Article:

Klein, Felix, Platt, Stephen M., Farren, Naomi J. orcid.org/0000-0002-5668-1648 et al. (14 more authors) (2016) Characterization of Gas-Phase Organics Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry:Cooking Emissions. Environmental Science and Technology. pp. 1243-1250. ISSN: 1520-5851

https://doi.org/10.1021/acs.est.5b04618

Characterization of gas-phase organics using proton transfer reaction time-of-flight mass spectrometry: cooking emissions

Felix Klein,[†] Stephen M. Platt,[†,§] Naomi J. Farren,[‡] Anais Detournay,[¶] Emily A. Bruns,[†] Carlo Bozzetti,[†] Kaspar R. Daellenbach,[†] Dogushan Kilic,[†] Nivedita K. Kumar,[†] Simone M. Pieber,[†] Jay G. Slowik,[†] Brice Temime-Roussel,[¶] Nicolas Marchand,[¶] Jacqueline F. Hamilton,[‡] Urs Baltensperger,[†] André S.H. Prévôt,[†] and Imad El Haddad[*,†]

†*Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, 5232, Switzerland*
‡*Wolfson Atmospheric Chemistry Laboratories, University of York, York, YO10 5DD, UK*
¶*Aix Marseille Université, CNRS, LCE FRE 3416, 13331 Marseille, France*
§*Now at: Department of Atmosphere and Climate, Norwegian Institute for Air Research, Kjeller, 100 2027, Norway*

E-mail: imad.el-haddad@psi.ch
Phone: +41 56 310 2785

Abstract

Cooking processes produce gaseous and particle emissions that are potentially deleterious to human health. Using a highly controlled experimental set-up involving a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS), we investigate the emission factors and the detailed chemical composition of gas phase emissions from a broad variety of cooking styles and techniques. A total of 95 experiments were conducted to characterize non-methane organic gas (NMOG) emissions from boiling, charbroiling, shallow frying and deep frying of various vegetables and meats, as well as emissions from vegetable oils heated to different temperatures. Emissions from boiling vegetables are dominated by methanol. Significant amounts of dimethyl sulfide are emitted from cruciferous vegetables. Emissions from shallow frying, deep frying and charbroiling are dominated by aldehydes of differing relative composition depending on the oil used. We show that the emission factors of some aldehydes are particularly large which may result in considerable negative impacts on human health in indoor environments. The suitability of some of the aldehydes as tracers for the identification of cooking emissions in ambient air is discussed.

Introduction

Cooking has recently been identified as a major pollution source in outdoor urban environments,[1–4] and in the absence of open solid fuel burning is generally recognized as the main source of organic aerosol in indoor environments.[5] Cooking fumes negatively impact human health e.g. by increasing the risk of cancer for professional chefs.[6] A recent study conducted on non-smoking Chinese women shows that cooking increases the risk of lung cancer.[7] Despite numerous aerosol mass spectrometry studies reporting the amount and chemical composition of primary organic aerosol emitted during cooking activities[8–12] only few studies have investigated the associated non-methane organic gases (NMOG). Schauer et al.[13] reported volatile organic compound (VOC) emissions from western style cooking (e.g. meat charbroiling) and Huang et al.[6] from cooking Asian style dishes. Other studies measured the emissions at the extraction stack of restaurants in Mexico,[14] Portugal[15] or Hong Kong.[16] While stack-based studies provide valuable data for the characterization of the bulk cooking emissions at large, such a setting is not well suited for the comparison of the emissions from different cooking processes. Additionally these studies are often unable to distinguish between emissions from the food itself and emissions from the heating source.[17] While some of the identified particle and gas phase products have been used as markers for the quantification of cooking emissions in ambient air, there are large uncertainties related to the relative contribution of these markers and their reactivity.[18,19] A part of these uncertainties may be related to the variability in the emission composition depending on the cooking process applied and the type of food cooked. This illustrates the need for a systematic characterization of the emission from different cooking processes. This study is the first detailed comparison of NMOG emission factors and chemical composition of a broad variety of cooking techniques including boiling, charbroiling, shallow frying and deep frying of different types of food (vegetables and meats) under different cooking conditions using the highly sensitive proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) alongside a comprehensive two-dimenional gas chromatograph with ToF-MS (GC×GC-ToF-MS) for structural confirmation.

Materials and Methods

Experimental set-up

Laboratory measurements were conducted at the Paul Scherrer Institute, Villigen, Switzerland. The food was cooked in a pan on an electric heating plate situated in a 60 L metal housing. Approximately 2 $\mathrm{L\,min^{-1}}$ out of the total flow (14 $\mathrm{L\,min^{-1}}$) going through the housing was diluted with zero air (737-250 series, AADCO Instruments, Inc., USA) through two sequential temperature controlled ejector diluters (Dekati Ltd., Kangasala, Finland), achieving a final dilution ratio of approximately 1:100. The metal housing was designed to provide a fast response time i.e. equilibrium was reached rapidly (Fig. S1) with residence times of the gases in both the metal containment and the sampling inlet of $<$120s and $<$10s, respectively. Gas phase NMOG emissions were measured with a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS). Methane, which is not emitted by cooking processes, was measured using cavity ring-down spectroscopy (G2401, Picarro, Inc.), before and after dilution to determine the exact dilution ratio. In total, 95 experiments were conducted including heating of vegetable oils, boiling of vegetables, charbroiling of meat, shallow frying of meat or vegetables and deep frying of fish and potato. A list of all experiments and experimental conditions can be found in the supplementary information (Tab. S1 and S2). All experiments were performed under controlled conditions using cooking times and temperatures as reported in cook books and the food was added to the already hot oils. The parameters explored include different foods, cooking methods, temperatures and vegetable oils used for frying.

PTR-ToF-MS

A PTR-TOF-8000 (Ionicon Analytik Ges.m.b.H., Innsbruck, Austria) operating in H_3O^+ mode was used. In this mode, the PTR-ToF-MS measures NMOG with a proton affinity higher than that of water. The sample is introduced into a drift tube and then protonated with H_3O^+ ions produced from water vapour in a hallow cathode ion source. The protonated NMOG are detected using a time-of-flight mass spectrometer (Tofwerk AG, Thun, Switzerland). A detailed description of the instrument can be found in Graus et al.[20] and Jordan et al.[21] For the 2012 experiments, the PTR-ToF-MS operated with a drift voltage of 480 V, a chamber temperature of 80 °C and a drift pressure of 2.2 mbar resulting in a reduced electric field (E/N) of about 120 td. In 2014 and 2015, the drift voltage was 545 V, the chamber temperature 60 °C and the drift pressure 2.2 mbar also resulting in an E/N of 120 td. The time resolution was 2 min in 2012 and 10 s in 2014 and 2015. The extraction voltage (Udx) was 35 V for all campaigns. The mass resolution, as well as the mass accuracy and the relative transmission efficiency, were routinely verified using a TO-14A aromatics gas standard mixture (100 ppb_V each in nitrogen) in 2012 and using a 12 compound gas standard including aldehydes, ketones and aromatics from m/z 45 to m/z 181 (100 ppb_V each in nitrogen) in 2014 and 2015. Data was analyzed using the Tofware post-processing software (version 2.4.2, TOFWERK AG, Thun, Switzerland; PTR module as distributed by Ionicon Analytik GmbH, Innsbruck, Austria), running in the Igor Pro 6.3 environment (Wavemetrics Inc., Lake Oswego, OR, USA).

