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Article

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Abstract

Many atmospheric organic compounds are long-lived enough to be transported from their sources to polar regions and high mountain environments where they can be trapped in ice archives. While inorganic components in ice archives have been studied extensively to identify past climate changes, organic compounds have rarely been used to assess paleo-environmental changes, mainly due to the lack of suitable analytical methods. This study presents a new method of direct injection HPLC-MS analysis, without the need of pre-concentrating the melted ice, for the determination of a series of novel biomarkers in ice-core samples indicative of primary and secondary terrestrial and marine organic aerosol sources. Eliminating a preconcentration step reduces contamination potential and decreases the required sample volume thus allowing a higher time resolution in the archives. The method is characterised by limits of detections (LODs) in the range of 0.01-15 ppb, depending on the analyte, and accuracy evaluated through an interlaboratory comparison. We find that many components in secondary organic aerosols (SOA) are clearly detectable at concentrations comparable to those previously observed in replicate preconcentrated ice samples from the Belukha glacier, Russian Altai Mountains. Some compounds with low recoveries in preconcentration steps are now detectable in samples with this new direct injection method significantly increasing the range of environmental processes and sources that become accessible for paleo-climate studies.

Keywords

Ice core, Biomarker, Organic Aerosol, Liquid Chromatography, Mass Spectrometry, Paleoclimate

1. Introduction

The analysis and quantification of non-anthropogenic marine and terrestrial organic compounds in ice cores is a developing field presenting a new suite of compounds potentially applicable to palaeoenvironmental reconstruction [1]. A small selection of studies obtaining new records of various novel organic compounds in ice has proven the concept; Kawamura et al. [2] detected lipid compounds in snow layers dating back 450 years at Site J, Greenland, using gas chromatography – mass spectrometry (GC-MS), Pokhrel et al. [3] detected oxidation products of isoprene and monoterpenes in ice up to 350 years old in Alaska using GC-MS on rotary evaporation-preconcentrated samples, and Muller-Tautges et al. [4] detected carboxylic acids and inorganic ions between 1942-1993 from Grenzgletscher (Monte Rosa Massif) in the southern Swiss Alps using high performance liquid chromatography-mass spectrometry (HPLC-MS) on stir-bar preconcentrated samples. Following this, King et al. [5] developed a method of HPLC-MS analysis for rotary evaporation-preconcentrated ice samples. We quantified concentrations of a wide range of novel organic compounds in ice core samples which had shown good potential for survival during transport to, and preservation within, ice core records, and relationships to environmental conditions [1]. These included a range of fatty acids, secondary oxidation aerosol compounds, and primary biogenic molecules at both detectable and reproducible concentrations.

Adaptation of methods towards those not requiring preconcentration has been previously successfully applied to levoglucosan, an organic compound produced by combustion of cellulose and used to indicate past biomass burning trends from ice core analysis. In order to both circumnavigate the need for preconcentration and to avoid more time consuming GC-MS methods, Gambaro et al. [6] developed the first method of direct injection HPLC-triple quadrupole mass spectrometry (HPLC/ESI-MS/MS) for quantification of levoglucosan in Antarctic ice samples, where concentrations are expected to be very low. They achieved detection limits as low as 0.003ppb in samples as small as 1mL, reproducible at 20-50%, while lowering analysis time and contamination risk, demonstrating the potential benefits of this process.

In this study we compare our previous method [5] for preconcentrated samples with a similar one for use on non-preconcentrated snow and ice samples, i.e. direct injection HPLC-MS, for an identical compound list (Table 1).

While preconcentration is still needed in many cases due to the very low levels of organic compounds in polar and alpine ice samples (typically parts per trillion (ppt, equivalent to ng/L) –

parts per billion (ppb, equivalent to µg/L)), some samples closer to source location may contain higher compound concentrations detectable without requiring such a step. Alternatively, new instrumentation presents the opportunity to analyse samples at detection levels as low as ppt, thus removing the need for preconcentration. The elimination of a preconcentration step would be beneficial for several reasons; reducing the processing steps of samples reduces the possibility for introduction of contamination, especially in the case of fatty acids where background contamination is generally high compared to SOA compounds [5]. Additionally, for some of the compounds on our target list, preconcentration has been ineffective, due to very low recovery. For example, the rotary evaporation method previously applied in King et al. (2018) showed very low recovery for oxidised biogenic aerosol markers such as MBTCA. Direct injection, if suitable detection limits can be achieved, opens up these additional compounds to ice core analysis, and therefore offers an enhanced suite of compounds for paleo-environmental reconstruction. Finally, the required sample volume for direct injection is also much smaller, in this case approximately 100 µL per sample rather than 10 mL for a sample requiring preconcentration, thus improving the depth and time resolution that can be attained from the ice core. As an example, this will often allow seasonally-resolved samples to be analysed, as opposed to annual or multi-annual records, which will be invaluable to develop an understanding of the processes and sources these novel organic paleo-environmental markers represent. This may also be particularly useful when evolving the method to analyse much older ice than currently tested, where annual ice layers are much thinner, due to ice flow, than those in younger, shallower counterparts. As a long-term perspective, methods requiring low sample volume may be amenable to adaptation for coupling with continuous flow analysis systems (e.g Kaufmann *et al*. 2008). Finally, the use of high-resolution MS without sample preconcentration would allow retrospective non targeted analysis, whereas the sample preconcentration step invariably alters the samples representatively.

Table 1: Target compound list for this study (adapted from King et al. [5]), by compound group and in order of increasing number of carbon atoms.

