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ABSTRACT SUBMISSION FORM

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Adding extra-dimensions to Tea (*Camellia sinensis* L.) volatiles profiling by GC×GC-TOF-MS and soft electron ionization: effects of climate changes on volatile metabolome

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Summary: The study implements the principles of sensomics into multidimensional platforms based on comprehensive two-dimensional gas chromatography ($GC \times GC$) coupled with Time of Flight Mass Spectrometry (TOF-MS) and tandem ionization. Extra-dimensions of information from sampling by High Concentration Capacity (HCC) sample preparation and from detection by tandem ionization (70 and 12 eV) provide unique signature(s) with an extremely powerful potential.

Keywords: Camellia sinensis L.; untargeted and targeted fingerprinting; comprehensive twodimensional gas chromatography-time-of-flight mass spectrometry and tandem ionization

1 Introduction

Climate changes are greatly impacting on agro-ecosystems, crops, and farmer livelihoods in communities worldwide. An increase in frequency and intensity of climate events in many areas result in a reduction in crop yields although the impact on crop quality is less acknowledged, yet it is fundamental for food systems [1]. Tea (*Camellia sinensis* L.) is a crop or great economic relevance and water infusion of dried leaves the most consumed beverage around the world.

The sensory quality of tea is the keyfactor affecting consumer preference, it relates with color, strength, taste and aroma [2]. Phenolic compounds (mainly present as glycosides in the plant) and xanthine condition tea color, taste and somato-sensations (astringency) while volatile compounds are

2. Experimental

Samples: environmental teas were from Yunnan and Fujian province (China) and collected at different timings before and after monsoon rains in 2014 and 2015. South Carolina (USA) tea "Bigelow" was collected in 2015 before and after hurricane Joaquin.

Head Space Solid Phase Micro Extraction sampling: samples were frozen in liquid nitrogen and ground up to $300 \ \mu m$ (Grindomix GM200, Retsch, Haan, Germany); precisely weighted (0.500 g) in headspace glass vials (20 mL) for HS-SPME sampling. fundamental for its aroma. More than 600 volatiles have been identified in green and black teas, with 41 of them considered as key contributors to the tea aroma [2].

This study presents a comprehensive and systematic investigation strategy for effective profiling and fingerprinting of volatiles from teas undergone to intense climate events: pre- and post- heavy rains (monsoon or hurricane). In particular, the effectiveness of fully automated head-space sampling by miniaturized extraction devices, based on either sorption and adsorption polymers, hyphenated to comprehensive twodimensional gas chromatography coupled with Time of Flight Mass Spectrometry (ToF-MS) with hard (70eV) and soft (12eV) electron ionization are shown.

SPME DVB/CAR/PDMS d_f 50/30 µm - 2 cm (Supelco, Bellefonte, PA, USA). Standard-infiber procedure was before sampling for 30 min at 50°C. Fibre thermal desorption into the S/SL injection port for 5 minutes at 250°C.

GC×GC-TOF-MS instrument set-up: Agilent 6890 GC coupled with Markes Bench-TOF SelectTM (Markes International. operating Llantrisant, UK) in tandem ionization (70 eV and 12 eV). Transfer line 270°C; Ion source 250°C. Thermal modulation by two-stage KT 2004 loop-type modulator (Zoex Corporation, Houston, TX) cooled with liquid N_2 and controlled by OptimodeTM V.2 (SRA Instruments, Italy). Hot jet pulse time 250 ms, modulation time 4s.

Column set: ¹D SE52 (30 m \times 0.25 mm d_c, 0.25 μ m d_f) and ²D OV1701 (86% PDMS, 7% phenyl, 7% cyanopropyl) (1 m \times 0.1 mm d_c, 0.10 μ m d_f), from J&W. Carrier gas: He, const flow 1.3 mL/min. Oven from 40°C (1 min) to

3. Results

Untargeted and Targeted fingerprinting (UT fingerprinting) is based on the template matching approach [3] and follows an original work-flow validated for olive oil volatiles investigation [4].

Targeted analysis includes targeted compounds identified by matching EI-MS fragmentation pattern (NIST MS Search algorithm, ver 2.2 with Direct Matching threshold 850 and Reverse Matching threshold 900) with those collected in commercial (NIST2014 and Wiley 7n) and in-house databases. Linear Retention Indices (I^{T}_{S}) were adopted as quality constraint for positive identification.

Untargeted analysis was based on peak-regions features [5] created over a selection of preprocessed 2D patterns (pre-targeted) covering the samples' set variability.

The process is performed automatically by GC Image InvestigatorTM R 2.7 (GC Image LLC, Lincoln NE, USA). **Figure 1** shows a 2D pattern from a Yunnan tea sample where targeted peaks (yellow circles) and peak-regions (red outlines) are mapped.

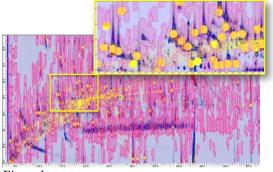


Figure1

Focusing on targeted analytes relative distribution, PCA shows samples sub-classes dominated by processing (black tea - Bigelow vs. environmental teas). Latent variables for Fujian contribute in the wide spreading of observations over the Cartesian plane - Figure 2. Most informative analytes are those related to LOXs pathways: decanal, (Z,E)-3,5octadien-2-one, (E,E) 2,4-heptadienal, (E)-2200°C at 3°C/min and to 270°C at 10°C/min (5 min).

Data acquisition and data elaboration: data were acquired by TOF-DS and processed by GC Image 2.7 (GC Image, LLC Lincoln NE, USA).

octenal, (E,E)-3,5-octadien-2-one, E-2hexenal, 3-Octen-2-one, (E,Z) 2,4-heptadienal. Analytes are ordered according to the correlation coefficient on F1.

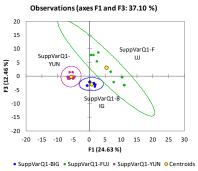


Figure 2

Figure 3 shows as heat-map, based on 2D Peaks Volume Response from 110 targeted peaks (mean and centering normalization), the effect of heavy rains on volatiles distribution -Fujian 2015 teas. Coloring from red (low abundance) to green (high abundance) shows analytes distribution across samples. Hierarchical clustering based on Euclidean distances, informs about those analytes up- or down-regulated by heavy rains

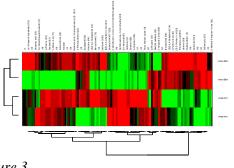


Figure 3

4. Conclusions

Comprehensive fingerprinting enables effective investigation of complex fractions and provides interesting insights on the effect of climate events on tea volatiles. Mass Spectrometry with tandem ionization as additional analytical dimension is fundamental for reliable profiling of samples and consistent fingerprinting.

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