Even though protonation with H_3O^+ is considered a soft ionization technique, fragmentation can still occur for many compounds present in cooking emissions (e.g., aldehydes, alcohols). Although fragmentation patterns have been reported for some of the detected compounds, these patterns are dependent on the specific conditions in the PTR-ToF-MS drift tube.[22–24] Therefore fragmentation patterns for the most abundant compounds were determined by headspace measurements of the pure standards with the PTR-ToF-MS, under the conditions described above. Due to the similar E/N during both measurement periods a similar fragmentation pattern is expected. All frying data has been corrected for fragmentation, as shown in the in the supplementary information (Tab. S3). Examples of corrected gas-phase mass spectra are presented in Fig. 1 for the different oils used. For the correction, the calculated values (see fragmentation table) were subtracted from the fragment ions and added to the parent ions. Only negligible amounts of fragments are left in the spectra after correcting the aldehydes for fragmentation, thus further fragmentation corrections (e.g. for alcohols) would only slightly change the emission factors and were not performed. The mixing ratios in ppb_V are calculated as described elsewhere[25] using the ratio between the signal of the individual ions (C^+) and the signal of the reagent ion (H_3O^+) taking into account the drift voltage (U_{drift}), drift temperature (T_{act}) and the drift pressure (p_{act},) as well as the reaction rate of the ion with the H_3O^+ ion (k) and the transmission of the compound (TR_{C+}) relative to the transmission of the reagent ion ($TR_{H_3O^+}$) (Equation 1).

$$C_{ppb_V} = \frac{C^+}{H_3O^+} * \frac{U_{drift}[V]\,T_{act}^2[K]}{k\left[\frac{cm^3}{s}\right]\,p_{act}^2[mbar]} * \frac{TR_{H_3O^+}}{TR_{C^+}} \tag{1}$$

Literature k values were applied where available.[26] Otherwise a reaction rate of $k = 3 \times 10^{-9}\ cm^3 s^{-1}$ was assumed for carbonyl compounds and a reaction rate of $k = 2 \times 10^{-9}\ cm^3 s^{-1}$ for all other compounds (Tab. S4). Water clusters were always less than 5% of the H_3O^+ ion and therefore not considered for the calculations. Mixing ratios were converted to concentrations by multiplying the mixing ratio of each ion by the corresponding molar mass and dividing by the molar volume under standard conditions.

Emission factor calculation

Before calculating emission factors (EF) the individual background (measured before putting the oils or foods) of every experiment was subtracted. The emissions were averaged over the duration of the experiment omitting times during which the metal container was opened for cooking operations. Emission factors were calculated by multiplying the average emissions (C) by the cooking time (t), the flow from the metal container (F), the dilution ratio (DR) and dividing by the amount of food used (M_{Food}) (Equation 2).

$$EF\left[\frac{\mu g}{kg}\right] = \frac{C\left[\frac{\mu g}{m^3}\right] * DR * t[min] * F\left[\frac{m^3}{min}\right]}{M_{Food}[kg]} \tag{2}$$

Enhancement factors

For the shallow frying and deep frying experiments, enhancement factors (EHFs) were calculated to determine the enhancement of emissions due to the food being cooked above the emissions of the oil heating alone. An EHF is calculated from the ratio of the average emission factor of the compound (X) to the average emission factor of a compound emitted only from the oil (Y) normalized to the same ratio measured during oil heating experiments. (Equation 3)

$$EHF_x = \frac{X_{fry}}{Y_{fry}} * \frac{Y_{oil}}{X_{oil}} \tag{3}$$

An EHF close to 1 means that almost all of the measured compound comes from the oil. Increasing EHF values correspond to a lower influence of the oil. Acrolein, which is formed from the dehydration of glycerol emitted during the breakdown of fatty acids,[27] is emitted almost exclusively from oil and was thus used as reference (Y).

GC×GC-ToF-MS

Additional measurements of vegetable oil were performed using a two dimensional gas chromatograph coupled to a time-of-flight mass spectrometer (GC×GC-ToF-MS) at the University of York. Cooking oils (olive, sunflower and canola) were individually placed in a 49 cm^3 stainless steel reactor with a stirrer, enclosed in a heater unit to simulate cooking. The oils were heated to 180 °C and the NMOG emissions were sampled onto thermal desorption tubes (Model 013010, Gerstel GmbH co.) packed with Tenax (0.5 g) for one minute using a flow rate of 40 $mL\,min^{-1}$ of synthetic air. The thermal desorption tubes were analyzed immediately using a Gerstel thermal desorption unit coupled to a GC×GC-ToF-MS system, incorporating an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) and a Pegasus III ToF-MS (LECO, St. Joseph, MI, USA). The primary column was a non-polar BPX5 column (30 m × 320 μm internal diameter × 0.25 μm film thickness) and the secondary column was a mid-polarity BPX50 column (4 m × 180 μm internal diameter × 0.20 μm film thickness). The carrier gas used was helium with a flow rate of 1 $mL\,min^{-1}$. The spectra were collected in the m/z range 45-500 at a rate of 200 Hz. The data were analysed using LECO ChromaTOF software. The compounds were identified using a combination of retention indices and reference to the NIST MS library. All NMOG emissions reported herein were measured by the PTR-ToF-MS (GCxGC-ToF-MS was used only for compound identification).

