Supporting Information

for

Evaluating a tap water contamination incident attributed to oil contamination by non-targeted screening strategies

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Table S1. Name, structure and retention time of model NA compounds in UPLC-QTOF-MS analysis.

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Reference

Chemicals and reagents.

Fourteen naphthenic acids (NAs) and three oxidized NAs (oxy-NAs) were used as model compounds for analysis of NA mixtures: 4-n-propylcyclohexanecarboxylic acid (*cis*- and *trans*-) ($C_{10}H_{18}O_2$), *trans*-4-pentylcyclohexane carboxylic acid ($C_{12}H_{22}O_2$), 12-oxochenodeoxycholic acid ($C_{24}H_{38}O_5$), cyclohexanecarboxylic acid ($C_7H_{12}O_2$), 1-pyrenebutyric acid ($C_{20}H_{16}O_2$), abietic acid ($C_{20}H_{30}O_2$), 1-adamantaneacetic acid ($C_{12}H_{18}O_2$), 2-hexyldecanoic acid ($C_{16}H_{32}O_2$) and 12-hydroxysteric acid ($C_{18}H_{36}O_3$) were purchased from TCI (Tokyo Chemical Industry Co., Tokyo, Japan); 1,2,3,4-tetrahydro-2-naphthoic acid ($C_{11}H_{12}O_2$), dicyclohexylacetic acid ($C_{14}H_{24}O_2$), 5-beta-cholanic acid ($C_{24}H_{40}O_2$), cyclohexane pentanoic acid ($C_{11}H_{20}O_2$) and 12-hydroxydodecanoic acid ($C_{12}H_{24}O_3$) were purchased from Sigma Aldrich (Oakville, ON, Canada); 1-methyl-1-cyclohexane carboxylic acid ($C_8H_{14}O_2$) was purchased from Alfa Aesar (Ward Hill, MA); *trans*-4-tert-butylcyclohexanecarboxylic acid ($C_{11}H_{20}O_2$) was purchased from Acros Organics (Morris Plains, NJ); 1-adamantane carboxylic acid ($C_{11}H_{16}O_2$) was purchased from J&K Chemical (Beijing, China). The commercial mixture of NAs and redistilled 2-pentene were from Acros Organics. Eleven polycyclic aromatic hydrocarbons (PAHs) standard including phenanthrene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indene benzene pyrene, benzo[ghi]perylene and dibenz[a,h]anthracene were purchased from Organic Standards Solutions International Smart Solution. Two surrogate standards of d-phenanthrene, d-chrysene, and four alkylated PAHs standards of 3-methylphenanthrene, 9-methylphenanthrene, methylpyrene, 4-methyldibenzothiophene were from Anpel

Laboratory Technologies (China). Methanol, ethyl acetate (EA), phenixin (CCl_4) n-hexane and dichloromethane (DCM) were obtained from Fisher Chemicals (Fair Lawn, NJ). HPLC grade ammonium acetate and formic acid were purchased from Dima Technology TNC (USA). Hydrochloric acid, bromine and ammonia were purchased from Beijing chemicals. Distilled water was prepared by a Milli-Q Synthesis water purification system (Millipore, Bedford, MA, USA).

Sample analysis of PAHs and alkyl-PAHs.

500 mL of water spiked with 25 ng of surrogate standards was extracted through an Oasis MAX cartridge. The sorbent of MAX cartridge is synthesized from the reversed-phase Oasis HLB copolymer and features two retention mechanisms: anion exchange and reversed phase. This makes the cartridge suitable for simultaneous extractions of PAHs and other charged compounds in water samples. 6 mL of methanol, 12 mL of ethyl acetate and 6 mL of n-hexane/DCM (2:1, v/v) were used to elute the analytes. The elutes were mixed, dried and redissolved in 0.1 mL of hexane and the injection volume was 1 μL for analyses by a GC-EI-MS detector (Shimadzu QP 2010 plus). The methods for GC/MS analyses has been reported previously.[1] Chromatographic separation was achieved on a HB-5MS capillary column (30 m × 0.32 mm × 0.25 μm film thickness). The carrier gas was helium at a constant flow rate of 1.0 mL/min. A splitless injector was used and held at 290 °C. The temperature program was from 50 °C (2 min) to 300 °C (20 min) at the rate of 5 °C/min. The interface and ion temperatures were maintained at 150 and 230 °C, respectively. The method detection limits (MDL) for individual PAHs and alkylated PAHs isomers were determined to be 0.04-1.9 ng/L in water samples. The efficiencies of the sample preparation procedure was

