Supporting Information

for

Occurrences of the typical agricultural nonionic surfactants tristyrylphenol ethoxylates in cherries (*Cerasus pseudocerasus*), peaches (*Amygdalus persica*), and kiwifruit (*Actinidia Chinensis*) and the implications of human exposure in China

Jie Zhou [a, b], Chunmei Li [b], Zejun Jiang [b], Lufang Wang [b], Hang Su [b], Hui Li [b], Chao Deng [b], Qi Wang [b], Jing Wang [b], Fen Jin [b,*], Ruyan Hou [a,*]

[a] State Key Laboratory of Tea Plant Biology and Utilization, International Joint Laboratory on Tea Chemistry and Health Effects, School of Tea and Food Science &Technology, Anhui Agricultural University, Anhui Province Key Lab of Analysis and Detection for Food Safety, Hefei 230036, PR China

[b] Key Laboratory of Agro-Product Quality and Safety, Institute of Quality Standard and Testing Technology for Agro-Products, Chinese Academy of Agricultural Sciences, Beijing 100081, China.

* Corresponding authors:

Fen Jin

E-mail: jinfenbj@163.com; Tel: +86–10–8210–6570

Ruyan Hou

E-mail: hry@ahau.edu.cn

Text S1 The calculation of the consumption of different fruits

At present, the dietary consumption data of cherries, peaches, and kiwifruit in China is not available. The consumption data of different fruits were calculated based on the yield, processing consumption, the amount of fresh fruit exported, the rate of storage loss, the number of days of concentrated consumption and the number of people in China. Fruit yield data was obtained from China's yield data from Food and Agriculture Organization of the United Nations (FAO). Fruit processing consumption, the rate of storage loss and the number of days of concentrated consumption are reported in the literatures [1-2]. The amount of fresh fruit exported was obtained from the export data of China Customs Information Network from January to December 2016. The population of China is 1.38 billion in terms of the national population in 2016.

According to China's peach yield (14469004 t), processing consumption (13%), the amount of fresh fruit exported (73466.435 t), the rate of storage loss (40%), the number of days of concentrated consumption (120 d) in 2016 and the total population of China in 2016 (1.38 billion), the daily average peach consumption of Chinese residents was converted to 0.045 kg. According to China's kiwifruit yield (2390287 t), processing consumption (10%), the amount of fresh fruit exported (4133.415 t), the rate of storage loss (25%), the number of days of concentrated consumption (150 d) in 2016 and the total population of China in 2016 (1.38 billion), the daily average kiwifruit consumption of Chinese residents was converted to 0.0078 kg. According to the literature [3], the per capita cherry consumption in China is 374 g. And the concentrated consumption days is 150 d. Therefore, the daily average cherry consumption of Chinese residents was calculated to be 0.0025 kg。

Table S1 Sources and quantities of fruit samples collected from the main growing areas in China from 2016 to 2017.

Location	cherry		peach		kiwifruit		Total
	2016	2017	2016	2017	2016	2017	
A	20	20	20	5	----	----	65
B	15	20	10	----	----	----	45
C	15	10	10	10	----	----	45
D	----	----	20	20	----	10	50
E	----	----	15	----	20	30	65
F	----	----	10	10	25	20	65
G	----	----	6	----	----	----	6
H	----	10	----	----	----	----	10
I	----	----	----	10	----	----	10
Total	110		146		105		361

Table S2 Names, retention times (RT, min), and MS/MS parameters for TSPnEOs.