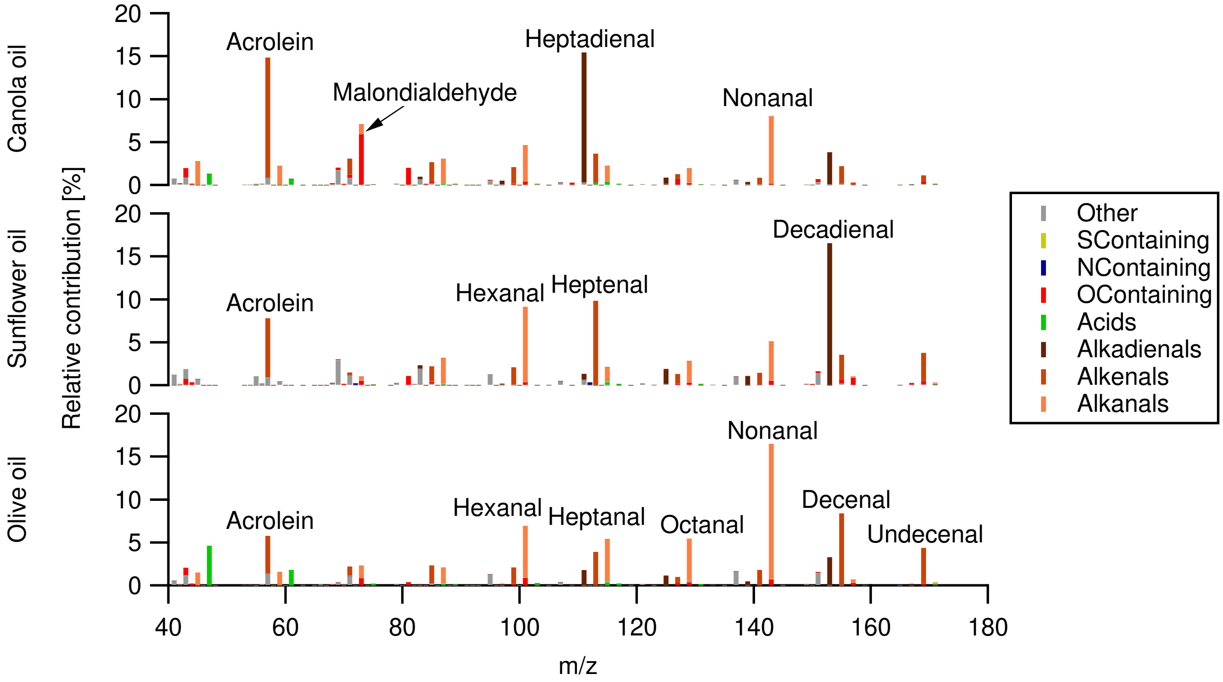

Figure 1: Relative contribution of different compounds to total NMOG emissions from canola, sunflower and olive oil at high temperatures (180 − 200 °C) as measured with the PTR-ToF-MS.

Results and discussion

Emissions from heated vegetable oils

Figure 1 shows the emissions from heated vegetable oils (canola, sunflower and olive oil). The compounds are classified into eight families: alkanals, alkenals, alkadienals, carboxylic acids, O-containing, N-containing, S-containing and other. The "other" family comprises everything not attributable to the other families and hydrocarbon fragments not attributable to their parent compound due to unknown fragmentation patterns. The O-, N- and S-containing denote compounds having an ambiguous structure but clearly containing oxygen, nitrogen or sulphur respectively, based on their accurate mass measurements. For the cooking processes alkanals, alkenals and alkedienals are included in the carbonyl families. The attribution of the individual ions to the families was achieved in a similar way to Kilic et al.,[28] by comparing with literature and the GC×GC-ToF-MS measurements, as shown in the supplementary information (Tab. S4). A list of all emission factors shown is included in the supplementary information (Tab. S5 and S6).

While saturated and unsaturated carbonyls dominate the NMOG emissions, unambiguous distinction between aldehydes and ketones is not possible with the PTR-ToF-MS data alone. The dominance of aldehydes in our study is confirmed using GC×GC-ToF-MS measurements (Tab. S7-S9 and Fig. S2), consistent with prior studies.[23,29,30] The highest signals for canola oil are at m/z 57.069, 73.064, 111.117 and 143.143; these correspond to acrolein (C_3H_4O), malondialdehyde ($C_3H_4O_2$), 2,4-heptadienal ($C_7H_{10}O$) and nonanal ($C_9H_{18}O$), respectively. For sunflower oil, the most dominant compounds are at m/z 57.069, 101.096, 113.096 and 153.127; these correspond to acrolein, hexanal ($C_6H_{12}O$), 2-heptenal ($C_7H_{12}O$) and 2,4-decadienal ($C_{10}H_{16}O$), respectively. For olive oil, the highest signals are m/z 57.069, 101.096, 115.112, 129.127, 143.143, 155.143 and 169.159; these correspond to acrolein, hexanal, heptanal ($C_7H_{14}O$), octanal ($C_8H_{16}O$), nonanal, 2-decenal ($C_{10}H_{18}O$) and 2-undecenal ($C_{11}H_{20}O$), respectively. While acrolein, common in all oil emissions, is formed through the dehydration of glycerol,[27] the other aldehydes are produced via peroxyl radical reactions of the fatty acids.[31] The different emission patterns of the oils are consistent with the varying composition of the triglycerides present in the oils.[32] Depending on the positions of the double bonds in the triglycerides and the place of fracture, different hydroperoxides are produced, resulting in decomposition to different alkanals, alkenals and alkadienals.

The relative composition of the emissions from sunflower and canola oil do not change significantly with temperature (Fig. 2). However, olive oil emissions show an increase in larger aldehydes with increasing temperature, especially nonanal and 2,4-decadienal (Fig. 3). It was observed that the oil emissions scale with the surface area of the oil layer rather than the mass of oil heated. In order to be able to compare the oil heating with the frying processes we chose for the calculations the mass of oil needed for frying 1 kg of food and integrated over 10 minutes of heating to calculate emission factors. The total NMOG emission factors for heating the three oils increased significantly when increasing the temperature (by 40 -

