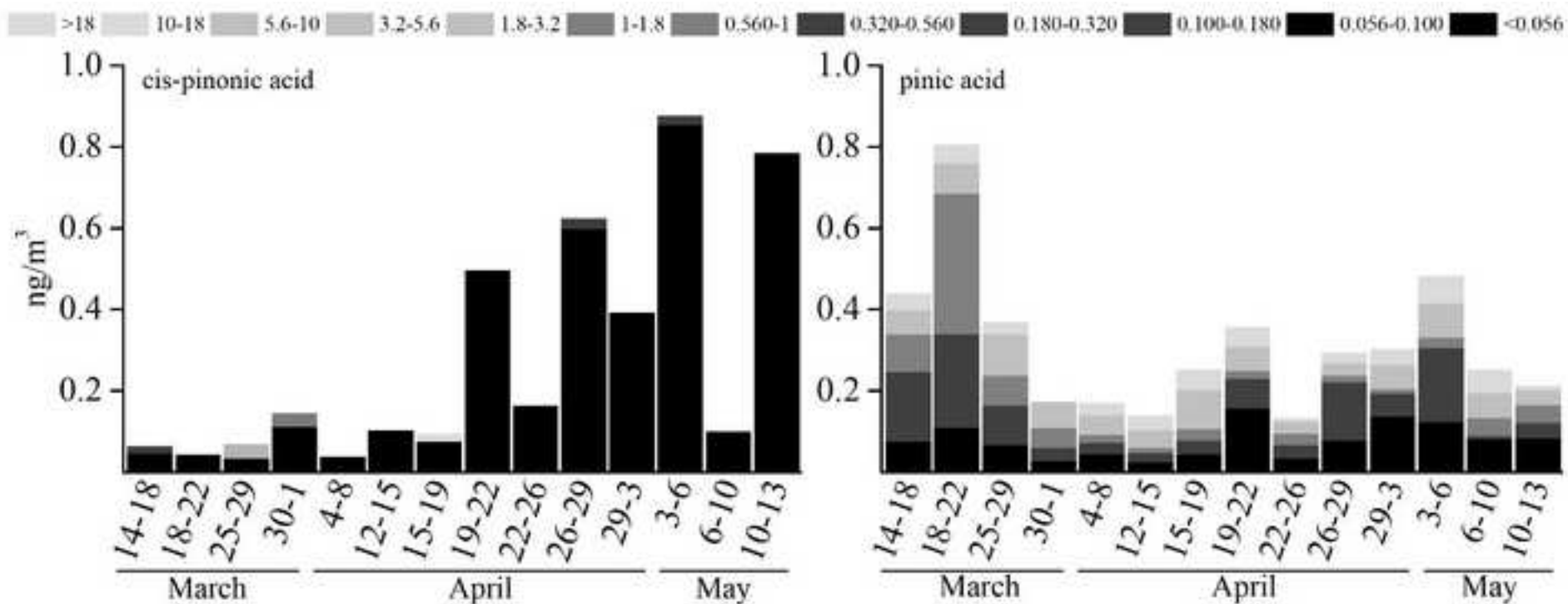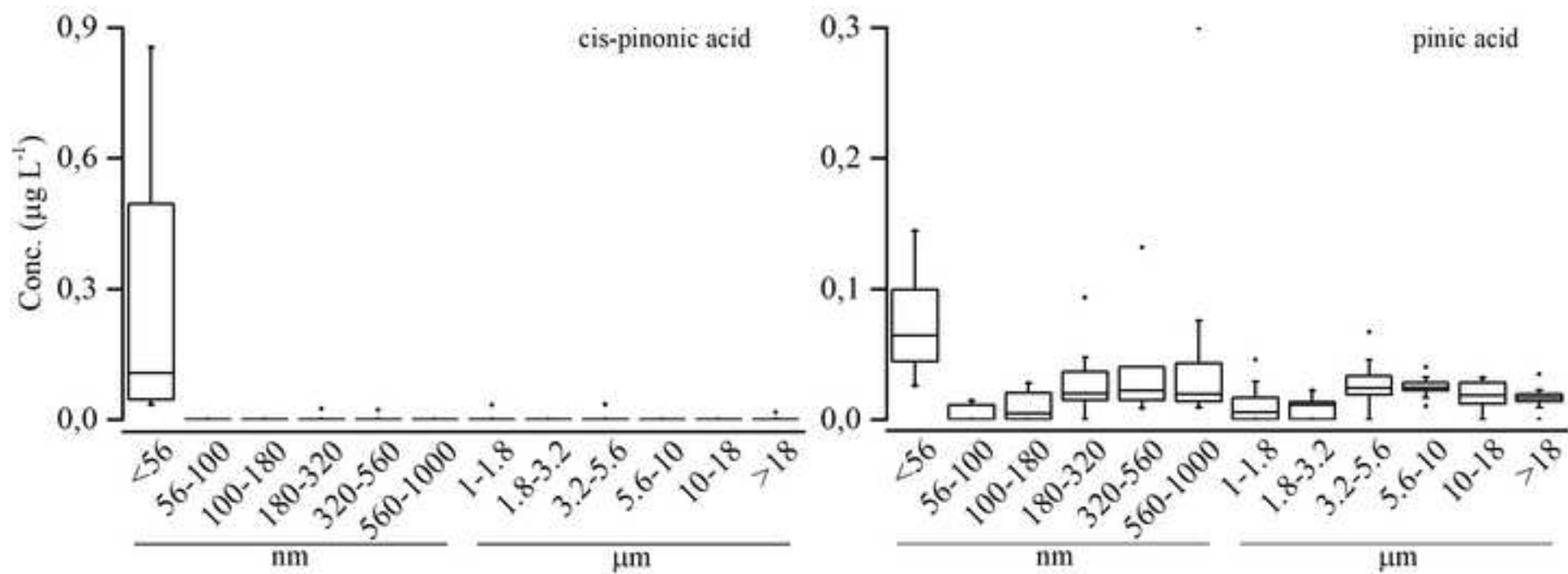**Click here to download high resolution image**

Figure 3
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	0.5 ± n.d.	San Bernadino, Canada, September 1998 (Yu et al., 1999)
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Supplementary Material