Compound Source	Neutral Formula	Name
Isoprene-derived SOA	$C_4H_{10}O_4$	Meso-erythritol*
Isoprene-derived SOA	$C_5H_{12}O_4$	Methyl-tetrols
Monoterpene-derived SOA	$C_7H_{12}O_4$	Pimelic acid*
Monoterpene-derived SOA	$C_7H_{10}O_6$	1,2,4-butanetricarboxylic acid (BTCA)*
Monoterpene-derived SOA	$C_8H_{12}O_6$	3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)
Monoterpene-derived SOA	$C_7H_{10}O_4$	Terebic acid
Monoterpene-derived SOA	$C_{10}H_{18}O_3$	Pinolic acid
Monoterpene-derived SOA	$C_{10}H_{16}O_3$	*Cis*-pinonic acid
Monoterpene-derived SOA	$C_{10}H_{14}O_3$	Keto-pinic acid
Sesquiterpene-derived SOA	$C_{14}H_{22}O_4$	β-caryophyllinic acid
Sesquiterpene-derived SOA	$C_{15}H_{24}O_3$	β-caryophyllonic acid
Sesquiterpene-derived SOA	$C_{14}H_{22}O_4$	β-nocaryophyllonic acid
Biogenic SOA	$C_4H_6O_5$	D-malic acid
Primary biogenic	$C_7H_6O_3$	Salicylic acid
Low molecular weight fatty acids (LFA) (<C24); marine / microbial sources	$C_{12}H_{24}O_2$	Lauric acid
	$C_{14}H_{28}O_2$	Myristic acid
	$C_{17}H_{34}O_2$	Heptadecanoic acid
	$C_{18}H_{34}O_2$	Oleic acid
	$C_{19}H_{38}O_2$	Nonadecanoic acid
	$C_{20}H_{32}O_2$	Arachidonic acid
	$C_{22}H_{44}O_2$	Behenic acid
	$C_{23}H_{46}O_2$	Tricosanoic acid
High molecular weight fatty acids (HFA) (>C24); terrestrial biomass	$C_{27}H_{54}O_2$	Heptacosanoic acid
	$C_{28}H_{56}O_2$	Octacosanoic acid
	$C_{30}H_{60}O_2$	Melissic acid

*surrogate standards (analytes chemically similar to those being extracted where actual standard not available)

2. Materials and methods

Sample analysis was carried out by direct injection ultra-high performance liquid chromatography (UHPLC) electrospray ionisation (ESI) high-resolution mass spectrometry (HRMS) with a post-column injection of ammonium hydroxide in methanol.

2.1 Standard solutions and eluents

Bulk standard solutions were prepared in dichloromethane (>99.9%, Optima™, HPLC/MS, Fisher Chemical), and acetonitrile (>99.9%, Optima™ HPLC/MS, Fisher Chemical), and then combined into a diluted standard mixture of all analytes at a concentration of 1 ppm in acetonitrile. Details of the sources and purities of each compound standard can be found in King et al. [5]. Final standards for instrument calibration, quantification of detection limits, and quantification of matrix effects were made at concentrations of 10 ppt, 100 ppt, 1 ppb,10 ppb and 100 ppb by dilutions with water (>99.9%, Optima™ UHPLC/MS, Fisher Chemical).

2.2 Decontamination protocols

All glassware was baked at 450°C for 8 hrs using the method of Müller-Tautges et al. (2014). Glassware was capped with PTFE lined lids. Solvents were also cleaned using ozonation following the method of King et al. [5], which has been shown to reduce background contamination of unsaturated fatty acids.

2.3 Instrumental analysis

Analysis was carried out using an UltiMate3000 UHPLC coupled with a Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap MS at the Department of Chemical Sciences, University of Padua, Italy. We utilise this more sensitive instrument than that used in the methodological development of the previous study. The interlaboratory comparison described in the previous study shows how this instrument lowered detection limits to the range of ppt for many compounds, in comparison to the HPLC-ESI-HRMS (with Accela system HPLC (Thermo Scientific, Bremen, Germany) coupled to an LTQ Velos Orbitrap (Thermo Scientific, Bremen, Germany)) at the University of Cambridge, UK, which did not achieve detection limits below ppb concentrations (Table 2). Given that concentrations of compounds detected in preconcentrated samples in King et al.[5] were in the order of ppb, this more sensitive instrument should allow detection not only of these compounds without preconcentration but may allow detection of previously undetected

compounds. This is due in part to the different detectors in the two instruments, which gives the Q-Exactive a better sensitivity and thus lower detection limits. Similarly, a triple quadrupole mass analyser may provide better sensitivity for SOA compounds while it would not give reliable determination of unsubstituted fatty acids when using HPLC with an ESI source. This is because the fragmentation used in the single and multiple reaction monitoring when using triple quadrupole mass analysers cannot be exploited for the determination of unsubstituted fatty acids which would lose the only functional group that can be easily ionised (the carboxylic group). Further factors giving the Q-Exactive better sensitivity are that the ionic path is much shorter than for the Velos, resulting in less ion scattering, and that the Q-Exactive has an enhanced vaccum, increasing the electronic performance. There are also factors which are unique to every instrument set-up and specific laboratory environment: the contamination introduced into the instrument is dependent on the working environment in which the instrument sits, the previous samples analysed and also the age of the instrument. Beside these, removing a sample pre-concentration procedure may reduce potential contaminations introduced during sample handling. In this study we account for these factors by repeating some optimisation steps applied to the previously used instrument, as discussed further in section 3.1.