assessed by analyzing water samples spiked with standard solutions of PAHs and alkyl-PAHs. Recoveries of PAHs and alkylated PAHs in triplicate spiked samples were 58-72% and 73-87%, respectively.

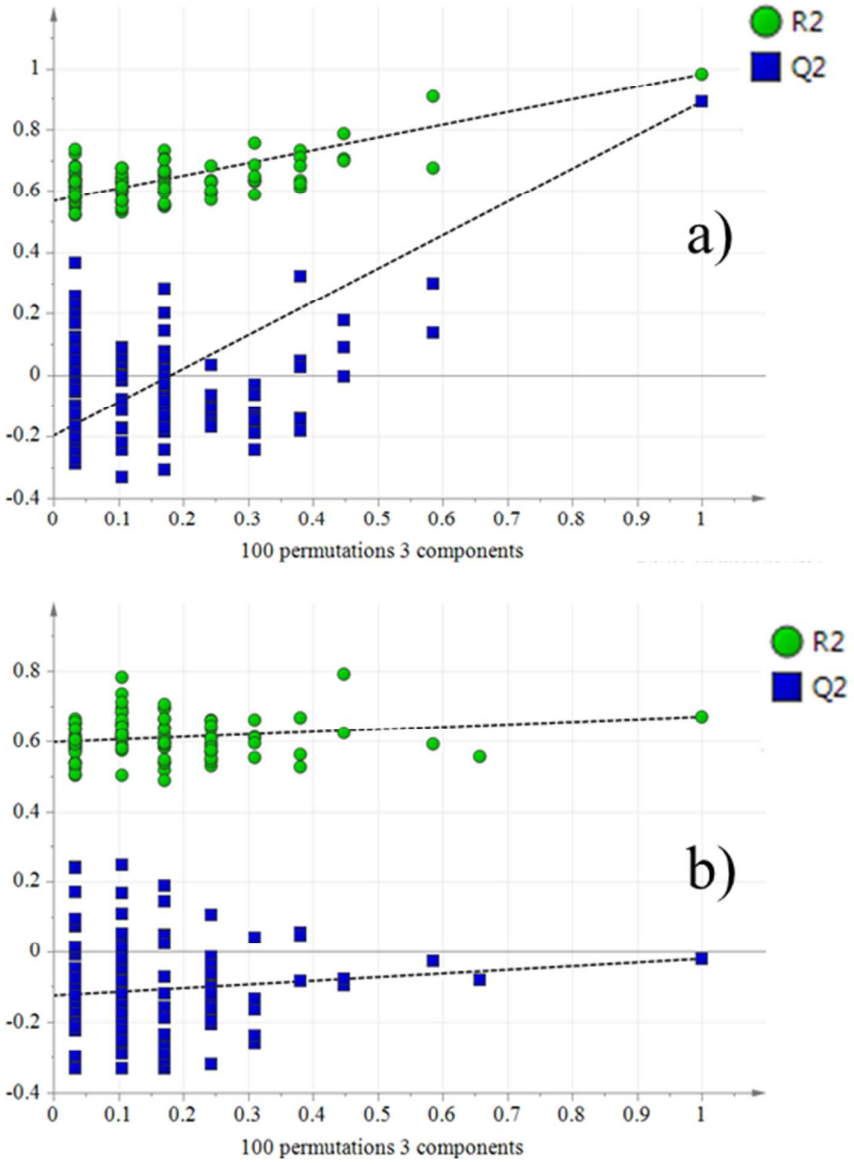


Figure S1. Validation plots obtained from 100 permutation tests by non-targeted analysis in tap water samples from the polluted period (a) and the non-pollution period (b).

