Formation Pathways of Aldehydes from Heated Cooking Oils

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Table S1: Total gas-phase aldehyde concentrations observed in the experiments performed in this study reported as mean ± standard deviation.

Exp. #	Cooking oil used	Antioxidants (ppm)	Cycle 1 (µg m^{-3})	Cycle 2 (µg m^{-3})	Cycle 3 (µg m^{-3})	Cycle 4 (µg m^{-3})
1		Control	1932±496	2369±514	2372±317	2471±415
2	Canola oil	γ-tocopherol (100)	913±241	1391±282	1598±203	1684±376
3		BHT (100)	848±169	1194±150	1311±86	1311±148
4		Control	835±163	1379±201	1458±190	1517±198
5	Sunflower oil	γ-tocopherol (100)	1629±234	1816±291	1800±159	1793±97
6		BHT (100)	1393±187	1529±118	1538±139	1661±149
7		Control	1629±257	1968±221	1881±221	1728±265
8	Olive oil	γ-tocopherol (100)	1555±367	1827±433	1691±278	1671±268
9		BHT (100)	972±139	1155±210	1436±108	1414±104
10		Control	1272±242	1560±200	1397±136	1409±128
11	Peanut oil	γ-tocopherol (100)	1598±179	1774±283	1699±98	1532±88
12		BHT (100)	1688±261	1821±200	1769±220	1659±146

Table S2: Rate constants for reaction scheme 1.

Reaction #	Rate constant	Value	Unit
R1	$k_i = k_1$	10^{-6}	s^{-1}
R2	$k_p = k_2$	10 [a,b]	$M^{-1}\ s^{-1}$
R3	$k_t = k_5$	10^5 [a,b]	$M^{-1}\ s^{-1}$
R4	k_4	10^{-5}	s^{-1}
R5	k_5	10^3 [a]	$M^{-1}\ s^{-1}$
R6	k_6	10^5–10^7 [a,b]	$M^{-1}\ s^{-1}$
R7	k_7	1[a]	$M^{-1}\ s^{-1}$

where, k_i is initiation reaction rate constant,
k_p is propagation reaction rate constant, and
k_t is termination reaction rate constant.

a: Salvador et al. (1995).
b: Kancheva and Kasaikina (2012).

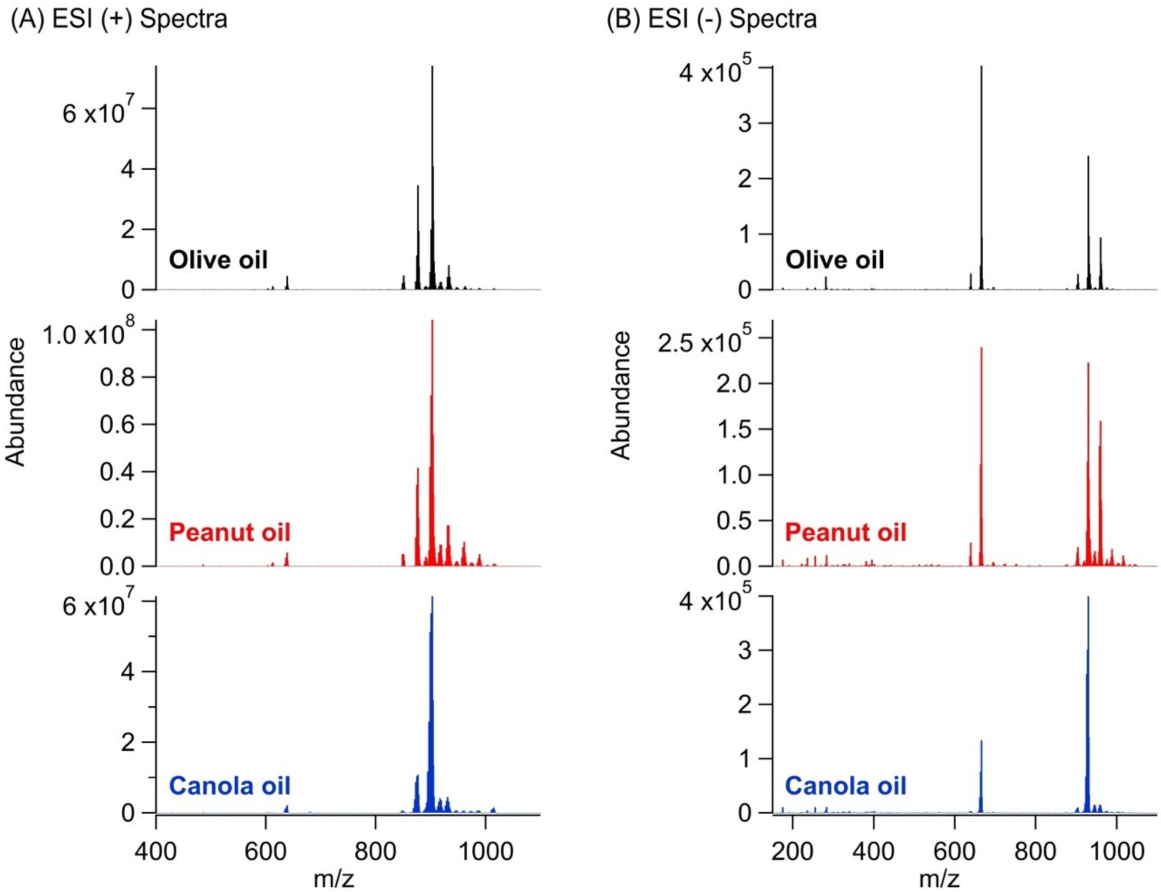


Figure S1. Composition of different triacylglycerols present in fresh oil as measured by ESI-MS in positive ionization mode (panel A) and negative ionization mode (panel B). The ion signals are 2 orders of magnitude higher in the positive mode, and there is very little fragmentation, allowing us to use the $[M+NH_4]^+$ signals to estimate TAG fractions in Table 1.