The optimised settings of the instrument were those developed by King et al. [5] and were as follows; the LC injected sample volumes of 20 µL and used a Waters XBridge™ C18 (3.5 µm, 3.0x150 mm) column with the mobile phases (A) water with 0.5 mM NH_4OH and (B) methanol with 0.5 mM NH_4OH. The gradient programme was 0–3 min 0% B, 3–4 min linear gradient from 0% to 30% B, 4–9 min 30% B, 9–10 min linear gradient from 30% to 100% B, 10–25 min 100% B, 25–26 min linear gradient from 100% to 0% B, 26–35 min 0% B, with a 250 µL/min flow rate at 20°C. We applied a post-column injection of methanol with 5 mM NH_4OH at a flow rate of 100 µL/min. MS analysis was performed in negative ionisation using the following ESI source parameters: 400°C source temperature, 40 arbitrary units (a.u.) sheath gas flow rate, 20 a.u. auxiliary gas flow rate, 3.5 kV needle voltage, 350°C transfer capillary temperature, S-Lens RF Level 50%. MS spectra were collected in full scan, with a resolution of 70 000 at *m*/*z* 400, in the mass range *m*/*z* 80–600 and in MS/MS for all target compounds with a collision-induced dissociation (CID) energy of 30 (normalized collision energy). Instrumental calibration was carried out routinely to within an accuracy of ± 2 ppm, using Pierce LTQ Velos ESI Positive Ion Calibration Solution and a Pierce ESI Negative Ion Calibration Solution (Thermo Scientific, Bremen, Germany).

Calibration for quantification of target analytes was carried out at the start of each sample series, for which analysis took approximately 60 continuous hours, using standard solutions of 10 ppt,100 ppt,1 ppb,10 ppb and 100 ppb. Deuterated internal standards d3-malic acid, d10-pimelic acid and d31-palmitic acid at a concentration of 10 ppb were used as internal standards to adjust concentrations accounting for methodological and instrumental variability. Quality check standards solutions at a concentration of 10 ppb have also been analysed every 10 samples to ensure no changes in detection sensitivity throughout the sequence of analysis.

2.4 Sample preparation

Ice samples analysed were from the Belukha glacier ice core, Russian Altai mountains, for which details on drilling, transportation and cutting can be found in Olivier et al. [8]. A total of 18 samples were tested representing ice from a range of ice-core ages, accounting for differences in ice chemistry and physical ice properties which may affect analysis. These were 12 samples from 1866-1869, and 6 samples from 1821-1823.

Sample sections were cut to avoid the outer-most ice of the core, which has been exposed to potential contamination. Additionally, once cut, samples for the analysis of organic compounds were scraped with a metal scalpel to remove cut surfaces and placed directly in pre-cleaned amber glass vials with PTFE lined caps. Samples were stored at -25^{o}C before melting in sealed vials inside a class 100 clean room, at approximately 16^{o}C. Each sample represented 10 cm ice core resolution, equivalent to sub-annual resolution. 1 mL of the well-mixed sample was transferred to a glass LC-MS vial and spiked with 10 ppb deuterated standards for immediate analysis.

3. Results and discussion

3.1 Methodological optimisation

While the HPLC-MS method was optimised in our previous study ([5]), some parameters were re-tested to ensure the methodology was appropriate for the new instrument (i.e. the Q Exactive™ Orbitrap MS). This particularly included steps in reducing background contamination, which can be different for individual compounds depending on the instrument and lab environment being used.

The repeated tests were: testing of non-ozonated and ozonated solvents, testing of the inclusion of a post-column injection, and the application of MS-MS analysis to ensure correct identification of peaks in the mass spectra.

On average, the application of a post column injection of 5 mM NH_4OH in methanol increased peak areas by 1.5 to 2 times compared to peak areas without a post-column injection. The use of ozonated solvents was again shown to be effective at reducing background contamination of unsaturated fatty acids which break down during ozonolysis; in non-ozonated solvents these compounds were present at contamination levels of ≥10 ppb, while ozonated solvents allowed detection at as low as 10 ppt.

Instrumental analysis showed that the retention time of some compounds shifted when comparing preconcentration/direct injection analysis. This is because the solvent of the final sample (and standard solutions) is different in the two cases; in the preconcentrated samples the solvent is methanol, used to re-dissolve the compounds from the rotary evaporation vial. In direct injection, the solvent is the snow melt water of the sample or LC-MS water for the standard solutions. The retention times for the direct injection, aqueous sample are presented in Table 2. In general, the retention times of SOA compounds are slightly shorter while retention times of fatty acids are longer for samples and standard solutions in water compared with methanol [5].

3.2 Methodological validation

Instrumental LODs were evaluated on standard solutions prepared in water to match the matrix of the ice samples. Calculation used the Hubaux-Vos method, following IUPAC recommendations [9,10]. Limits of quantifications (LOQs) are 10/3*LODs. Sensitivity (slope of the calibration line) and linearity range were tested using both the r-Pearson correlation test and the F-test to compare linear and quadratic fits. Results showed a good linearity in the tested range (10 ppt-100 ppb) for all compounds. Method/instrumental repeatability was evaluated in real ice core samples. Validation parameters are reported in Table 2.

Matrix effects of direct-injection samples were tested by comparing the linear calibration lines of two different sets of prepared standards, each analysed in triplicate; one set of 1 ppb, 10 ppb, and 100 ppb concentrations diluted with water (external calibration), and another of the same concentrations diluted with ice-sample melt made by pooling together aliquots of the different ice samples analysed in this study (internal calibration). Comparison of the slopes of the lines, using a t-test, was used to evaluate the difference in values quantified between the two standard types.