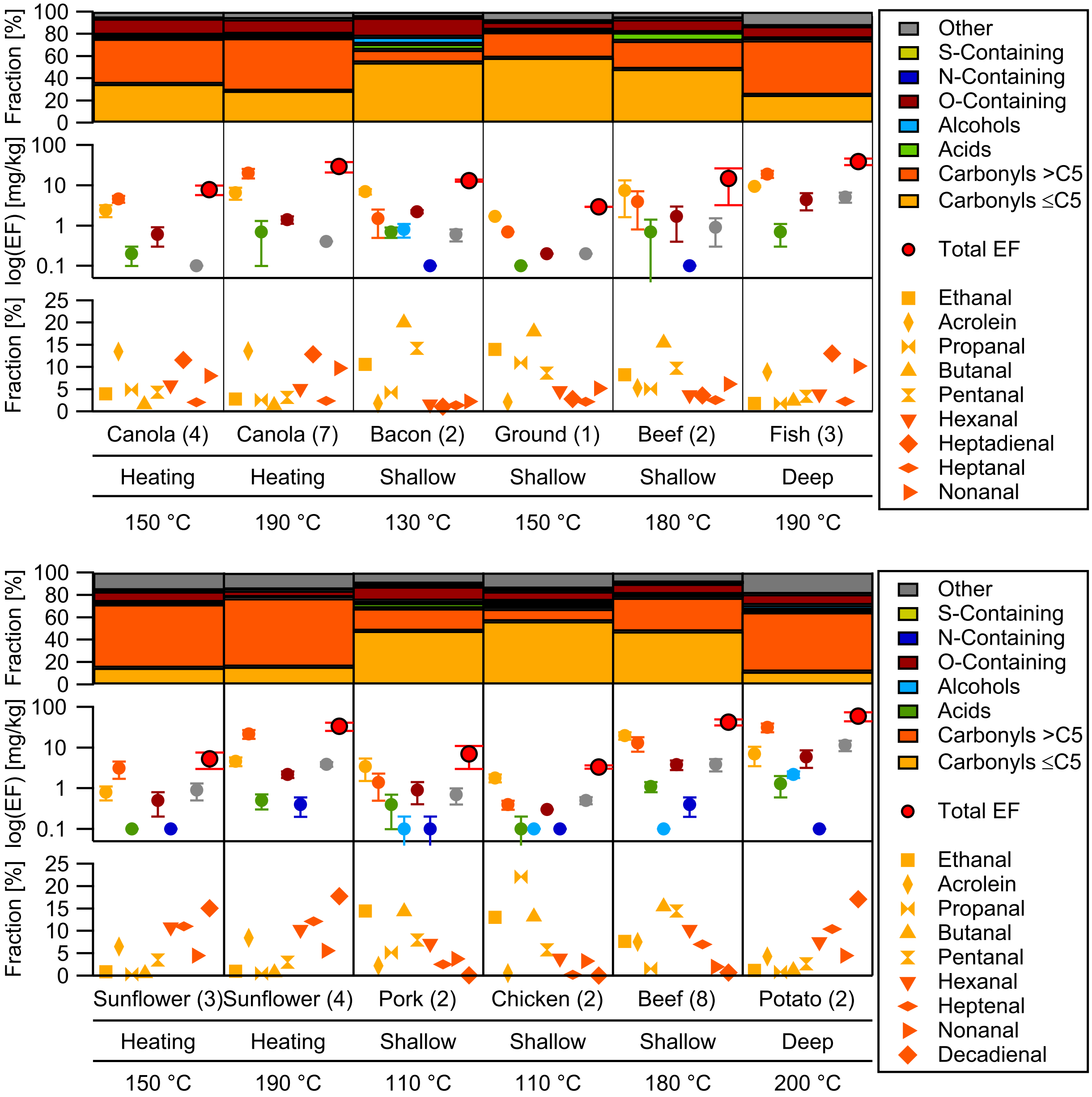

Figure 2: Relative composition (upper panel), emission factors (middle panel) and compounds contributing to more than 5% to the total mass (lower panel) of cooking with canola oil (upper graph) and sunflower oil (lower graph) as measured with the PTR-ToF-MS. The axis labels represent from top to bottom, the kind of food cooked, the cooking method and the oil temperature at the beginning of the experiment. Numbers in brackets represent the number of experimental repeats.

$60°C$) from 8 mg kg^{-1} to 29 mg kg^{-1}, from 5 mg kg^{-1} to 33 mg kg^{-1} and from 12 mg kg^{-1} to 78 mg kg^{-1} for canola, sunflower and olive oil, respectively. In general, the higher emission factors for olive oil are due to the higher temperature used during these experiments (160 °C and 220 °C) compared to canola oil and sunflower oil (150 °C and 190 °C). The increase of emission factors due to increasing temperature can be explained by the acceleration of the chemical processes (breaking of fatty acids) which lead to the formation of the emitted aldehydes.

Emissions from charbroiling, frying and deep frying

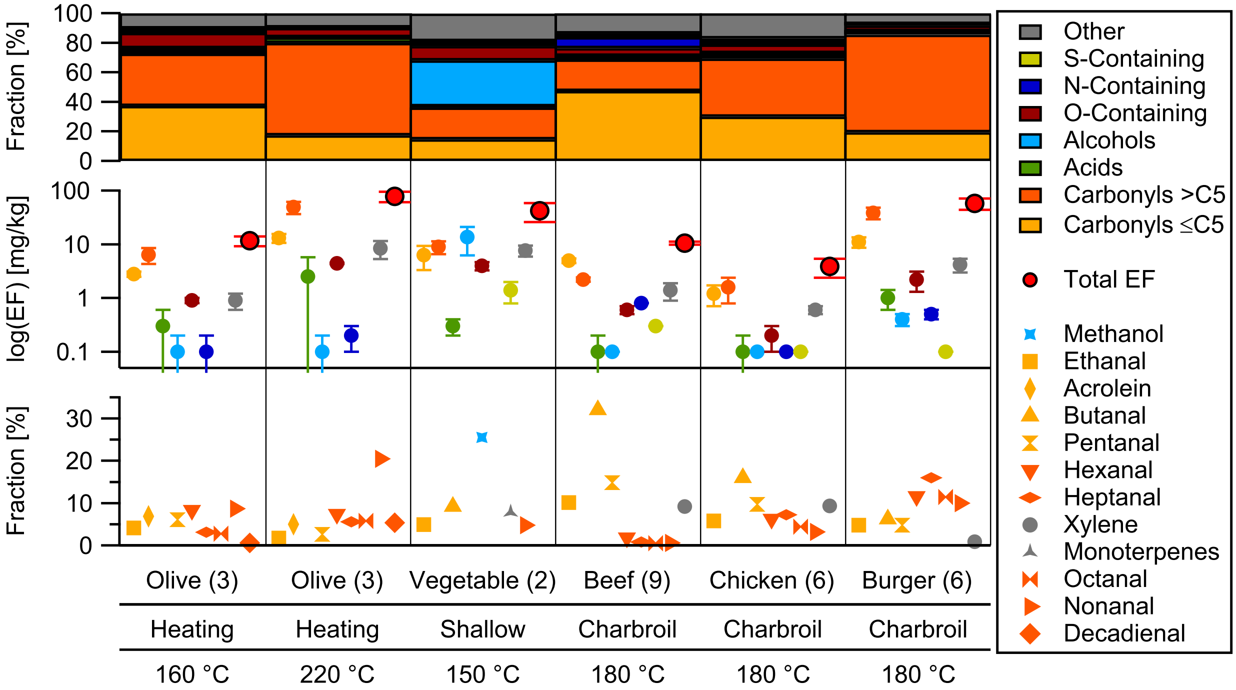

Figure 3: Relative composition (upper panel), emission factors (middle panel) and compounds contributing to more than 5% to the total mass (lower panel) of cooking with olive oil and charbroiling as measured with the PTR-ToF-MS. The axis labels represent from top to bottom, the kind of food cooked, the cooking method and the temperature at the beginning of the experiment. Numbers in brackets represent the number of experimental repeats.