No.	Compound	MW	Retention time (min)	Adduct ion	MRM transitions*	Q1 pre bias (V)	CE (V)	Q3 pre bias (V)
1	TSP1EO	450.26	1.708	$[M+NH_4]^+$	**468.4>105.2**	-23	-29	-17
					468.4>269.1	-23	-14	-41
2	TSP2EO	494.28	1.739	$[M+NH_4]^+$	**512.4>105.1**	-28	-39	-29
					512.4>183.2	-24	-21	-32
3	TSP3EO	538.31	1.765	$[M+NH_4]^+$	**556.4>105.1**	-20	-41	-17
					556.4>227.3	-26	-21	-23
4	TSP4EO	582.33	1.866	$[M+NH_4]^+$	**600.4>105.1**	-29	-46	-17
					600.4>271.3	-27	-26	-44
5	TSP5EO	626.36	1.813	$[M+NH_4]^+$	**644.5>105.1**	-32	-50	-38
					644.2>419.3	-27	-23	-47
6	TSP6EO	670.39	1.968	$[M+NH_4]^+$	**688.5>105.2**	-35	-63	-44
					688.5>567.4	-35	-20	-41
7	TSP7EO	714.41	2.145	$[M+NH_4]^+$	**732.5>105.1**	-35	-55	-27
					732.5>611.3	-35	-17	-33
8	TSP8EO	758.44	2.378	$[M+NH_4]^+$	**776.6>105.1**	-29	-33	-47
					776.6>551.4	-29	-25	-38
9	TSP9EO	802.47	2.666	$[M+NH_4]^+$	**820.6>105.1**	-32	-60	-41
					820.6>329.2	-41	-30	-14
10	TSP10EO	846.49	3.046	$[M+NH_4]^+$	**864.7>105.1**	-44	-65	-41
					864.7>89.1	-26	-38	-14
11	TSP11EO	890.52	3.498	$[M+NH_4]^+$	**908.7>105.2**	-31	-59	-17
					908.7>177.0	-35	-31	-10
12	TSP12EO	934.54	3.923	$[M+NH_4]^+$	**952.7>105.1**	-38	-65	-23
					952.7>89.0	-40	-46	-14
13	TSP13EO	978.57	4.305	$[M+NH_4]^+$	**996.7>105.1**	-38	-65	-17
					996.7>329.3	-29	-36	-20
14	TSP14EO	1022.60	4.703	$[M+NH_4]^+$	**1040.8>105.1**	-41	-61	-17
					1040.8>89.3	-32	-51	-38
15	TSP15EO	1066.62	5.136	$[M+NH_4]^+$	**1084.8>105.1**	-32	-64	-17
					1084.8>89.1	-32	-45	-35
16	TSP16EO	1110.65	5.532	$[M+NH_4]^+$	**1128.8>105.1**	-44	-65	-17
					1128.8>133.1	-44	-38	-47
17	TSP17EO	1154.68	5.887	$[M+2NH_4]^{2+}$	**595.6>105.2**	-30	-22	-42
					595.6>89.2	-30	-29	-34
18	TSP18EO	1198.70	6.266	$[M+2NH_4]^{2+}$	**617.6>105.2**	-24	-23	-16
					617.6>89.2	-24	-31	-36
19	TSP19EO	1242.73	6.640	$[M+2NH_4]^{2+}$	**639.6>105.2**	-42	-26	-32
					639.6>89.2	-38	-31	-14
20	TSP20EO	1286.75	6.910	$[M+2NH_4]^{2+}$	**661.7>105.2**	-26	-40	-40
					661.7>89.2	-34	-33	-34

21	TSP21EO	1330.78	7.198	$[M+2NH_4]^{2+}$	**683.7>105.2**	-26	-38	-14
					683.7>89.2	-26	-33	-34
22	TSP22EO	1374.81	7.524	$[M+2NH_4]^{2+}$	**705.7>105.2**	-32	-37	-40
					705.7>89.2	-36	-34	-32
23	TSP23EO	1418.83	7.850	$[M+2NH_4]^{2+}$	**727.7>105.1**	-28	-44	-16
					727.7>89.2	-28	-35	-34
24	TSP24EO	1462.86	8.169	$[M+2NH_4]^{2+}$	**749.8>105.1**	-38	-55	-16
					749.8>89.1	-28	-35	-14
25	TSP25EO	1506.89	8.540	$[M+2NH_4]^{2+}$	**771.8>105.1**	-38	-48	-16
					771.8>89.2	-38	-36	-36
26	TSP26EO	1550.91	8.882	$[M+2NH_4]^{2+}$	**793.8>105.1**	-30	-52	-16
					793.8>89.2	-30	-36	-34
27	TSP27EO	1594.94	9.205	$[M+2NH_4]^{2+}$	**815.9>105.1**	-42	-54	-16
					815.9>89.2	-32	-37	-14
28	TSP28EO	1638.96	9.556	$[M+2NH_4]^{2+}$	**837.9>105.2**	-32	-49	-31
					837.9>89.2	-32	-38	-20
29	TSP29EO	1682.99	9.901	$[M+2NH_4]^{2+}$	**859.9>105.1**	-32	-50	-41
					859.9>89.2	-32	-42	-35
30	TSP30EO	1727.02	10.199	$[M+2NH_4]^{2+}$	**881.9>105.1**	-44	-51	-41
					881.9>89.2	-44	-40	-35

Note: * Quantifier transition in bold

Table S3 Frequency of detection and concentrations of pesticides in cherry samples.