This approach was used instead of the post-column infusion and post-extraction addition protocols [11] due to unavailability of blank samples (i.e. melted ice samples free from target analytes). Results show (Table 2) the presence of a small but significant matrix effect for most of the analytes. Analytes with lower background contaminations are generally also less affected by matrix effects while compounds with higher background contaminations are more affected by matrix effects (e.g. fatty acids). Isotopically labelled (deuterated) standards do not compensate for matrix effects, probably due to slight differences in lipophilicity and ion suppression effects, as observed in previous studies [12,13].

Table 2: Parameters of methodological validation of the direct injection HPLC-MS analysis, which are presented in order of increasing LOD. Also presented are LOQ, retention time, repeatability (presented as residual standard deviation from three repeat injections of calibration samples each of 10 ppt, 100 ppt, 1 ppb, 10 ppb and 100 ppb), intralaboratory comparison (presented as R^2 values of a linear trend line of preconcentrated-direct injection samples, see also Figure 1) and matrix effects (presented as the change in calibration slope between the standards diluted in ice sample melt compared to those diluted in water). NA=not applicable. Calibration curves and respective plots showing instrumental repeatability for example compounds are shown in Figure S1 of the supplementary information.

Compound	LOD (ppb)	LOQ (ppb)	LOD of previous study (ppb)	Retention time (min)	Instrumental Repeatability (%RSD)	Intralaboratory comparison (R^2)	Matrix effect (%±%RSD)
BTCA*	0.01	0.03	3.09	1.70	5	NA	13.5±9.1[a]
MBTCA**	0.02	0.06	2.68	1.70	5	NA	5.7±9.2[a]
Keto-pinic acid	0.02	0.07	2.62	7.85	7	0.68	4.9±4.8[a]
β-caryophyllinic acid	0.02	0.08	2.91	7.79	6	NA	5.6±4.3[a]
D-malic acid	0.04	0.13	2.61	1.76	4	0.75	3.9±6.8[a]
β-caryophyllonic acid	0.10	0.32	2.73	13.12	6	NA	-2.0±3.5[a]
Methyl-tetrols	0.13	0.43	4.57	3.57	4	0.92	11.4±2.3[b]
Terebic acid	0.14	0.46	5.65	3.22	3	0.64	-9.4±5.5[a]
Pimelic acid	0.22	0.74	2.32	1.79	5	0.50	-4.2±8.4[a]
***Cis*-pinonic acid**	0.35	1.16	8.94	7.61	6	NA	4.3±6.9[a]
Arachidonic acid	0.44	1.46	4.69	14.09	9	NA	1.1±3.1[b]
Pinolic acid	0.59	1.96	8.38	7.40	12	NA	-5.5±8.0[a]
Meso-erythritol	2.57	8.62	5.94	2.93	17	NA	9.9±3.8[b]
β-nocaryophyllonic acid	3.02	10.06	2.52	12.88	5	NA	6.8±8.6[a]
Tricosanoic acid	3.82	12.74	4.73	19.27	6	NA	16.8±5.3[b]
Salicylic acid	5.44	18.15	10.23	7.61	12	NA	7.5±6.0[a]

Behenic acid	5.68	18.93	5.93	18.19	5	NA	20.6±2.9[b]
Melissic acid	6.08	20.28	17.03	28.22	10	NA	18±53[b]
Nonadecanoic acid	6.32	21.07	2.00	15.91	12	NA	30±23[b]
Heptacosanoic acid	6.97	23.19	12.21	25.29	7	NA	3.0±3.4[b]
Octacosanoic acid	9.99	33.28	11.73	27.46	8	NA	11.7±6.5[b]
Lauric acid	10.91	36.35	4.47	13.56	5	NA	15.6±6.6[b]
Heptadecanoic acid	12.83	42.76	6.27	14.92	5	NA	10±27[b]
Myristic acid	15.74	52.46	19.14	13.94	6	NA	8.0±7.6[b]
Oleic acid	15.75	52.49	20.13	14.60	3	NA	-9±15[b]

[a] Evaluated in the concentration range 0-10 ppb; [b] Evaluated in the concentration range 0-100 ppb. * Butane-1,2,3,4-tetracarboxylic acid. ** 3-methyl-1,2,3-butanetricarboxylic acid.

3.3. Method comparison

A method comparison was done to assess the accuracy of the direct injection UHPLC-ESI-HRMS method, comparing ice samples from the Belukha glacier ice core measured both with the method developed in this study and with the method developed by King et al. [5]. The method of King et al. [5] used rotary-evaporation to preconcentrate the samples before analysis with HPLC-ESI-HRMS using an Accela system HPLC (Thermo Scientific, Bremen, Germany) coupled to an LTQ Velos Orbitrap (Thermo Scientific, Bremen, Germany) [5]. An inter-laboratory comparison has already been carried in King et al. [5] showing that sample concentrations measured on the previously used instrument are reliably reproduced on the instrument used in this study, and therefore our sample concentrations of the preconcentrated method are accurate and may be reliably compared to the direct injection samples.

Compounds detected in the preconcentrated Belukha samples were as follows; D-malic acid, terebic acid, methyl-tetrols, pimelic acid, keto-pinic acid, cis-pinonic acid, heptacosanoic acid, octacosanoic acid, and melissic acid. MBTCA was detected in a very few samples above detection limits. In the direct injection method compounds detected were MBTCA, D-malic acid, terebic acid, methyl-tetrols, pimelic acid and keto-pinic acid. BTCA and cis-pinonic acid were detected in some of the direct injection samples, but in others were below LODs. In comparison, the direct injection promoted BTCA and MBTCA detection, as recovery percentage for both compounds in preconcentrated samples was only 3%, the lowest value observed for all compounds [5], which results in values falling below LOD in these samples. Avoiding this drawback, the direct injection method successfully detects MBTCA in all samples well above LODs.