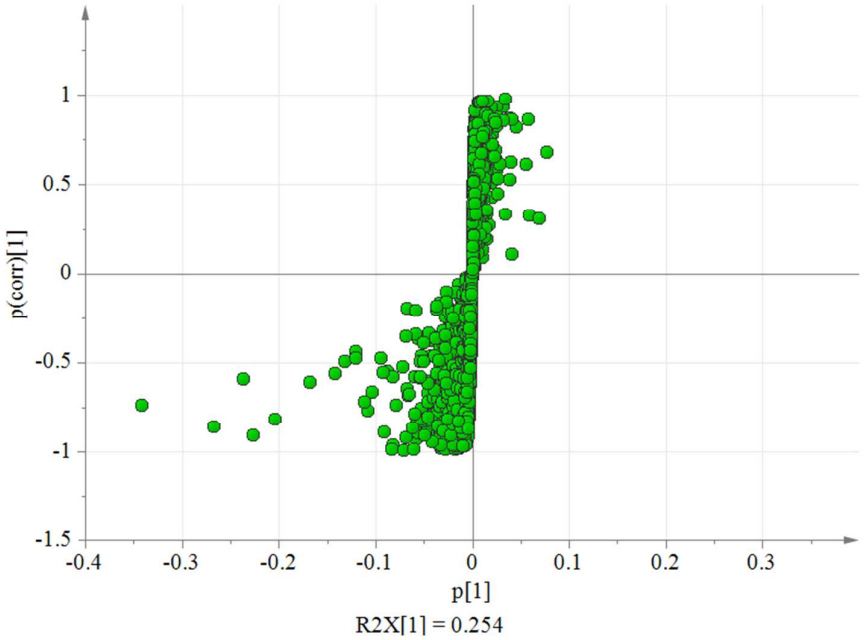


Figure S2. S-plots of OPLS-DA based on UPLC-QTOFMS spectra of water samples from polluted and reference regions during the event.

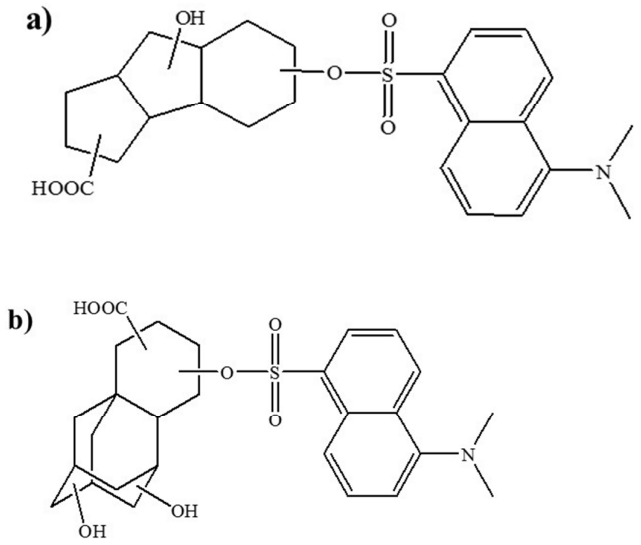


Figure S3. The proposed structures of $C_{13}H_{20}O_4$+$C_{12}H_{11}NO_2S$ a) and $C_{15}H_{22}O_5$+$C_{12}H_{11}NO_2S$ b), of which the mass spectrum are shown in Figure 3e and 3f, respectively.

