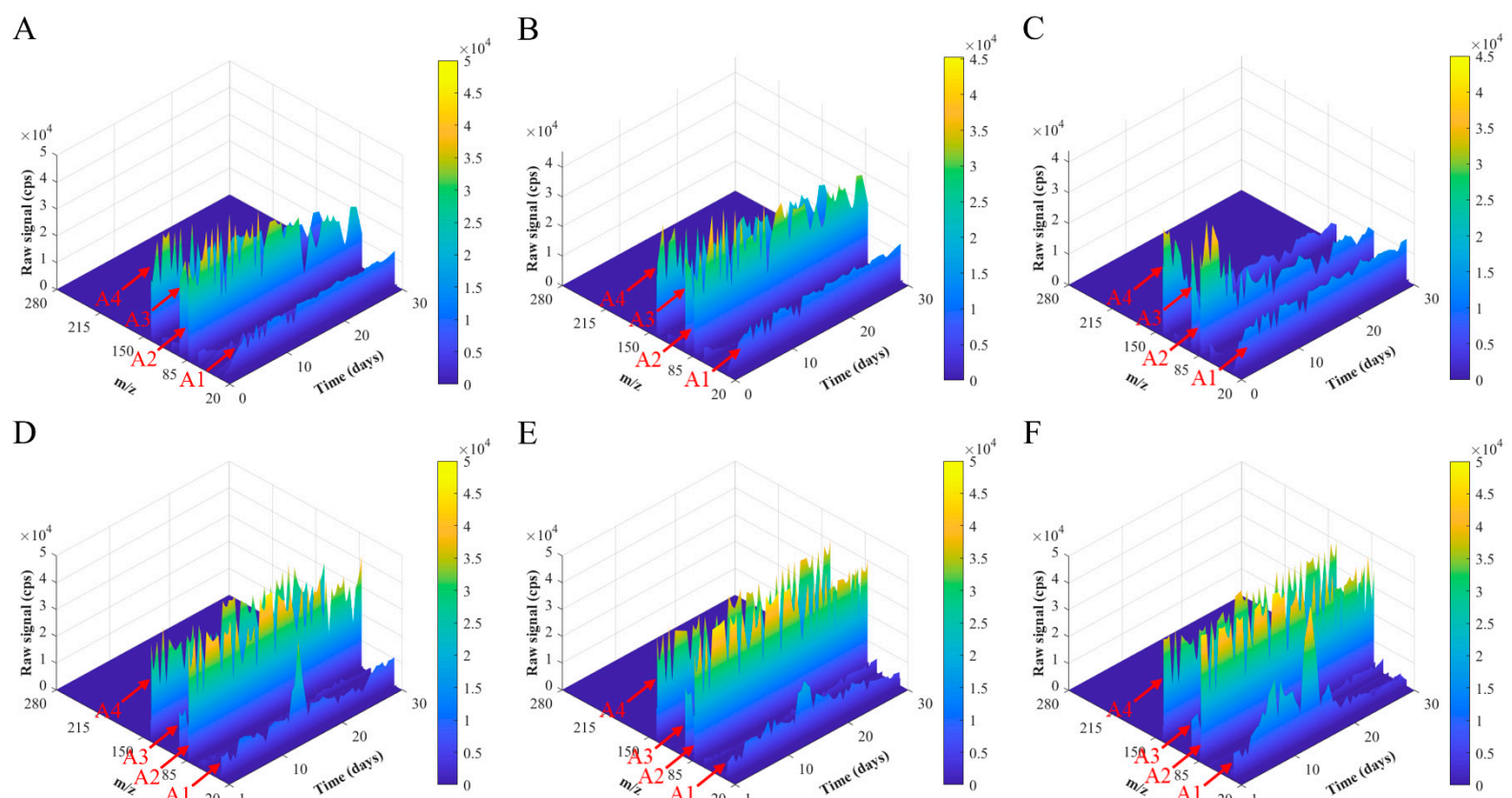


## Supporting Information

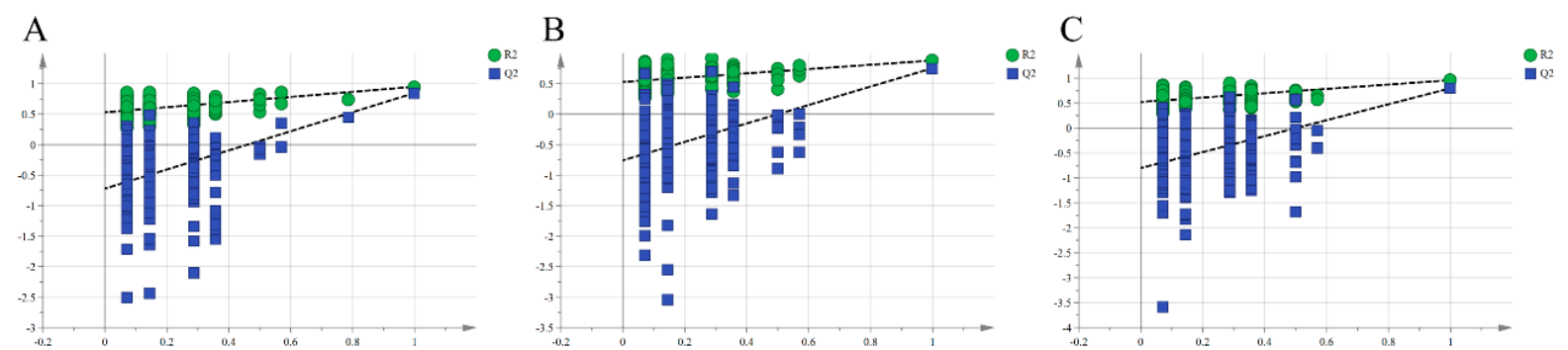
**Table S1.** Calibration curve data for five reference compounds hesperidin, didymin, nobiletin, tangeretin, and 3,5,6,7,8,3',4'-heptamethoxyflavone (HMF) (n = 2)