For shallow frying in a pan, the dominant compounds are aldehydes (more than 60%). The contribution of smaller ($\leq$ C5) aldehydes to the total emissions increases, from about

30% to about 50% when frying food with canola oil and from about 15% to about 50% when frying food with sunflower oil, compared to the heating of the pure oils alone. The fractional contribution of the smaller aldehydes decreases with increasing oil temperature. The total NMOG emission factors for shallow frying of meat range from 3 $\mathrm{mg\,kg^{-1}}$ for chicken to 42 $\mathrm{mg\,kg^{-1}}$ for beef in sunflower oil. During vegetable frying lower relative amounts of aldehyde emissions were observed as a result of low temperatures (150°C). Due to the long cooking time of 20 minutes (meat was fried for 10 minutes), the total NMOG emission was 42 $\mathrm{mg\,kg^{-1}}$, higher than EF measured during other shallow frying experiments. The most abundant aldehyde from vegetable frying is butanal (4 $\mathrm{mg\,kg^{-1}}$) which is low compared to the emission of methanol (11 $\mathrm{mg\,kg^{-1}}$), a reported by-product from cell wall synthesis.[33] The frying of vegetables releases monoterpenes (3 $\mathrm{mg\,kg^{-1}}$) which may be attributed to emissions from condiments (e.g. oregano, basil), used as seasoning for this experiment,[34] as these compounds were not observed during vegetable boiling.

The total NMOG emission factors from deep frying processes are 59 $\mathrm{mg\,kg^{-1}}$ for potato and 39 $\mathrm{mg\,kg^{-1}}$ for the fish, comparable to the total emission factors expected from heating the pure oils at the same temperature (200 °C) and (190 °C). In addition the chemical composition of deep frying emissions is comparable to the composition of the pure oils besides an increase in alcohol emissions for the potato frying and an increase of O-containing compounds for fish frying. For all the frying experiments except the vegetables, negligible amounts of acids, alcohols, N-containing and S-containing species were observed (below 5% contribution to total NMOG).

The absolute emission factors of carbonyls from oils depend not only on the cooking temperature but also on the oil surface. For shallow frying the last parameter is hard to control and to assess. Therefore, in order to separate oil emissions from those due to the food used, we have calculated enhancement factors of different compounds normalized to acrolein expected to be emitted solely from oil heating (Fig. 4). Aldehyde emissions from deep frying of potato and fish strongly resemble the corresponding oil emissions with all the

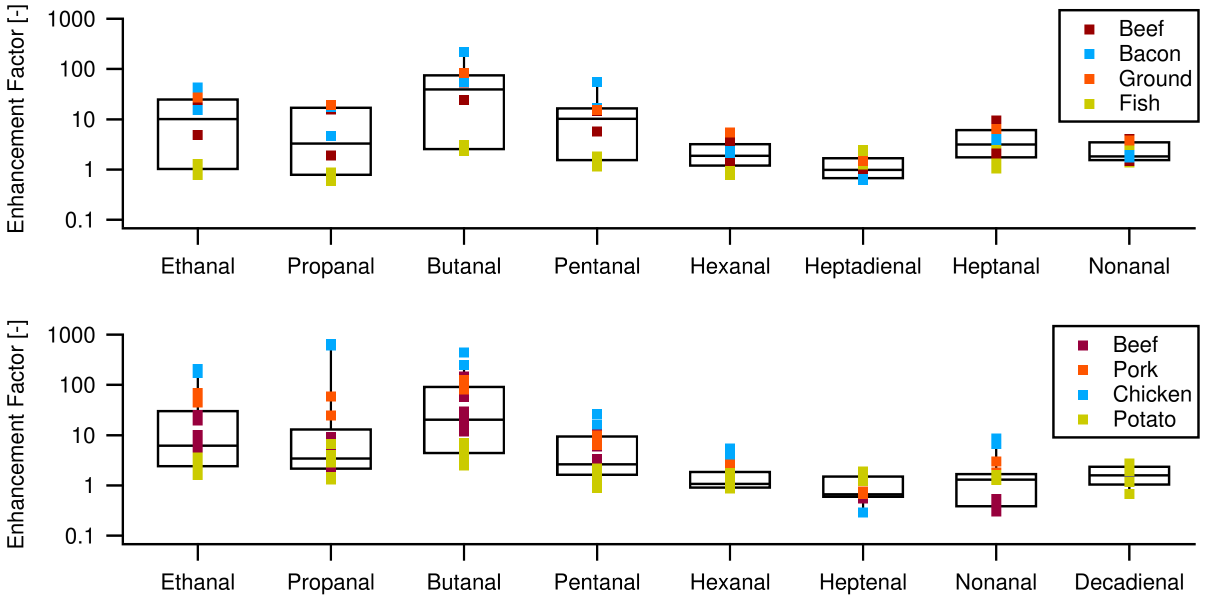

Figure 4: Enhancement of aldehyde emissions from frying processes compared to oils only for experiments with canola oil (upper graph) and experiments with sunflower oil (lower graph). An enhancement factor equal 1 means all the emissions can be attributed to heating of oil. Enhancement factors for decadienal could only be calculated for deep frying of potato most likely due to lower temperatures $(\leq 180^{\circ}C)$ during shallow frying. Pentanal could also comprise emissions of pentanone.

enhancement factors around 1 and the ratio between smaller and larger aldehydes matching the ratio of the pure oils. For shallow frying experiments, the enhancement factors for aldehydes with more than 5 carbons are mostly around 1, by contrast the smaller aldehydes show significant enhancement factors ranging from 5 to almost 1000. This demonstrates that the smaller aldehydes observed during shallow frying are mostly generated by the foods and not the oils used. These small aldehydes most probably originate from the decomposition of the fatty acids in the meat.[35] The relative contributions of individual aldehydes to the total emissions show only slight differences between the different foods which seems to be caused by different frying temperatures. The emissions from shallow frying are lower than the deep frying emissions due to the lower temperatures used (130 °C to 180 °C) and the smaller surface of the oil but higher than what would be expected from only heating the oils (Fig. 2).