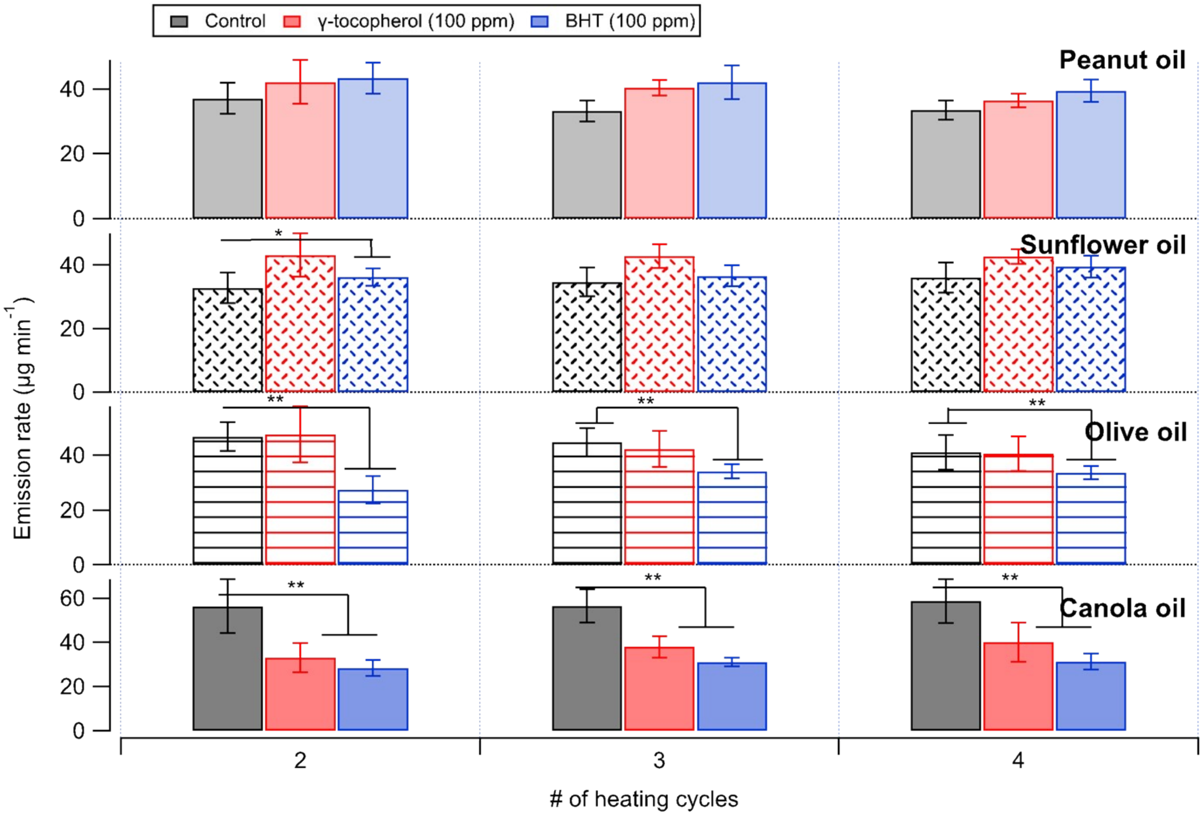
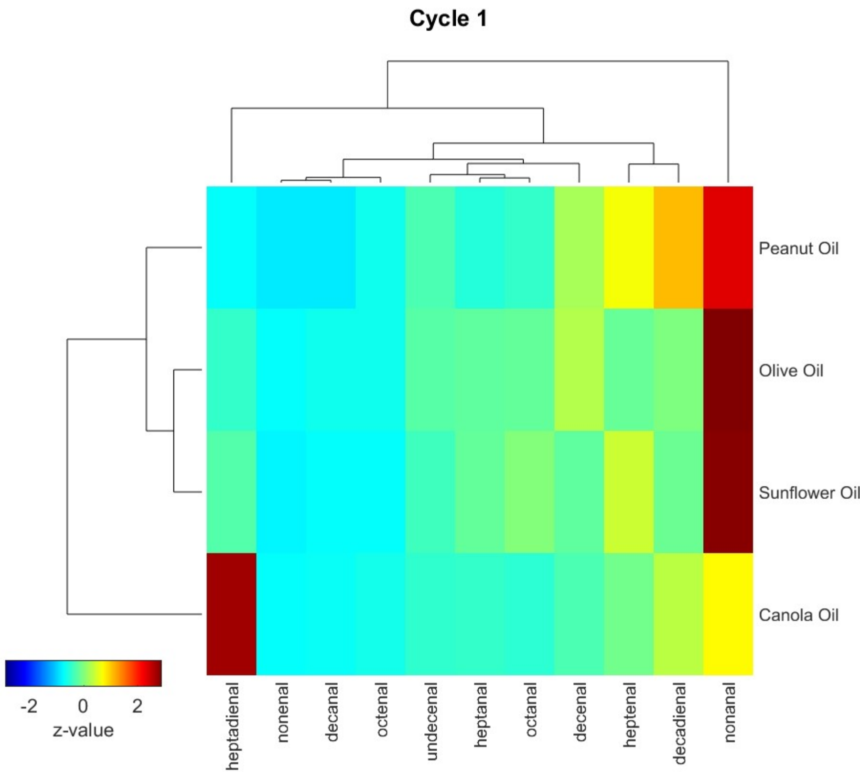
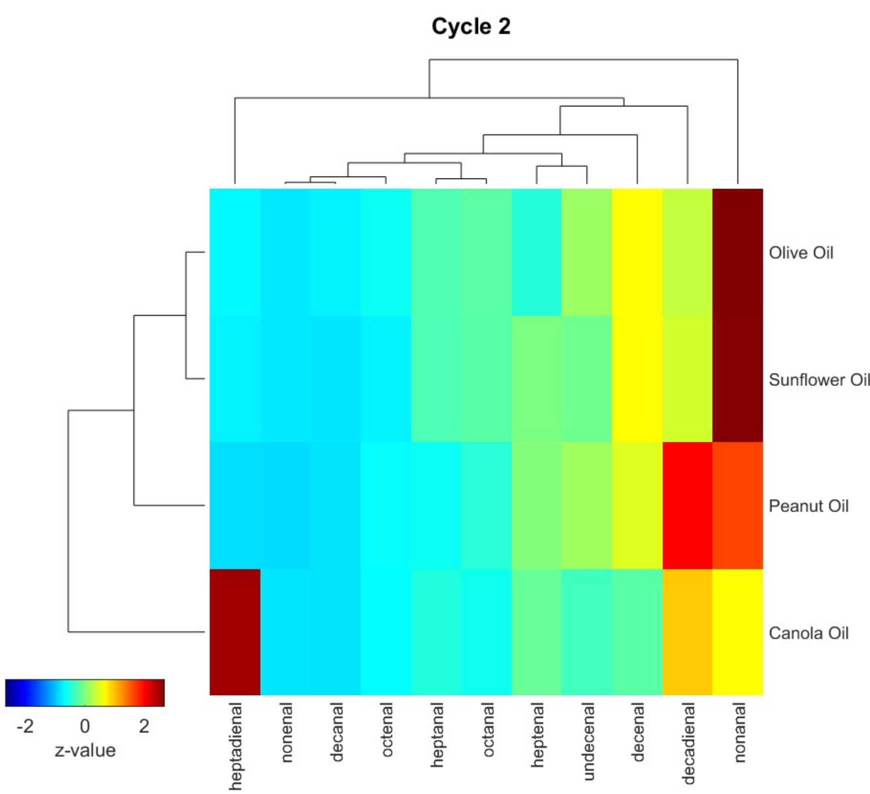