Compounds	Regression equation ( $y = ax + b$ ) *	R <sup>2</sup>	Retention time (min)	Signal (nm)
Section 2.3.3				
Hesperidin	$y = 6.1597x + 19.082$	0.9997	13.57	283
Didymin	$y = 5.9937x + 23.748$	0.9997	14.42	283
Nobiletin	$y = 14.194x + 4.8444$	0.9999	30.03	330
HMF	$y = 9.0761x - 1.4144$	0.9996	34.49	330
Tangeretin	$y = 14.886x + 6.9411$	0.9999	40.63	330
Section 2.4.2				
Hesperidin	$y = 5.8163x + 5.2308$	0.9992	18.09	283

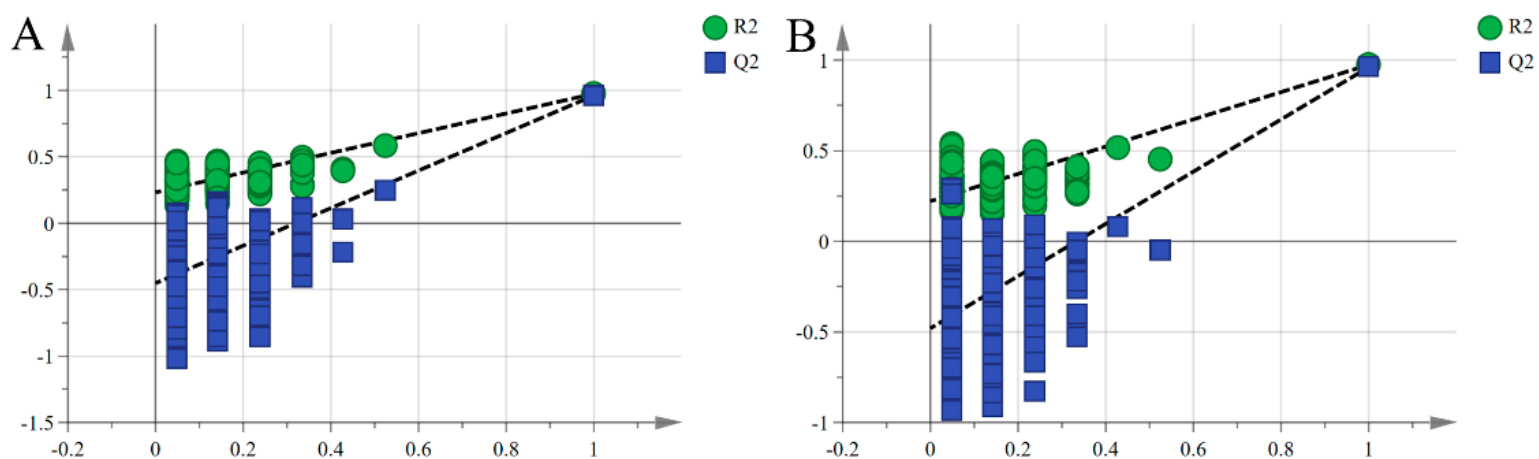
\* y and x denoted the peak area (mAU·s) and the corresponding injection concentration (μg/ml), respectively. a and b denoted the slope and intercept of the regression line, respectively. The calibration curves exhibit good linearity ( $R^2 > 0.9990$ ).



**Figure S1.** Three-dimensional (3D) plots of the detected spectra ( $m/z$  from 20 to 280) of the VOCs' emission from samples (A) Y2015, (B) Y2016, and (C) Y2018 during the simulated storage (25 °C and 60% RH), and from samples (D) Y2015, (E) Y2016, and (F) Y2018 during the accelerated spoilage (35 °C and 90% RH) during a month. The arrows marked the peaks of the compounds with  $m/z$  of 32, 81, 95 and 137 (compounds A1~A4 shown in Table 3).



**Figure S2.** Performed permutations test ( $n = 200$ ) with statistic parameters of [ $R^2 = (0.0, 0.53)$ ,  $Q^2 = (0.0, -0.721)$ ] for (A) Y2015, [ $R^2 = (0.0, 0.528)$ ,  $Q^2 = (0.0, -0.757)$ ] for (B) Y2016, and [ $R^2 = (0.0, 0.523)$ ,  $Q^2 = (0.0, -0.802)$ ] for (C) Y2018 at the first week of simulated storage in the OPLS-DA model.



**Figure S3.** Performed permutations test (n = 200) with statistic parameters of [ $R^2 = (0.0, 0.232)$ ,  $Q^2 = (0.0, -0.452)$ ] for (A) samples at the first week and [ $R^2 = (0.0, 0.222)$ ,  $Q^2 = (0.0, -0.48)$ ] for (B) samples at the fourth week of accelerated spoilage in the OPLS-DA model.