All of the fatty acids detected with the pre-concentration technique were below detection limits in the direct injection samples; this is because background contamination levels were high in these experiments, and consequently so are LODs.

The results of the comparison between the preconcentrated and direct injection samples are shown in Figure 1, as scatterplots representing the reproducibility of final concentration values in the samples. The scatterplots show good linearity for all compounds, indicating that trends in the sample timeseries are reliably reproduced. For some compounds, the linear trend lines deviate from the 1:1 ratio line, for example terebic acid. This difference is not accounted for by matrix effects evaluated using a test ice-sample melt (see section 3.2 for details). However, each

individual ice sample would be characterized by a different matrix composition, which may affect quantification differently from one sample to another. In each case, the deviation from the 1:1 ratio line suggests either a lower-than-expected sample concentration in the direct injection samples, or higher-than-expected concentration in the preconcentrated samples. This may be because preconcentrated samples are finally analysed in methanol, used to re-dissolve the samples from the dried vial following rotary evaporation, whereas direct injection samples are measured in the original snow melt. It would be expected that methanol is an overall cleaner sample as the lower solubility discourages the presence of inorganics in the sample which may otherwise interfere with the ionisation of the analytes in the ESI source. Ideally, matrix effects could be accounted for by using an internal calibration. However, this is not a viable alternative for this application due to limited amount of sample available for the analysis.

The observed offset, where large enough to be significant such as for terebic acid, may be quantified and accounted for in further analysis.

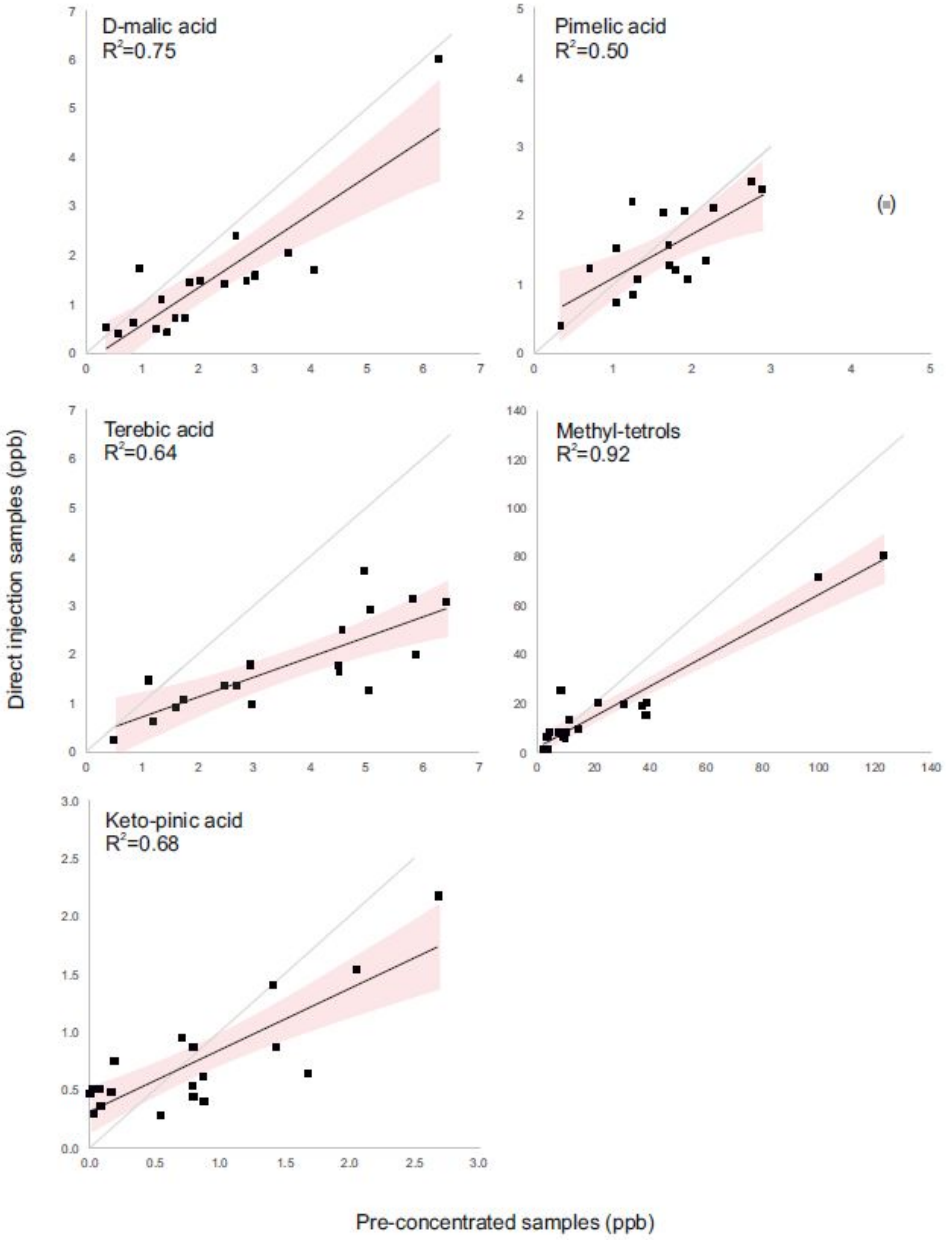

Figure 1: Scatterplots representing comparisons between final sample concentrations of each of direct injection and preconcentration methods of analysis of replicate environmental samples. Linear trendlines and associated R^2 values are presented to assess reproducibility, and error bands at 95% confidence intervals shown in pink. The bracketed outlying point in the pimelic acid plot is shown but not included in the trend line and R^2 value. Compounds shown are those with a complete dataset (i.e. no sample concentrations below detection limits).