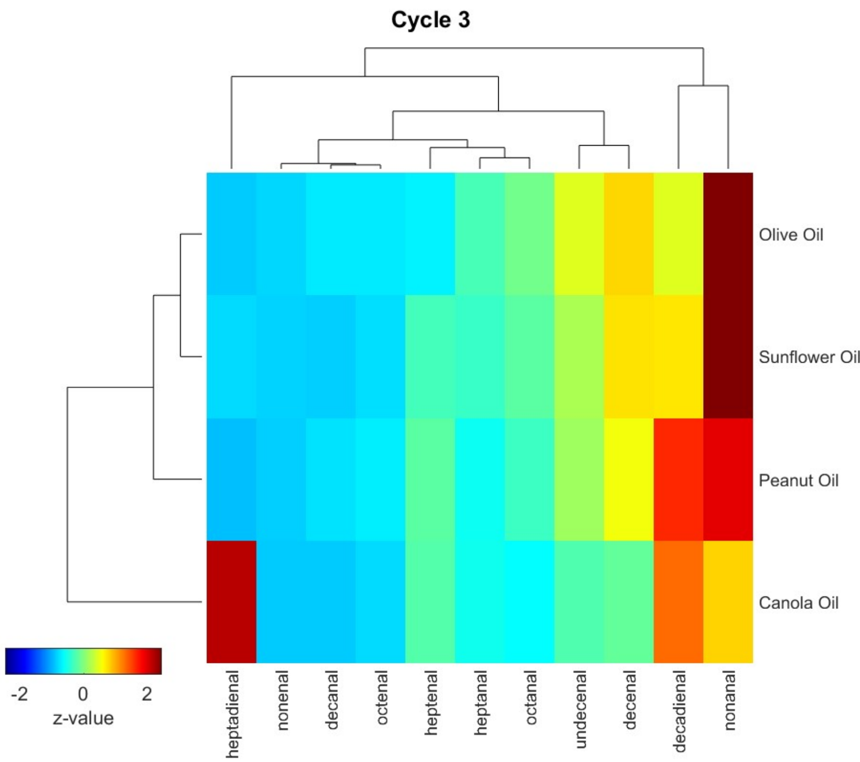
Figure S2. Emission rates of total aldehydes in presence and absence of antioxidants from heating cycles 2 through 4. * denotes $p < 0.05$, and ** denotes $p < 0.005$.


Cycle 1
Peanut Oil
Olive Oil
Sunflower Oil
Canola Oil
heptadienal
nonenal
decanal
octenal
undecenal
heptanal
octanal
decenal
heptenal
decadienal
nonanal
-2
0
2
z-value

42


Cycle 2
Olive Oil
Sunflower Oil
Peanut Oil
Canola Oil
heptadienal
nonenal
decanal
octenal
heptanal
octanal
heptenal
undecenal
decenal
decadienal
nonanal
-2
0
2
z-value

43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Olive Oil
Sunflower Oil
Peanut Oil
Canola Oil
heptadienal
nonenal
decanal
octenal
heptenal
heptanal
octanal
undecenal
decenal
decadienal
nonanal
-2
0
2
z-value

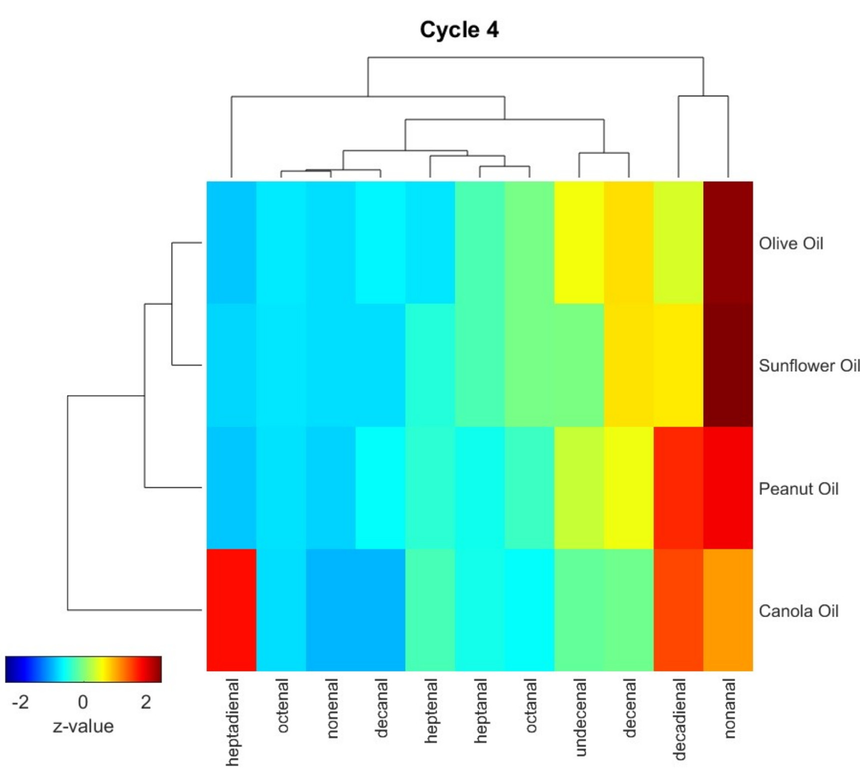

Cycle 4
Olive Oil
Sunflower Oil
Peanut Oil
Canola Oil
heptadienal
octenal
nonenal
decanal
heptenal
heptanal
octanal
undecenal
decenal
decadienal
nonanal
-2
0
2
z-value

Figure S3. Hierarchical clustering analysis (HCA) performed on aldehydes from cycles 1 through 4 shows that canola oil is significantly different from olive, sunflower and peanut oil which are shown to cluster together. Canola oil emissions are significantly higher in 2,4-heptadienal, while olive, sunflower and peanut oil produces nonanal in highest concentrations suggesting that the type of TAGs in cooking oils play an important role in determining its emission profile.