The total emission factors from charbroiling beef (11 mg kg^{-1}) and chicken (4 mg kg^{-1}) are lower than those from frying processes, indicating that a higher amount of the emissions come from the use of oils. Furthermore, the charbroiling of burger patties releases total NMOG emissions of 58 mg kg^{-1} which is comparable to heated vegetable oils at the same temperature ($180°C$). This can be explained by the high fat content of the burger patties. Since fat in ground beef mostly consists of saturated or singly unsaturated fatty acids[36] we observe mostly saturated aldehydes in contrast to more unsaturated aldehydes associated with frying with oils. The burger patties are the only significant emitters of octanal (7 mg kg^{-1}). The emissions from charbroiling beef (without oil) are dominated by small aldehydes (about 50%) indicating again that the small aldehydes are produced from the meat rather then from the heated oils. Other compounds emitted during the charbroiling of beef and chicken are C8 aromatics (C_8H_{10}, e.g. xylene) and a nitrogen containing compound ($C_5H_6N_2$, e.g. aminopyridine).

Frying and charbroiling processes are very common in domestic and commercial kitchens and are associated with large emissions of reactive NMOG and therefore expected to dominate gas phase cooking emissions. We observed that hexanal and nonanal were ubiquitous in all emissions from shallow and deep frying using different oils and also from charbroiling. With their relatively long atmospheric life-times against the OH radical (18 h for hexanal and 15 h for nonanal, for OH concentrations of $2 \times 10^6\, molec\, cm^{-3}$),[37] we suggest that hexanal and nonanal may potentially constitute suitable markers for identifying gas and particle phase cooking emissions in ambient air, using a PTR-ToF-MS. Future ambient studies should inspect this hypothesis, by examining the stability of emission ratios between these markers and total emissions and by assessing contributions from other processes that may emit these compounds (e.g. grass cutting may emit hexanal[38]). Raw spectra of all cooking processes can be found in the supplementary information (Fig. S3-5).

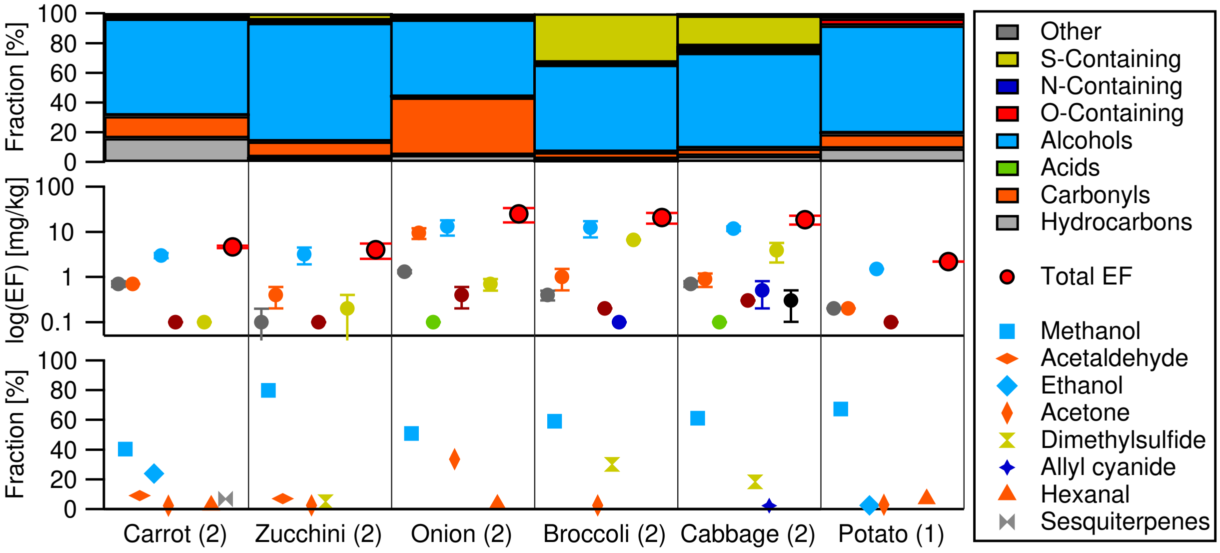

Figure 5: Relative composition (upper panel), emission factors (middle panel) and compounds contributing more than 5% to the total mass (lower panel) of boiling vegetables as measured with the PTR-ToF-MS. The cooking method is boiling in water for all experiments. Numbers in brackets represent the number of experimental repeats. The error bars indicate the standard deviation of the samples.

Emissions from boiling vegetables

The total NMOG emission factors observed from boiling vegetables were between 4 mg kg^{-1} and 21 mg kg^{-1}, lower than the emission factors from frying. Similar to vegetable frying, vegetable boiling emits large amounts of methanol (2 mg kg^{-1} to 13 mg kg^{-1}), corresponding to 40-80% of the total NMOG emissions. During vegetable boiling, unique compounds specific to different vegetables can be detected. High ethanol emissions (1 mg kg^{-1}) from carrots and acetaldehyde emissions from carrots (0.5 mg kg^{-1}) and zucchini (0.3 mg kg^{-1}) could originate from drought stress conditions during the growth, mechanical stress after the harvest or storage under low oxygen conditions.[39] Boiling carrots additionally emits considerable amounts of sesquiterpenes (0.3 mg kg^{-1}) which are formed during root development in the plants.[40] When boiling onions, high amounts of acetone (9 mg kg^{-1}) were measured due to the high acetone content in onions.[41] Broccoli and cabbage were found to emit between 20 and 30% of C_2H_6S (3 mg kg^{-1} to 6 mg kg^{-1}). This is consistent with the detection of dimethyl sulfide in cruciferous vegetable oil extracts reported by Buttery et al.[42] However, the contribution of ethanethiol from the hydrolysis of glucosinolate cannot be excluded.[43] Allyl cyanide emitted by boiling cabbage (0.4 $\mathrm{mg\,kg^{-1}}$) is formed as antifeedant in the plant.[44] Emission factors from boiling pasta and rice were determined but are not shown here because they were not significantly higher than the background.

Implications for indoor air

Aldehydes are known to irritate the eyes and the respiratory tract at high concentrations.[45] Based on the calculated emission factors, we have estimated the potential concentrations of individual aldehydes in a 40 $\mathrm{m^3}$ kitchen without ventilation after cooking 1 kg of food for 10 min, and compared them to exposure limits in place in some countries or thresholds reported in literature. Air exchange rates typical of residential kitchens (0.6 h-1) during the short cooking time have only a minor effect (<20%) and therefore will not be taken into account. Acetaldehyde is classified by the IARC as a group 2b carcinogen (possibly carcinogenic), at chronic exposure of 0.003 $\mathrm{mg\,m^{-3}}$.[46] Frying in sunflower oil leads to 20-fold higher concentrations of acetaldehyde. The German statutory accident insurance sets a workplace limit of 0.03 $\mathrm{mg\,m^{-3}}$ for hexanal (as an average over 8 hours) which is exceeded by up to 5 times, when cooking burger patties. The Australian government sets a workplace eight-hour average limit for exposure to acrolein of 0.23 $\mathrm{mg\,m^{-3}}$ and the EPA AGEL-1 limit is 0.07 $\mathrm{mg\,m^{-3}}$. Both limits can be readily exceeded by most of the frying processes. Deep frying in sunflower oil would result in a concentration of 0.25 $\mathrm{mg\,m^{-3}}$ of 2,4-decadienal, which is suspected to increase the risk of lung cancer.[47] In general, a large number of the detected compounds including unsaturated aldehydes from heated fats or sulphur and nitrogen containing species from vegetable boiling are notorious for their deleterious impact on human health. While such impact can be diminished with a proper ventilation system further studies are required for assessing the health effects of cooking emissions and the influence of the kitchen set-up.