Pesticides	Frequency of detection	concentrations (mg/kg)			
		Mean	Median	Min	Max
Carbendazim	63.64%	0.0763	0.0421	0.0006	0.3363
Tebuconazole	32.73%	0.0626	0.0331	0.0008	0.2505
Thiophanate	31.82%	0.1521	0.0298	0.0008	3.2190
Buprofezin	19.09%	0.0079	0.0029	0.0004	0.0592
Imidacloprid	17.27%	0.0615	0.0154	0.0011	0.7220
Difenoconazole	13.64%	0.0905	0.0113	0.0020	0.9783
Cypermethrin	13.64%	0.0404	0.0145	0.0019	0.1349
Acridine	12.73%	0.0076	0.0021	0.0004	0.0330
Cyhalothrin	11.82%	0.0241	0.0120	0.0009	0.1029
Emamectin benzoate	10.91%	0.0011	0.0006	0.0002	0.0055
Isocarbazide	8.18%	0.0605	0.0509	0.0021	0.1271
Procymidone	7.27%	0.0265	0.0018	0.0010	0.1915
Cypermethrin	7.27%	0.0171	0.0034	0.0010	0.1015
Spiroester	6.36%	0.1713	0.0125	0.0036	1.0153
Avermectin	4.55%	0.0117	0.0038	0.0015	0.0423
Bifenthrin	3.64%	0.0291	0.0318	0.0018	0.0509
Prochloraz	3.64%	0.1335	0.0628	0.0067	0.4017
Diflubenzuron	3.64%	0.0692	0.0290	0.0252	0.1934
Fenvalerate	3.64%	0.1031	0.1107	0.0091	0.1820
Chlorpyrifos	2.73%	0.0047	0.0022	0.0012	0.0106
Deltamethrin	2.73%	0.0095	0.0054	0.0041	0.0191
Pyridaben	1.82%	0.0733	0.0733	0.0577	0.0888
Fluorosilazole	1.82%	0.0010	0.0010	0.0006	0.0014
Carbide	1.82%	0.0347	0.0347	0.0016	0.0677
Chlorothalonil	0.91%	0.0200	0.0200	0.0200	0.0200
Nitrile azole	0.91%	0.1271	0.1271	0.1271	0.1271
Malathion	0.91%	0.0014	0.0014	0.0014	0.0014
Azoxystrobin	0.91%	0.0015	0.0015	0.0015	0.0015
Thiamethoxam	0.91%	0.0381	0.0381	0.0381	0.0381
Triazophos	0.91%	0.0308	0.0308	0.0308	0.0308
Amphetamine	0.91%	0.0494	0.0494	0.0494	0.0494
Dimethomorph	0.91%	0.0012	0.0012	0.0012	0.0012
Oxazol	0.91%	0.0020	0.0020	0.0020	0.0020

Table S4 Frequency of detection and concentrations of pesticides in peach samples.