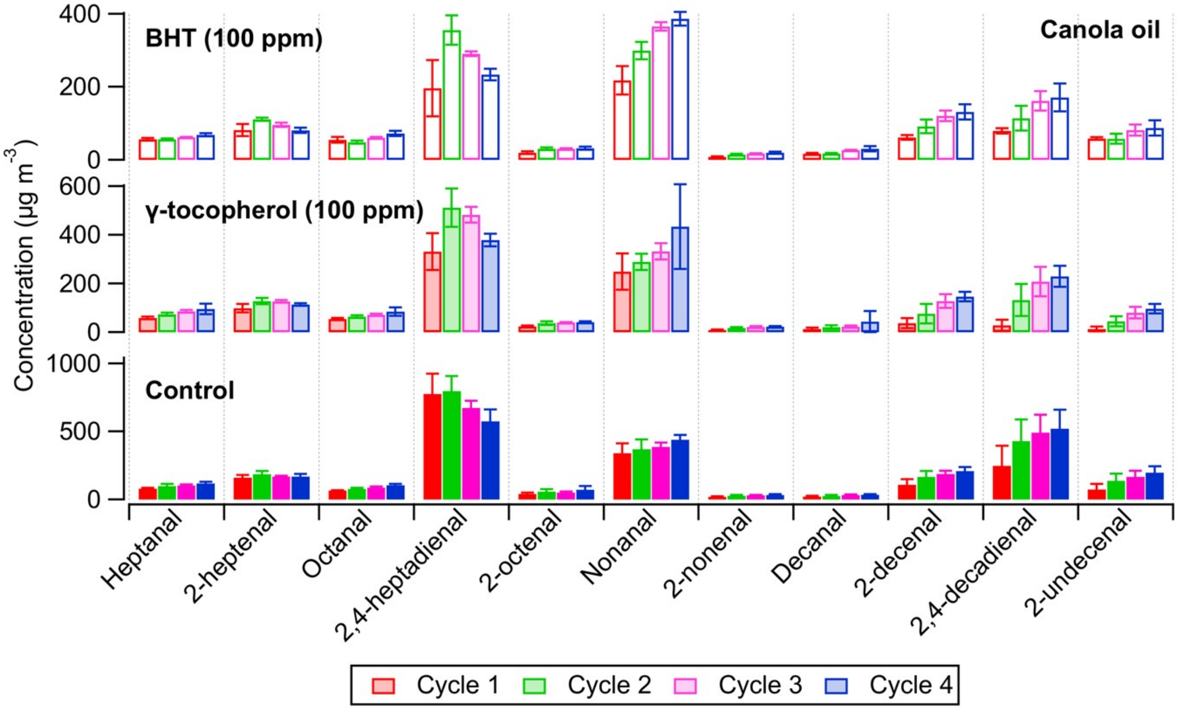


Figure S4. Concentration of aldehydes measured during canola oil autoxidation. Significant decrease in aldehyde emissions were observed upon addition of γ-tocopherol and BHT. 2,4-heptadienal showed highest emissions of all the aldehydes quantified. With repeated heating of canola oil, smaller aldehydes tended to drop, while aldehydes >C8 showed an increase in concentrations.

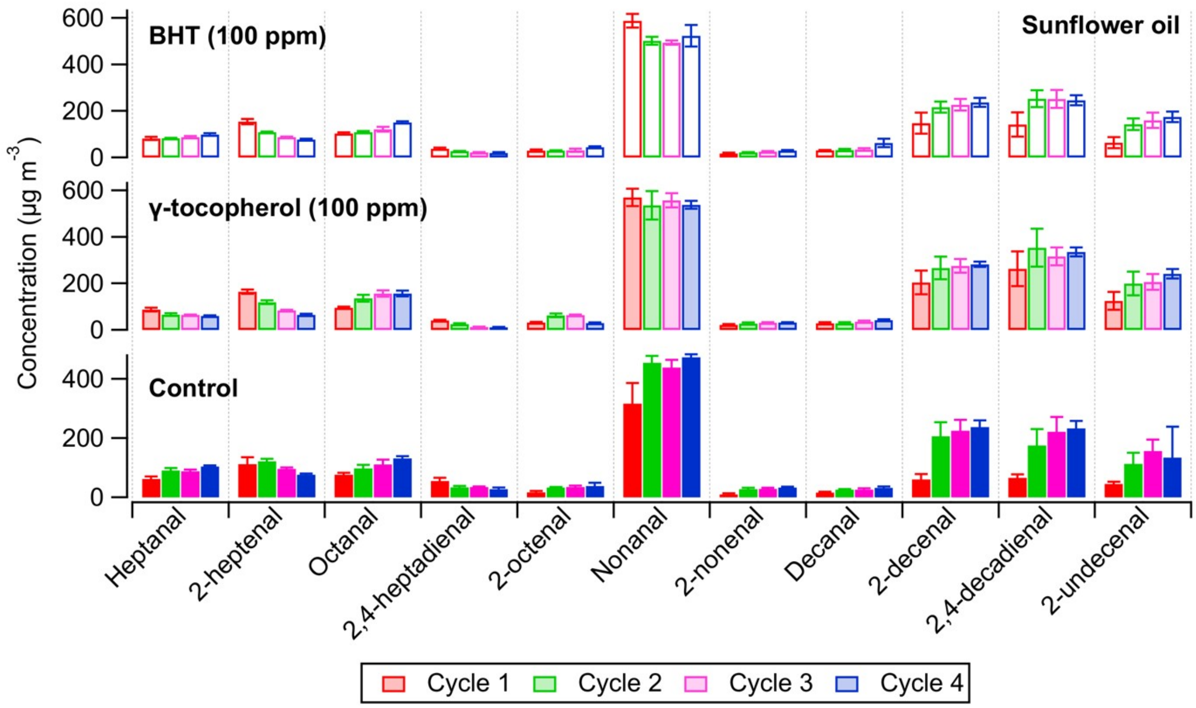


Figure S5. Concentration of aldehydes measured during sunflower oil autoxidation. Increase in aldehyde emissions were observed upon addition of γ-tocopherol and BHT. Nonanal showed highest emissions of all the aldehydes quantified. Aldehydes with <C8 showed a decline in concentrations, while aldehydes having >C8 showed an increase in concentrations upon repeated heating of oil.

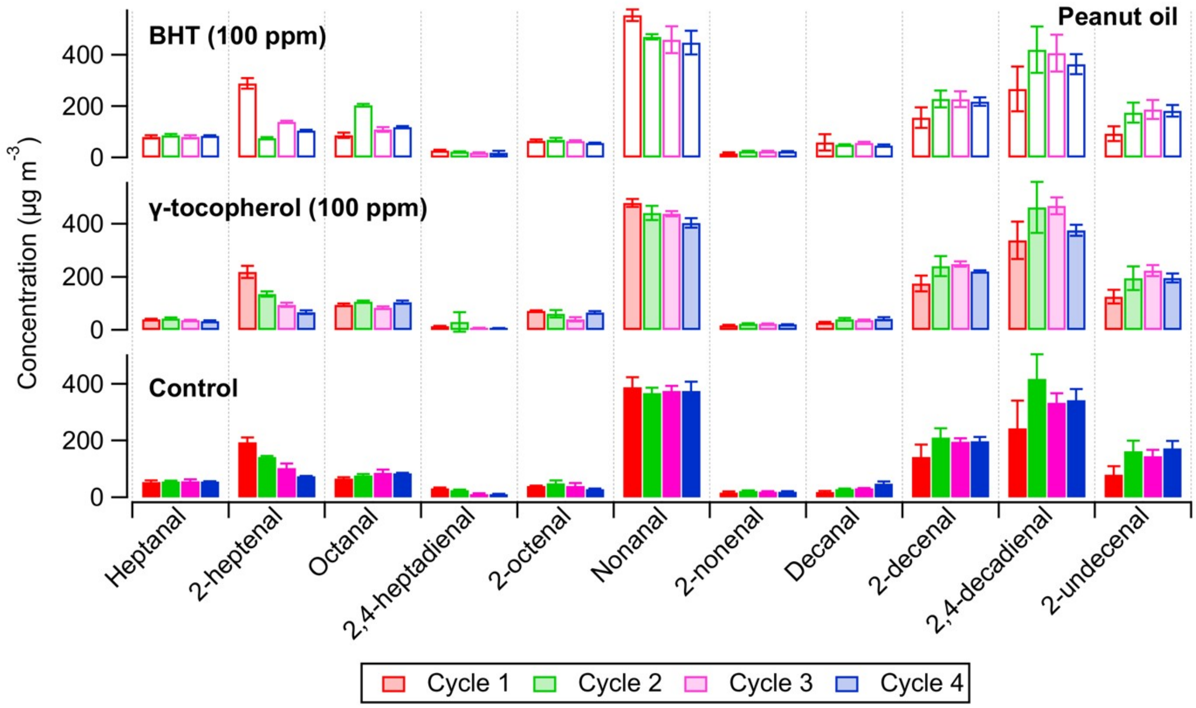


Figure S6. Concentration of aldehydes measured during peanut oil autoxidation. Increase in aldehyde emissions were observed upon addition of γ-tocopherol and BHT. Peanut oil showed a similar trend to sunflower oil in emission pattern of aldehydes with repeated heating of oil.