Because of the poor detection of MBTCA in the preconcentrated samples, we cannot assess the reproducibility of this compound compared to direct injection. We instead compare to previously reported ions in the ice core [14] to see if overall trends detected in the sample series appear reasonable. Figure 2 compares MBTCA to sulfate. Sulfate was chosen for comparison as it showed the most significant correlation to MBTCA of all other measured ions in the core (R^2=0.55). We display only the corresponding sample numbers since environmental interpretation is outside the scope of this study. The record shows that both compounds display similar trends over time, with peaks coinciding with mid-year summertime. Therefore MBTCA measured by direct injection produces results that are reasonable with previous findings. Indeed, this is also the case for all other new organic compounds detected i.e. trends match those of previously detected ions. However we save presentation of thee results for future work alongside environmental interpretation.

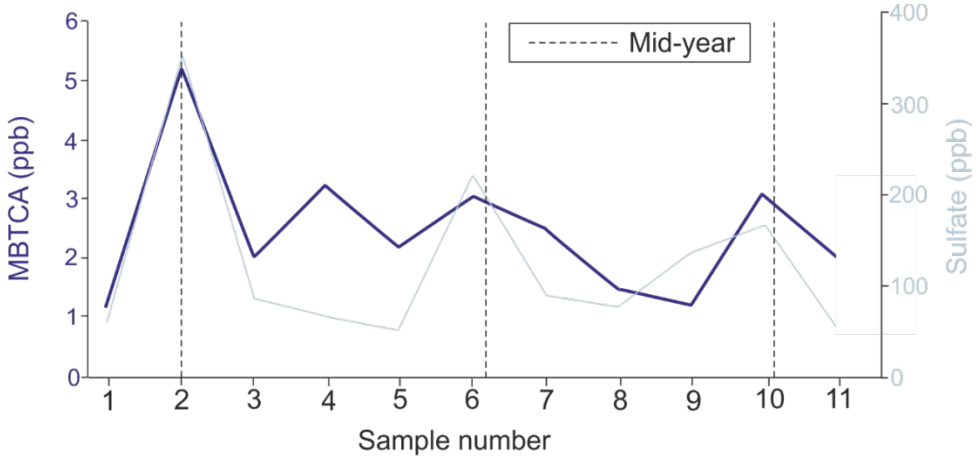

Figure 2: MBTCA and sulfate concentrations measured in a time series of ice core samples.

4. Conclusions

A method for analysing a series of organic compounds in ice core samples by direct injection UHPLC-ESI/HRMS is presented. This method is beneficial in reducing the required sample volume and the potential for contamination generated by sample preconcentration steps. The method provides LODs of 0.01-3.02 ppb for SOA compounds, and 0.44-15.75 ppb for fatty acids, with average instrumental repeatability of 7%. Small, but significant, matrix effects (~10% on average) were determined.

This direct injection analytical method is particularly suitable for SOA compounds which showed low recoveries in preconcentrated samples, e.g. MBTCA, and which are significantly above detection limits only with direct injection analysis. Other SOA compounds, detected more clearly than MBTCA in preconcentrated samples, were also detected with similar sensitivity in direct injection samples. Many of the studied tracers showed good reproducibility in final sample concentrations in both analytical methods, while others showed a lower-than-expected concentration in direct injection samples compared with pre-concentrated samples. This can be accounted for by differences in sample matrices or ionisation efficiency in samples analysed with the two techniques, and can be adjusted for in final sample concentrations.

Direct injection is less suitable for fatty acid compounds; their high background contamination results in high detection limits, and thus these compounds are more suited to analyses after a preconcentration. Alternatively, detection limits for these compounds require new, tailored, cleaning protocols to reduce background contaminations in the solvents and in the instrument itself before direct injection analysis.

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Supporting Information: Figure showing calibration curves and respective error of instrumental repeatability plots for example compounds representing a range of compounds classes and percentage relative standard deviation values.