Pesticides	Frequency of detection	concentrations (mg/kg)			
		Mean	Median	Min	Max
Carbendazim	60.29%	0.4259	0.2401	0.0019	8.3867
Imidacloprid	47.06%	0.0873	0.0796	0.0013	0.3960
Pyridaben	41.18%	0.0405	0.0331	0.0013	0.2297
Chlorpyrifos	38.97%	0.1114	0.0501	0.0010	0.4121
Acridine	36.03%	0.1429	0.1393	0.0006	0.3744
Spiroester	32.35%	0.0342	0.0309	0.0008	0.1370
Difenoconazole	30.15%	0.0317	0.0281	0.0003	0.1588
Fenvalerate	24.26%	0.0501	0.0395	0.0021	0.2675
Emamectin benzoate	19.85%	0.0157	0.0169	0.0008	0.0395
Chlorbenzuron	18.38%	0.0643	0.0592	0.0111	0.1814
Tebuconazole	17.65%	0.0898	0.0102	0.0012	0.5427
Cyhalothrin	16.91%	0.0807	0.0752	0.0083	0.2132
Cypermethrin	12.50%	0.1210	0.0450	0.0057	0.6514
Dimethomorph	12.50%	0.0419	0.0039	0.0006	0.2330
Endosulfan	11.76%	0.0285	0.0250	0.0010	0.0682
Profenofos	9.56%	0.1477	0.1300	0.0007	0.4499
Flucythrinate	8.09%	0.0254	0.0154	0.0043	0.0679
Buprofezin	6.62%	0.1228	0.0561	0.0070	0.5602
Bifenthrin	5.88%	0.0263	0.0233	0.0116	0.0550
Prochloraz	5.88%	0.4244	0.2519	0.0314	1.2938
Fenpropathrin	5.15%	0.2832	0.0301	0.0170	1.4224
Thiophanate	4.41%	0.3520	0.0124	0.0011	1.5410
Krut	4.41%	0.4698	0.2519	0.0314	1.2938
Pyrimethanil	4.41%	0.0368	0.0260	0.0109	0.0856
Propiconazole	3.68%	0.2189	0.0187	0.0105	1.0187
Pyridaben	3.68%	0.2109	0.0912	0.0561	0.5602
Fluorosilazole	3.68%	0.2989	0.1097	0.0070	1.1097
Fipronil	2.94%	0.0092	0.0092	0.0057	0.0126
Nitrile azole	2.94%	0.8518	0.6182	0.0854	2.0854
Azoxystrobin	2.94%	0.0148	0.0111	0.0010	0.0360
Phoxim	2.94%	0.0471	0.0456	0.0275	0.0698
Pyraclostrobin	2.21%	0.0088	0.0101	0.0030	0.0132
Avermectin	1.47%	0.0477	0.0477	0.0153	0.0801
Method	1.47%	0.5444	0.5444	0.0444	1.0444
Thiamethoxam	1.47%	0.0035	0.0035	0.0010	0.0060
Cumulus	1.47%	0.6454	0.6454	0.1454	1.1454

Chlorothalonil	0.74%	0.0014	0.0014	0.0014	0.0014
Malathion	0.74%	0.0695	0.0695	0.0695	0.0695
Triazophos	0.74%	0.0025	0.0025	0.0025	0.0025
Insecticide	0.74%	0.0217	0.0217	0.0217	0.0217
Azathioprine	0.74%	0.0020	0.0020	0.0020	0.0020

Table S5 Frequency of detection and concentrations of pesticides in kiwifruit samples.