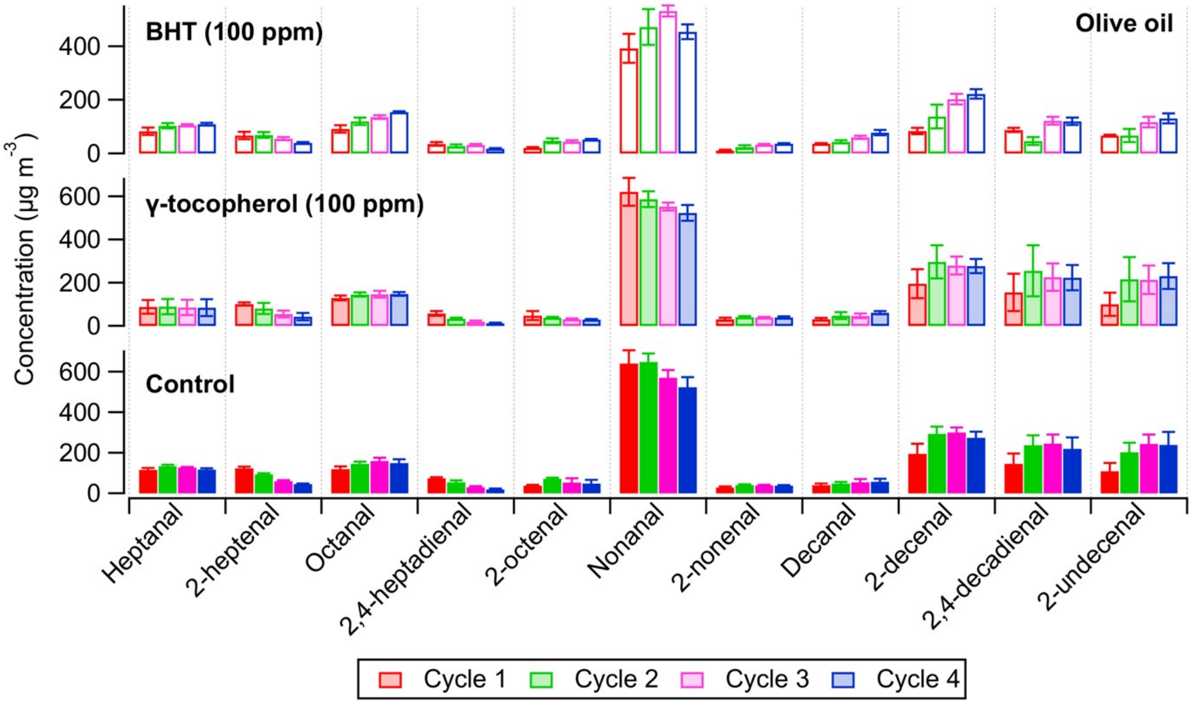


Figure S7. Concentration of aldehydes measured during olive oil autoxidation. No significant change in aldehyde concentrations was observed in presence of γ-tocopherol, while aldehyde concentrations declined in presence of BHT. Similar to sunflower and peanut oil, nonanal was found to be emitted in highest quantities. Aldehydes >C8 showed an increase in concentrations upon repeated heating of oil.