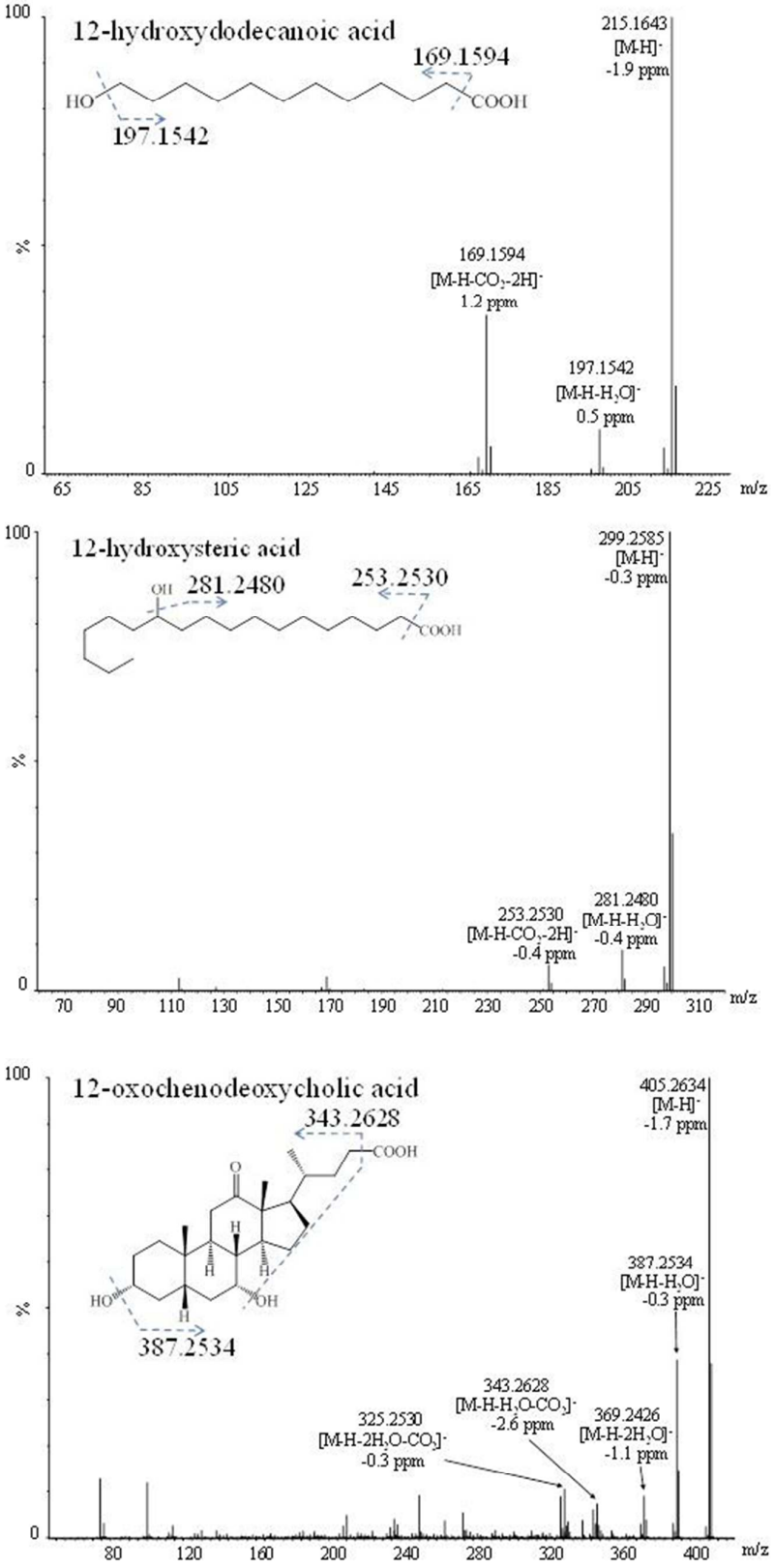
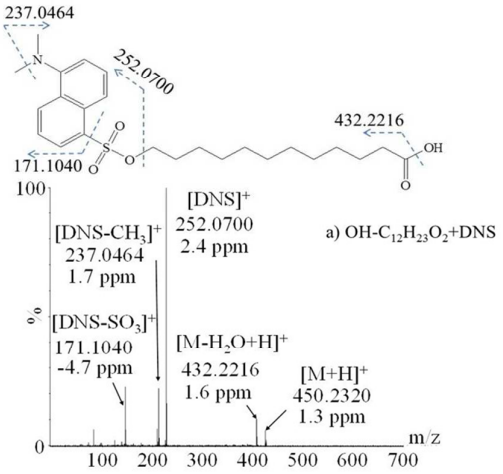
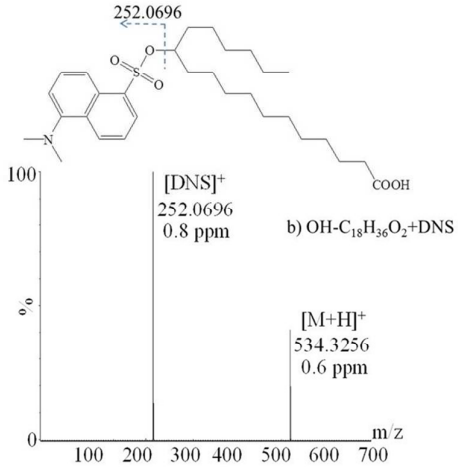


Figure S4. MS/MS spectra of model compounds of oxy-NAs.