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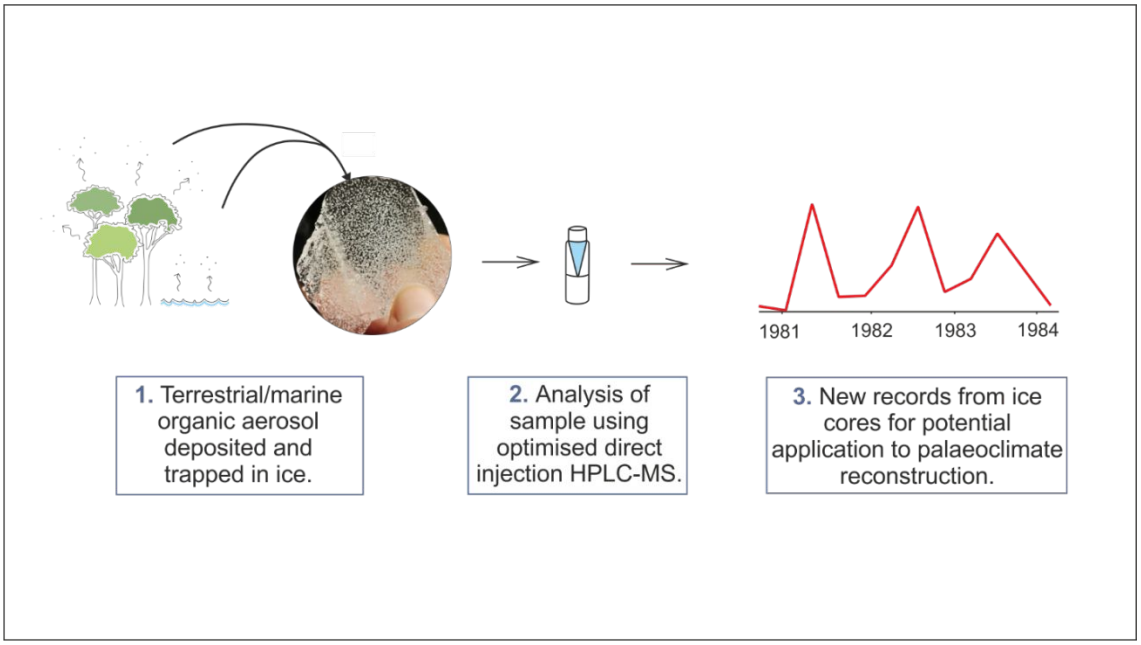
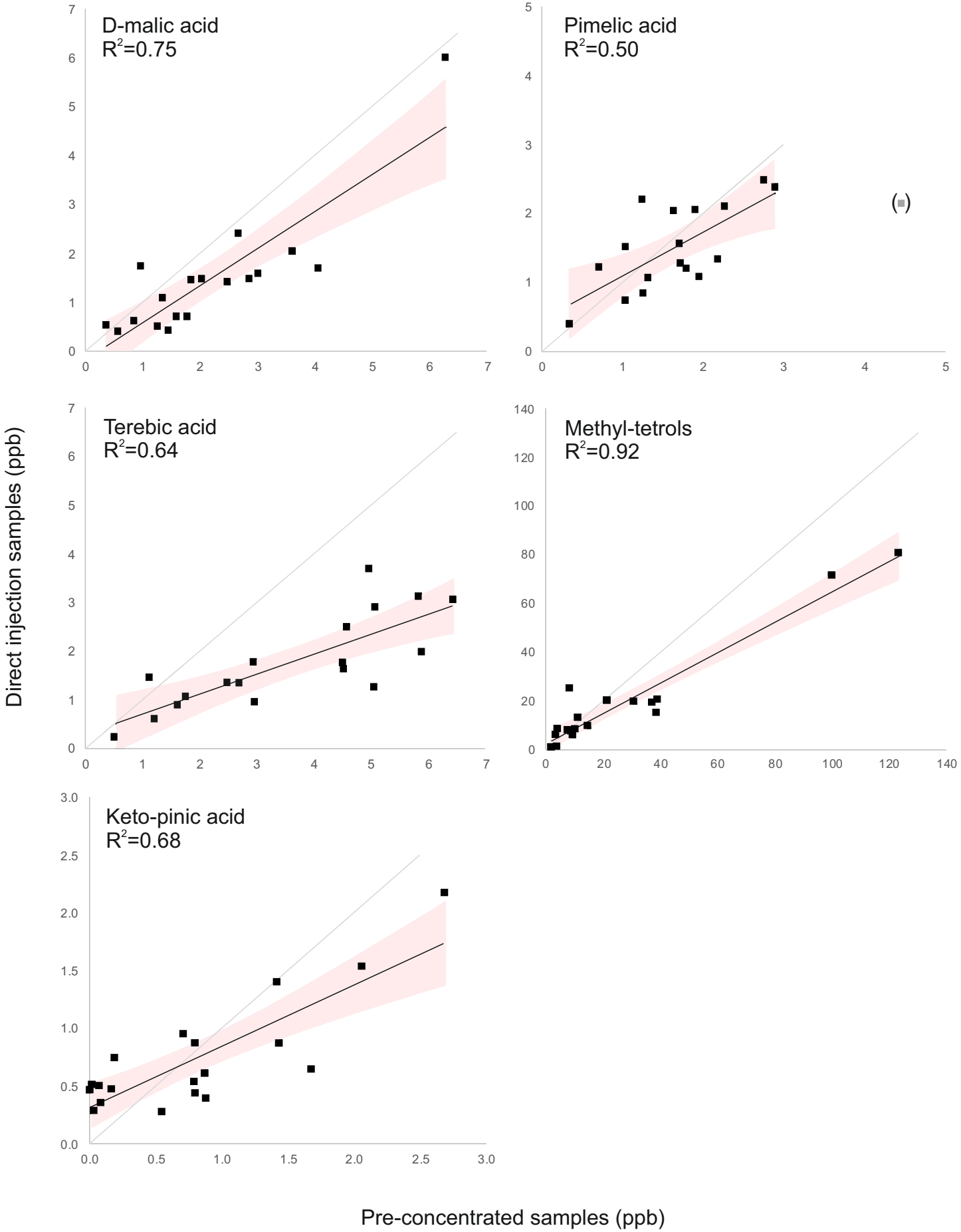
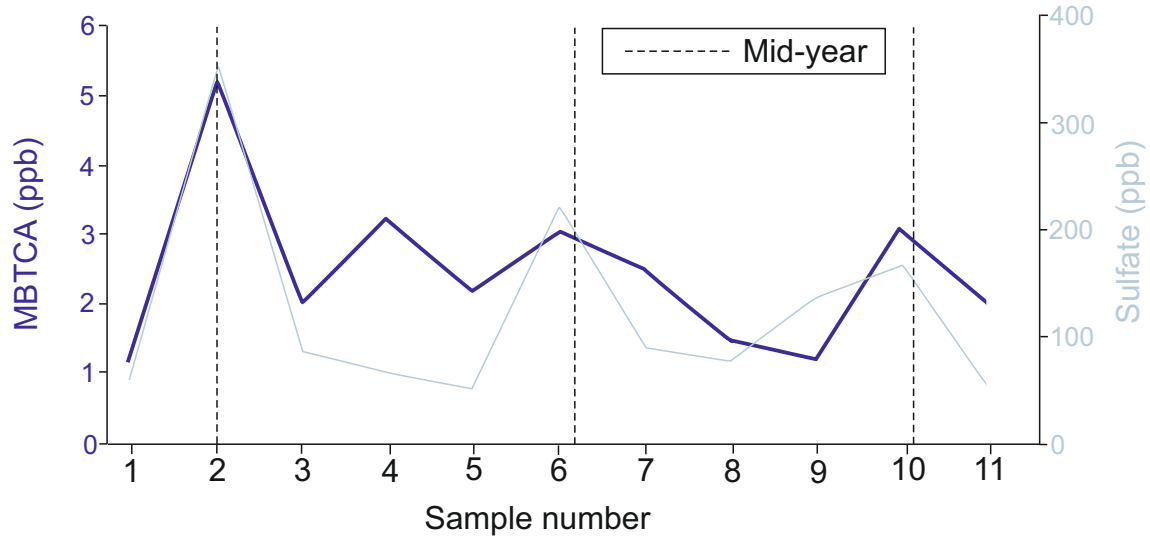
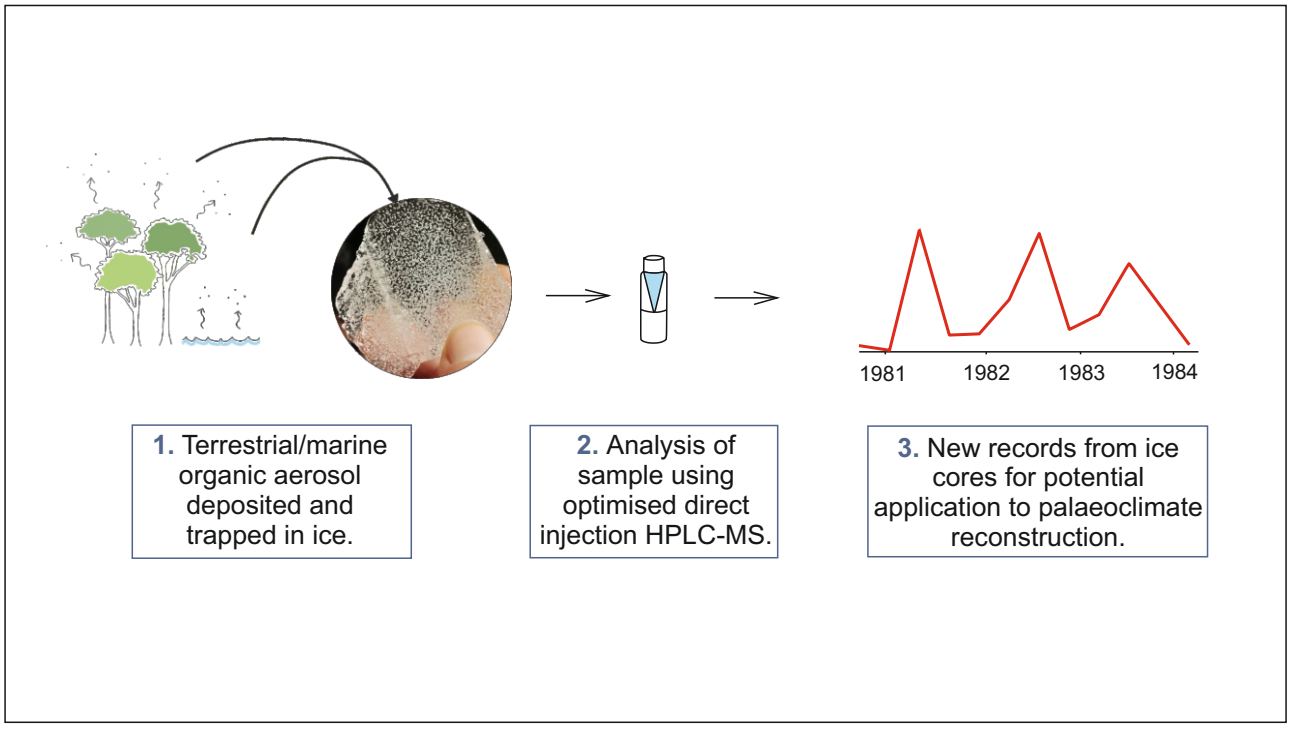
For TOC only


1981
1982
1983
1984
1. Terrestrial/marine organic aerosol deposited and trapped in ice.
2. Analysis of sample using optimised direct injection HPLC-MS.
3. New records from ice cores for potential application to palaeoclimate reconstruction.


D-malic acid
R²=0.75
Pimelic acid
R²=0.50
Terebic acid
R²=0.64
Methyl-tetrols
R²=0.92
Keto-pinic acid
R²=0.68
Direct injection samples (ppb)
Pre-concentrated samples (ppb)


Mid-year
MBTCA (ppb)
Sulfate (ppb)
Sample number
0
1
2
3
4
5
6
0
100
200
300
400
1
2
3
4
5
6
7
8
9
10
11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