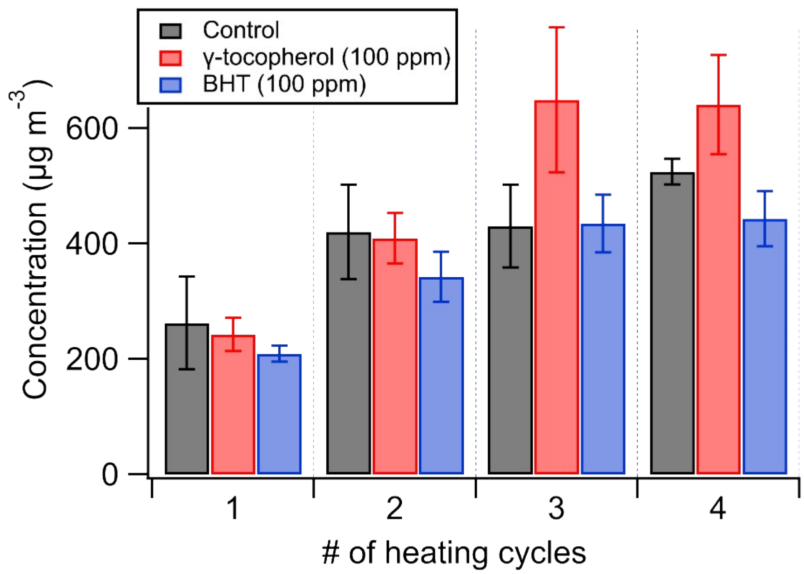
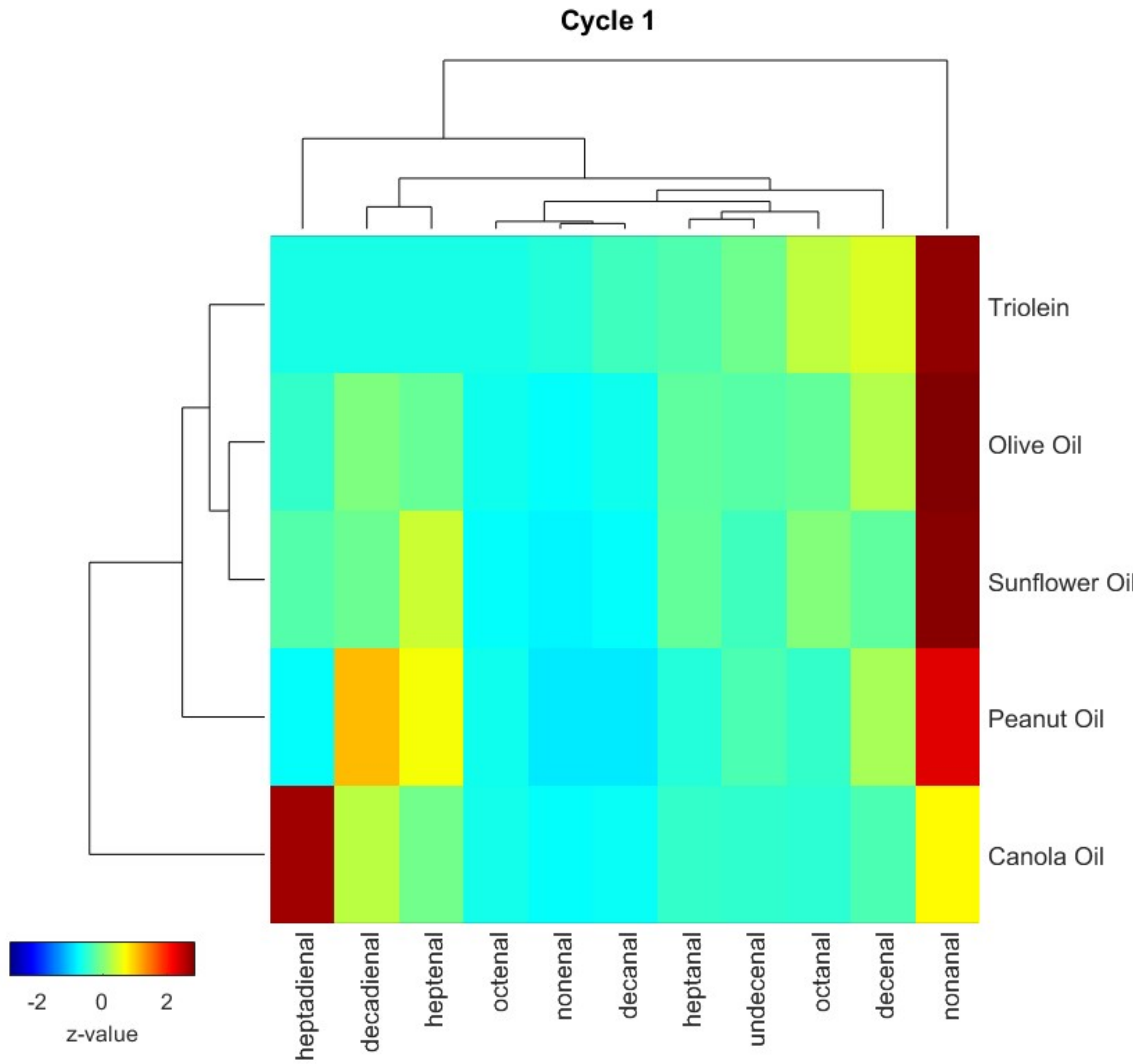
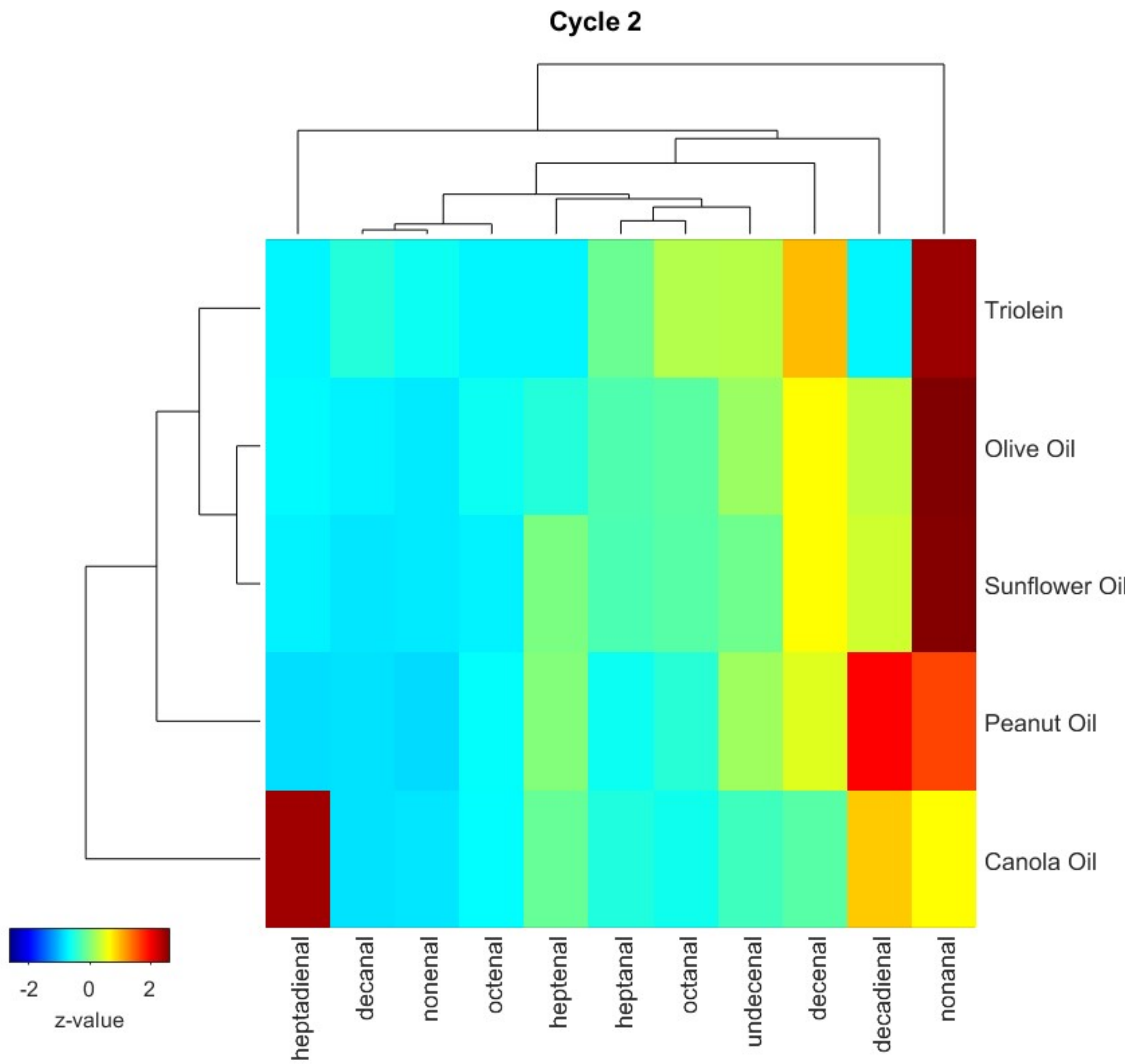