Acknowledgement

This work was supported by the Swiss National Science Foundation as well as the Swiss Federal Office for the Environment. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n.° 290605 (COFUND: PSI-FELLOW). Naomi Farren thanks the Natural Environment Research Council (NERC) for a PhD studentship. A special thank to René Richter for his valuable technical assistance during the campaigns. We would also like to thank Neil Harris, University of York for use of the stainless steel reactor. We also acknowledge the MASSALYA instrumental platform (Aix Marseille Université, lce.univ-amu.fr) for PTR-ToF-MS measurements.

Supporting Information Available

The supplementary information includes GC×GC-ToF-MS results from heating vegetable oils, a fragmentation table for aldehydes, the list of all cooking experiments including the experiment conditions, the list of all emission factors, the list with the exact *m/z*, *k* values and family attribution for all ions and raw PTR-ToF-MS spectra for all cooking processes.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Allan, J. D.; Williams, P. I.; Morgan, W. T.; Martin, C. L.; Flynn, M. J.; Lee, J.; Nemitz, E.; Phillips, G. J.; Gallagher, M. W.; Coe, H. Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities. *Atmos. Chem. Phys.* **2010**, *10*, 647–668.

(2) Slowik, J. G.; Vlasenko, A.; McGuire, M.; Evans, G. J.; Abbatt, J. P. D. Simulta-

neous factor analysis of organic particle and gas mass spectra: AMS and PTR-MS measurements at an urban site. *Atmos. Chem. Phys* **2010**, *10*, 1969–1988.

(3) Mohr, C. et al. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. *Atmos. Chem. Phys.* **2012**, *12*, 1649–1665.

(4) Crippa, M. et al. Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris. *Atmos. Chem. Phys.* **2013**, *13*, 961–981.

(5) Abdullahi, K. L.; Delgado-Saborit, J. M.; Harrison, R. M. Emissions and indoor concentrations of particulate matter and its specific chemical components from cooking: A review. *Atmos. Environ.* **2013**, *71*, 260–294.

(6) Huang, Y.; Ho, S. S. H.; Ho, K. F.; Lee, S. C.; Yu, J. Z.; Louie, P. K. K. Characteristics and health impacts of VOCs and carbonyls associated with residential cooking activities in Hong Kong. *J. Hazard. Mater.* **2011**, *186*, 344–351.

(7) Ko, Y. C.; Cheng, L. S. C.; Lee, C. H.; Huang, J. J.; Huang, M. S.; Kao, E. L.; Wang, H. Z.; Lin, H. J. Chinese food cooking and lung cancer in women nonsmokers. *Am. J. Epidemiol.* **2000**, *151*, 140–147.

(8) Buonanno, G.; Morawska, L.; Stabile, L. Particle emission factors during cooking activities. *Atmos. Environ.* **2009**, *43*, 3235–3242.

(9) Huboyo, H. S.; Tohno, S.; Cao, R. Q. Indoor PM2.5 Characteristics and CO Concentration Related to Water-Based and Oil-Based Cooking Emissions Using a Gas Stove. *Aerosol. Air. Qual. Res.* **2011**, *11*, 401–411.

(10) Mohr, C.; Huffman, J. A.; Cubison, M. J.; Aiken, A. C.; Docherty, K. S.; Kimmel, J. R.; Ulbrich, I. M.; Hannigan, M.; Jimenez, J. L. Characterization of Primary Organic

Aerosol Emissions from Meat Cooking, Trash Burning, and Motor Vehicles with High-Resolution Aerosol Mass Spectrometry and Comparison with Ambient and Chamber Observations. *Environ. Sci. Tech.* **2009**, *43*, 2443–2449.

(11) Wan, M. P.; Wu, C. L.; To, G. N. S.; Chan, T. C.; Chao, C. Y. H. Ultrafine particles, and PM2.5 generated from cooking in homes. *Atmos. Environ.* **2011**, *45*, 6141–6148.

(12) He, L. Y.; Lin, Y.; Huang, X. F.; Guo, S.; Xue, L.; Su, Q.; Hu, M.; Luan, S. J.; Zhang, Y. H. Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning. *Atmospheric Chemistry and Physics* **2010**, *10*, 11535–11543.

(13) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 1. C-1 through C-29 organic compounds from meat charbroiling. *Environ. Sci. Tech.* **1999**, *33*, 1566–1577.

(14) Mugica, V.; Vega, E.; Chow, J.; Reyes, E.; Sánchez, G.; Arriaga, J.; Egami, R.; Watson, J. Speciated non-methane organic compounds emissions from food cooking in Mexico. *Atmos. Environ.* **2001**, *35*, 1729–1734.

(15) Alves, C.; Evtyugina, M.; Cerqueira, M.; Nunes, T.; Duarte, M.; Vicente, E. Volatile organic compounds emitted by the stacks of restaurants. *Air Qual. Atmos. Health.* **2015**, *8*, 401–412.

(16) Lee, S. C.; Li, W. M.; Chan, L. Y. Indoor air quality at restaurants with different styles of cooking in metropolitan Hong Kong. *Sci. Total. Environ.* **2001**, *279*, 181–193.

(17) Ellegard, A. Cooking fuel smoke and respiratory symptoms among women in low-income areas in Maputo. *Environ. Health. Perspect.* **1996**, *104*, 980–985.

(18) Robinson, A. L.; Subramanian, R.; Donahue, N. M.; Bernardo-Bricker, A.; Rogge, W. F.

Source apportionment of molecular markers and organic aerosol. 3. Food cooking emissions. *Environ. Sci. Tech.* **2006**, *40*, 7820–7827.

(19) Weitkamp, E. A.; Hartz, K. E. H.; Sage, A. M.; Donahue, N. M.; Robinson, A. L. Laboratory measurements of the heterogeneous oxidation of condensed-phase organic molecular makers for meat cooking emissions. *Environ. Sci. Tech.* **2008**, *42*, 5177–5182.

(20) Graus, M.; Muller, M.; Hansel, A. High Resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time. *J. Am. Soc. Mass. Spectrom.* **2010**, *21*, 1037–1044.