12-hydroxydodecanoic acid derivatives



12-hydroxysteric acid derivatives



12-oxochenodeoxycholic acid derivatives

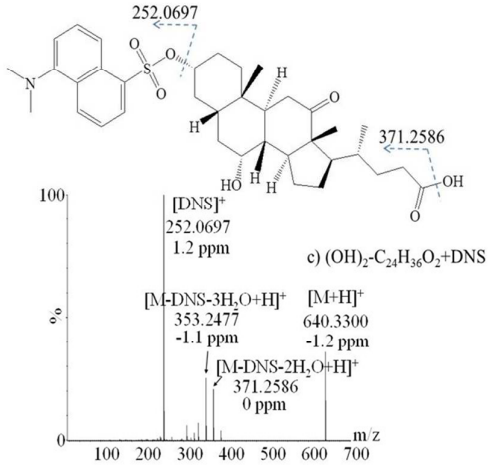


Figure S5. MS/MS spectra of model oxy-NAs derivatized with DNS.

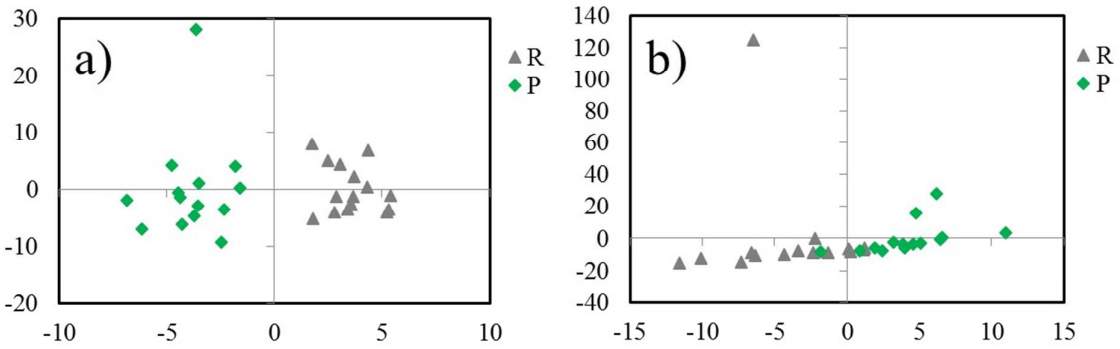


Figure S6. The score plots of OPLS-DA model by targeted analysis of NA mixtures in tap water samples from the polluted period (a) and the non-pollution period (b).