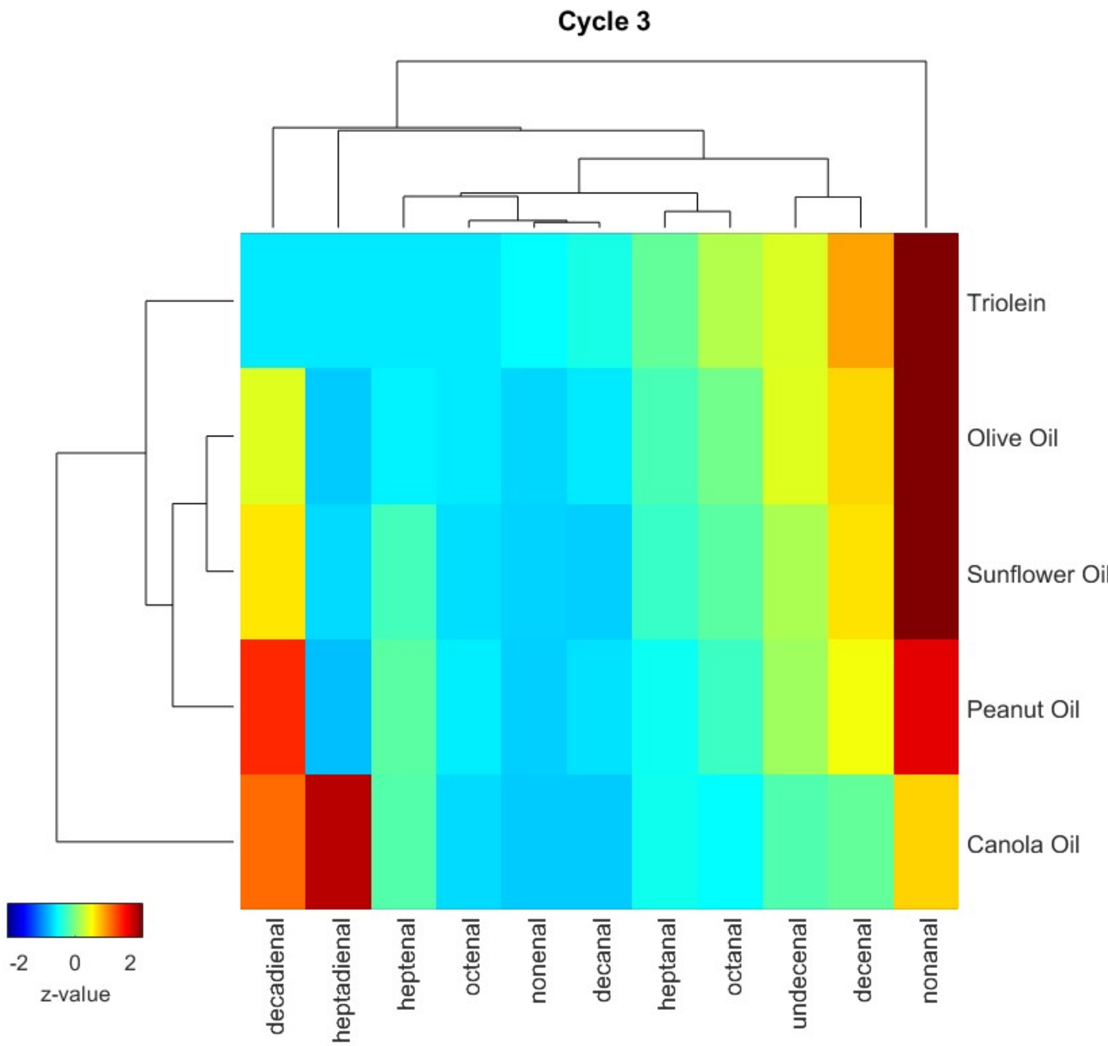
Figure S8. Concentration of total aldehydes emitted in presence and absence of antioxidants upon triolein heating at 170 °C. The aldehydes emissions increased in presence of γ-tocopherol, while they declined in presence of BHT fairly consistent with that of olive, peanut and sunflower oil suggesting that the type of TAGs in these are similar to triolein.


Cycle 1
Triolein
Olive Oil
Sunflower Oil
Peanut Oil
Canola Oil
heptadienal
decadienal
heptenal
octenal
nonenal
decanal
heptanal
undecenal
octanal
decenal
nonanal
-2
0
2
z-value



Cycle 2
Triolein
Olive Oil
Sunflower Oil
Peanut Oil
Canola Oil
heptadienal
decanal
nonenal
octenal
heptenal
heptanal
octanal
undecenal
decenal
decadienal
nonanal
-2
0
2
z-value

91


Cycle 3
Triolein
Olive Oil
Sunflower Oil
Peanut Oil
Canola Oil
-2
0
2
z-value
decadienal
heptadienal
heptenal
octenal
nonenal
decanal
heptanal
octanal
undecenal
decenal
nonanal