(21) Jordan, A.; Haidacher, S.; Hanel, G.; Hartungen, E.; Mark, L.; Seehauser, H.; Schottkowsky, R.; Sulzer, P.; Mark, T. D. A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). *Int. J. Mass. Spectrom.* **2009**, *286*, 122–128.

(22) Buhr, K.; van Ruth, S.; Delahunty, C. Analysis of volatile flavour compounds by Proton Transfer Reaction-Mass Spectrometry: fragmentation patterns and discrimination between isobaric and isomeric compounds. *Int. J. Mass. Spectrom.* **2002**, *221*, 1–7.

(23) Fullana, A.; Carbonell-Barrachina, n. A.; Sidhu, S. Volatile aldehyde emissions from heated cooking oils. *J. Sci. Food. Agr.* **2004**, *84*, 2015–2021.

(24) Gueneron, M.; Erickson, M. H.; VanderSchelden, G. S.; Jobson, B. T. PTR-MS fragmentation patterns of gasoline hydrocarbons. *Int. J. Mass. Spectrom.* **2015**, *379*, 97–109.

(25) de Gouw, J.; Warneke, C. Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry Reviews* **2007**, *26*, 223–257.

(26) Cappellin, L.; Probst, M.; Limtrakul, J.; Biasioli, F.; Schuhfried, E.; Soukoulis, C.; Märk, T. D.; Gasperi, F. Proton transfer reaction rate coefficients between H3O+ and some sulphur compounds. *International Journal of Mass Spectrometry* **2010**, *295*, 43–48.

(27) Umano, K.; Shibamoto, T. Analysis of acrolein from heated cooking oils and beef fat. *J. Agr. Food. Chem.* **1987**, *35*, 909–912.

(28) Kilic, D.; Brem, B.; Klein, F.; El-Haddad, I.; Durdina, L.; Rindlisbacher, T.; Huang, R.; Slowik, J.; Baltensperger, U.; Prevot, A. S. H. Characterization of non-methane volatile organic compound (NMVOC) emissions from aircraft turbine engines. **2015**, in prep.

(29) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 4. C-1-C-27 organic compounds from cooking with seed oils. *Environ. Sci. Tech.* **2002**, *36*, 567–575.

(30) Katragadda, H. R.; Fullana, A.; Sidhu, S.; Carbonell-Barrachina, A. A. Emissions of volatile aldehydes from heated cooking oils. *Food. Chem.* **2010**, *120*, 59–65.

(31) Gardner, H. W. Oxygen radical chemistry of polyunsaturated fatty acids. *Free. Radic. Biol. Med.* **1989**, *7*, 65–86.

(32) Choe, E.; Min, D. B. Mechanisms and Factors for Edible Oil Oxidation. *Compr. Rev. Food. Sci. Food. Saf.* **2006**, *5*, 169–186.

(33) Fall, R.; Benson, A. A. Leaf methanol - the simplest natural product from plants. *Trends. Plant. Sci.* **1996**, *1*, 296–301.

(34) Loza-Tavera, H. *Monoterpenes in Essential Oils In Chemicals via Higher Plant Bioengineering*; Advances in Experimental Medicine and Biology; Springer US, 1999; Vol. 464; Chapter 5, pp 49–62.

(35) Wood, J. D.; Richardson, R. I.; Nute, G. R.; Fisher, A. V.; Campo, M. M.; Kasapidou, E.; Sheard, P. R.; Enser, M. Effects of fatty acids on meat quality: a review. *Meat Science* **2004**, *66*, 21–32.

(36) Jiang, T.; Busboom, J. R.; Nelson, M. L.; Mengarelli, R. Omega-3 fatty acids affected human perception of ground beef negatively. *Meat Science* **2011**, *89*, 390–399.

(37) Hellen, H.; Hakola, H.; Reissell, A.; Ruuskanen, T. M. Carbonyl compounds in boreal coniferous forest air in Hyytiala, Southern Finland. *Atmos. Chem. Phys.* **2004**, *4*, 1771–1780.

(38) Fall, R.; Karl, T.; Hansel, A.; Jordan, A.; Lindinger, W. Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry. *Journal of Geophysical Research: Atmospheres* **1999**, *104*, 15963–15974.

(39) Seljasen, R.; Kristensen, H. L.; Lauridsen, C.; Wyss, G. S.; Kretzschmar, U.; Birlouez-Aragone, I.; Kahl, J. Quality of carrots as affected by pre- and postharvest factors and processing. *J. Sci. Food. Agr.* **2013**, *93*, 2611–2626.

(40) Yahyaa, M.; Tholl, D.; Cormier, G.; Jensen, R.; Simon, P. W.; Ibdah, M. Identification and Characterization of Terpene Synthases Potentially Involved in the Formation of Volatile Terpenes in Carrot (Daucus carota L.) Roots. *J. Agric. Food Chem.* **2015**, *63*, 4870–4878.

(41) White, R. K. Handbook of environmental fate and exposure data for organic-chemicals, Vol 2, Solvents - Howard,PH. *Risk. Anal.* **1992**, *12*, 163–163.

(42) Buttery, R. G.; Guadagni, D. G.; Ling, L. C.; Seifert, R. M.; Lipton, W. Additional volatile components of cabbage, broccoli, and cauliflower. *J. Agr. Food. Chem.* **1976**, *24*, 829–832.

(43) Bhattacharjee, P.; Singhal, R. S. *Asparagus, Broccoli, and Cauliflower: Production, Quality, and Processing In Handbook of Vegetables and Vegetable Processing*; Wiley-Blackwell, 2010; pp 505–523.

(44) Tanii, H.; Takayasu, T.; Higashi, T.; Leng, S.; Saijoh, K. Allylnitrile: generation from cruciferous vegetables and behavioral effects on mice of repeated exposure. *Food. Chem. Toxicol.* **2004**, *42*, 453–458.

(45) Cassee, F. R.; Arts, J. H. E.; Groten, J. P.; Feron, V. J. Sensory irritation to mixtures of formaldehyde, acrolein, and acetaldehyde in rats. *Arch. Toxicol.* **1996**, *70*, 329–337.

(46) O'Brien, P. J.; Siraki, A. G.; Shangari, N. Aldehyde sources, metabolism, molecular toxicity mechanisms, and possible effects on human health. *Crit. Rev. Toxicol.* **2005**, *35*, 609–662.

(47) Wang, C. K.; Chang, L. W.; Chang, H.; Yang, C. H.; Tsai, M. H.; Tsai, H. T.; Lin, P. Pulmonary changes induced by trans,trans-2,4-decadienal, a component of cooking oil fumes. *Eur. Respir. J.* **2010**, *35*, 667–675.

Graphical TOC Entry