Pesticides (mg/kg)	Frequency of detection	concentrations (mg/kg)			
		Mean	Media	Min	Max
Tebufenozide	32.63%	0.0778	0.0301	0.0070	0.2350
Carbendazim	24.21%	0.0188	0.0096	0.0012	0.1175
Tebuconazole	18.95%	0.0178	0.0109	0.0006	0.0609
acetamiprid	13.68%	0.0044	0.0030	0.0008	0.0175
Chlorpyrifos	13.68%	0.0200	0.0070	0.0020	0.1127
Azoxystrobin	13.68%	0.0122	0.0066	0.0011	0.0516
Myclobutanil	11.58%	0.0213	0.0018	0.0003	0.1684
Difenoconazole	9.47%	0.0744	0.0319	0.0065	0.2760
Imidacloprid	9.47%	0.0503	0.0143	0.0057	0.1534
Pyraclostrobin	8.42%	0.0482	0.0281	0.0100	0.1317
Pyridaben	8.42%	0.0108	0.0118	0.0024	0.0178
Malathion	8.42%	0.0222	0.0179	0.0027	0.0492
Trifloxystrobin	7.37%	0.0129	0.0091	0.0062	0.0244
Pyridyl	6.32%	0.0606	0.0102	0.0019	0.2969
Propiconazole	5.26%	0.0524	0.0127	0.0060	0.1480
Pyrimethanil	5.26%	0.0154	0.0100	0.0018	0.0451
Procymidone	4.21%	0.0254	0.0108	0.0050	0.0750
Thiophanate	3.16%	0.0879	0.0755	0.0404	0.1479
Cypermethrin	3.16%	0.0748	0.0265	0.0113	0.1865
Prochloraz	3.16%	0.0152	0.0076	0.0058	0.0323
Dicofol	3.16%	0.0391	0.0434	0.0230	0.0508
Fenthion	2.11%	0.0484	0.0484	0.0168	0.0800
Profenofos	2.11%	0.0012	0.0012	0.0011	0.0013
Fluorosilazole	2.11%	0.0004	0.0004	0.0003	0.0004
Metalaxyl	2.11%	0.0033	0.0033	0.0003	0.0063
Bifenthrin	2.11%	0.0442	0.0442	0.0240	0.0643
Thiamethoxam	2.11%	0.0097	0.0097	0.0084	0.0109
Cyhalothrin	2.11%	0.0160	0.0160	0.0144	0.0176
Chlorothalonil	1.05%	0.0550	0.0550	0.0550	0.0550
Dibutyl ether urea	1.05%	0.0001	0.0001	0.0001	0.0001
Nitrile azole	1.05%	0.0126	0.0126	0.0126	0.0126
Carbide	1.05%	0.0045	0.0045	0.0045	0.0045
Buprofezin	1.05%	0.0265	0.0265	0.0265	0.0265
Isoprocarb	1.05%	0.0006	0.0006	0.0006	0.0006

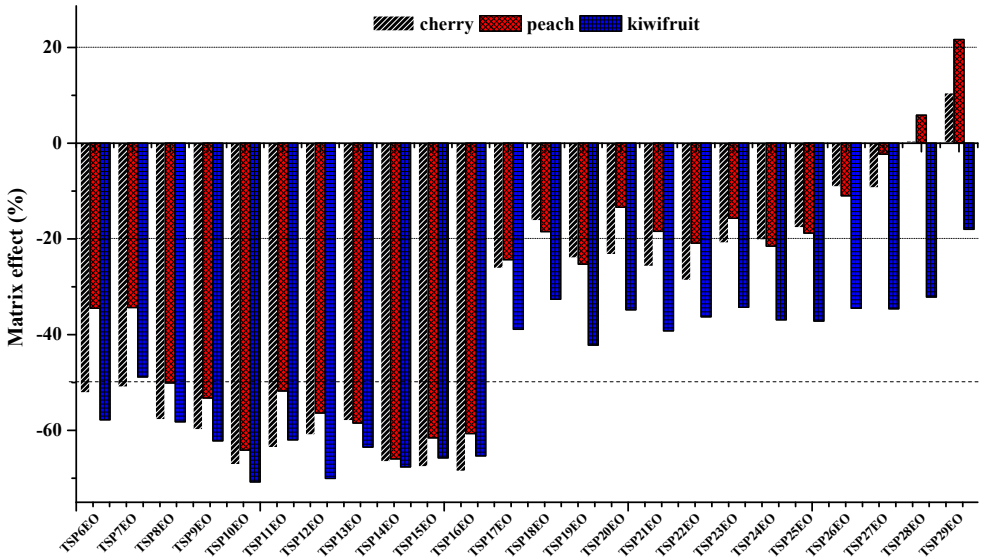

Figure S1 ME values for TSPEO oligomers (n = 6-29) in cherry, peach and kiwifruit samples.

References

1. Nie, J.; Yan, L.; Li, Z., Selenium content and dietary exposure assessment of main deciduous fruit trees in China. *Chinese Agricultural Sciences* **2015,** *48* (15), 3015-3026.

2. Wang, D.; Pan, D.; Hua, X., Risk assessment of dietary intake of peach pesticide residues. *Anhui Agricultural Sciences* **2016,** *44* (21), 126-130.

3. Huang, S.; Liu, C.; Li, M.; Zhao, G.; Li, Y., The development trend of sweet cherry industry at home and abroad in the past 20 years and its prediction for the future. *Journal of Fruit Science* **2014,** *31*, 1-6.