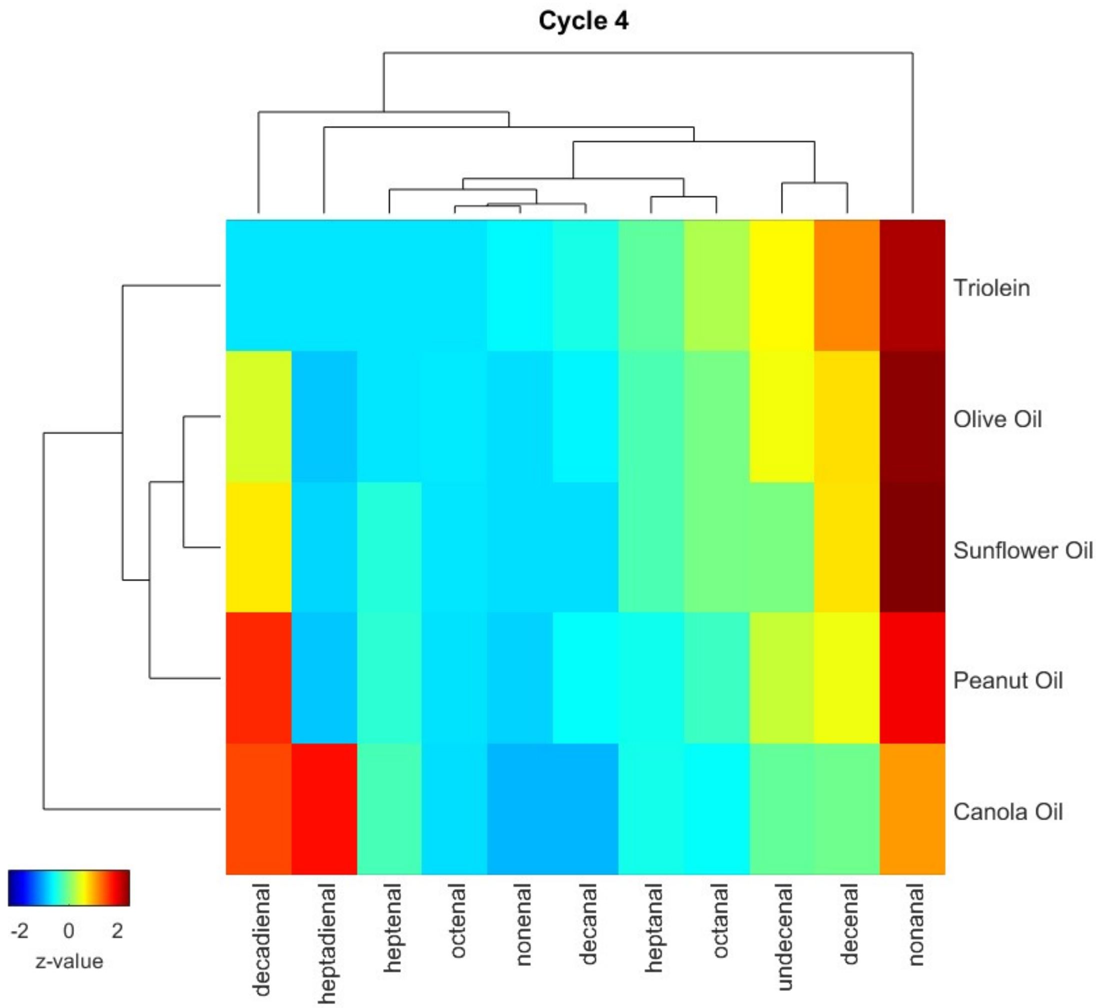
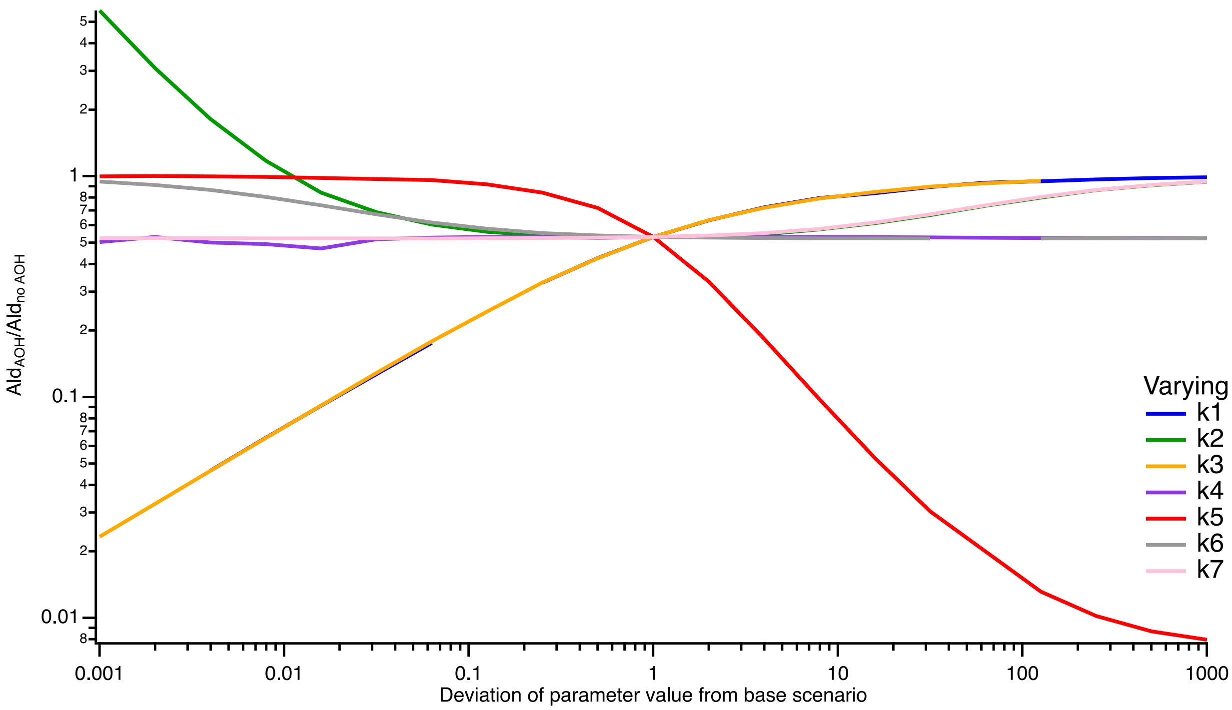


Figure S9. HCA performed on aldehydes emitted from triolein and cooking oils used in this study. HCA shows that oils containing higher fraction of stable TAGs cluster together with triolein suggesting that the type of TAGs present in oils are important in determining their emission profile. Furthermore, cluster analysis is consistent with repeated heating cycle of oils and triolein from cycle 1 through cycle 4.

(a)



(b)

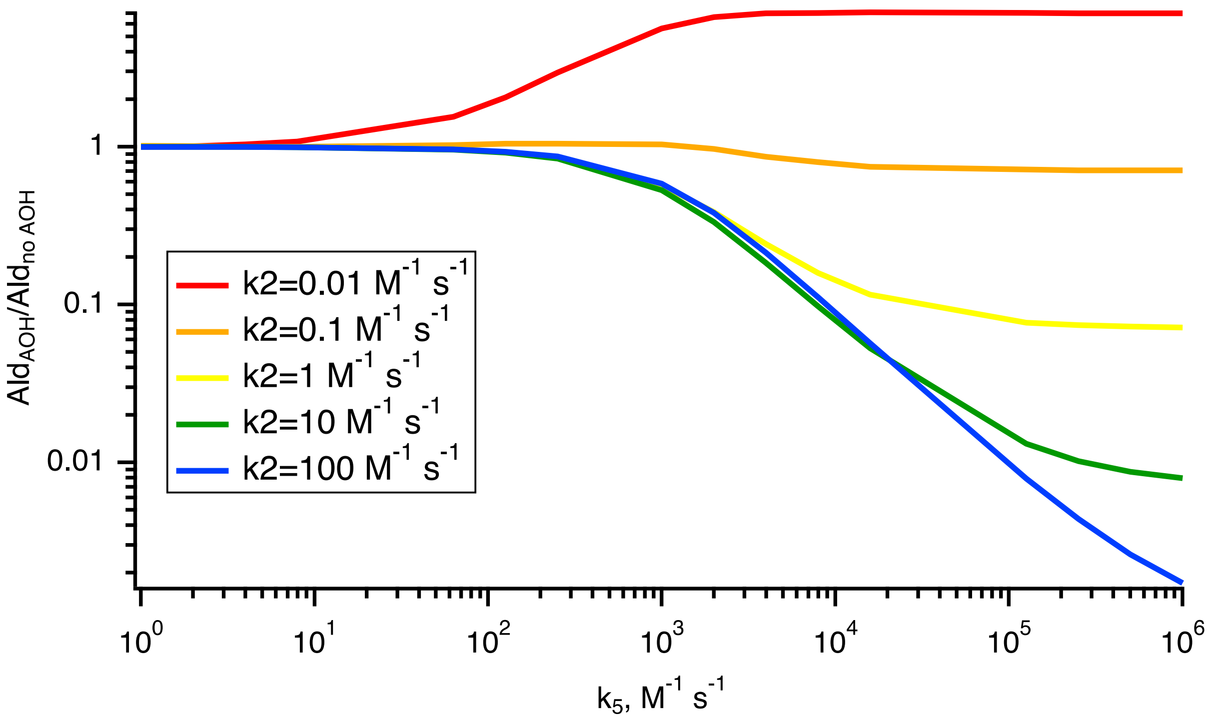


Figure S10. (a) Ratio of aldehydes with antioxidants to without antioxidants for varying values of rate constants. The rate constants k_2 and k_5 shows the greatest effect aldehydes concentration upon addition of antioxidants. (b) Ratio of aldehydes with antioxidants to without antioxidants as a function of k_5 for different k_2.

References

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