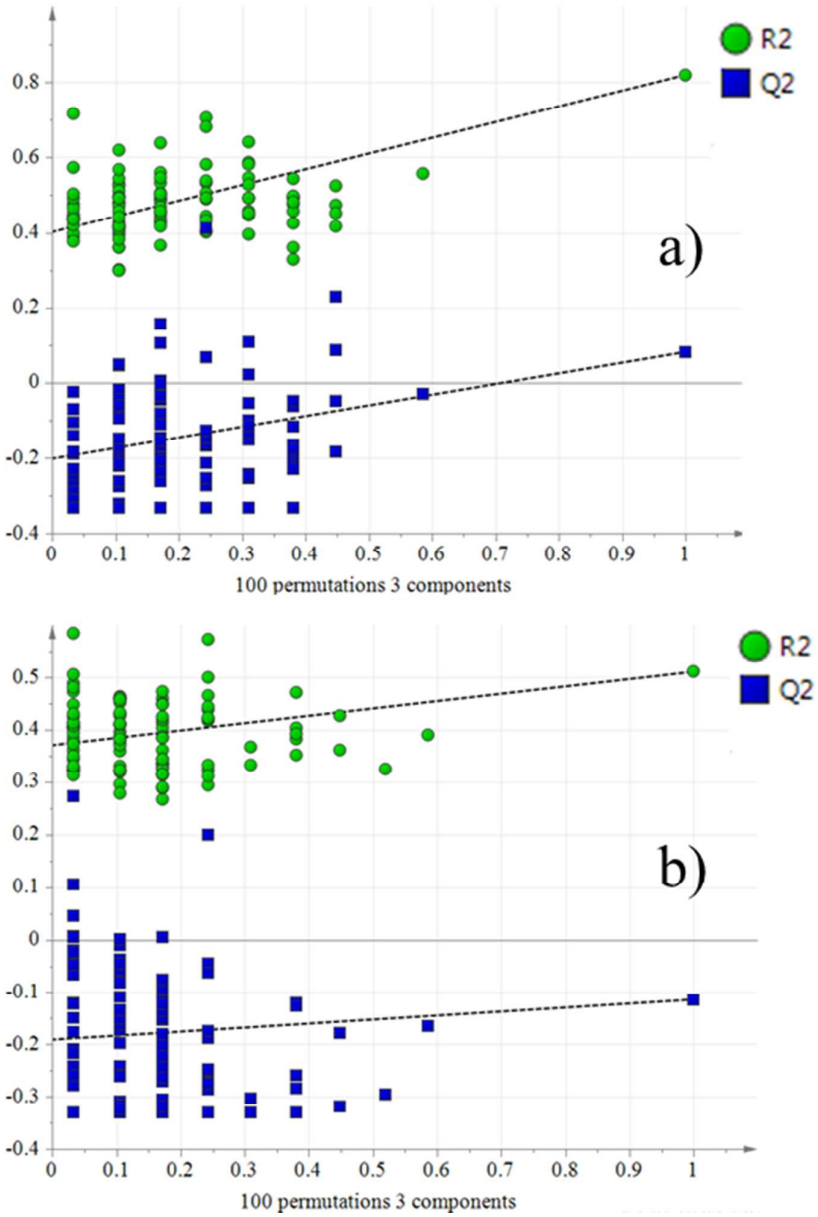
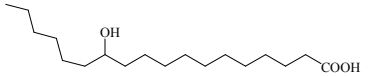
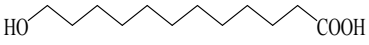
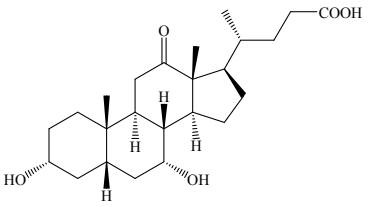
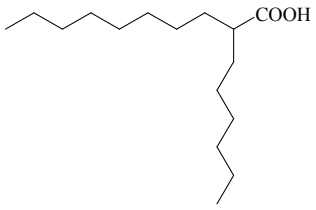
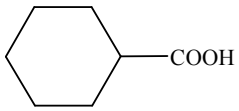
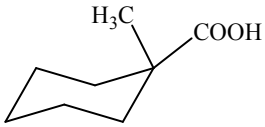
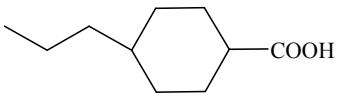
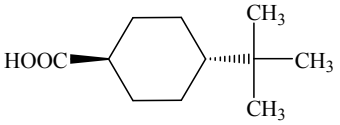
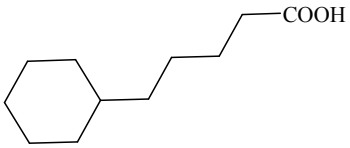


Figure S7. Validation plots obtained from 100 permutation tests by targeted analysis in tap water samples from the polluted period (a) and the non-pollution period (b).

Table S1. Name, structure and retention time of model NA compounds in UPLC-QTOF-MS analysis.

Name	CAS No.	Molecular Weight	RT (min)	Structure
12-hydroxysteric acid	106-14-9	$C_{12}H_{24}O_3$, MW= 300.2664	9.32	
12-hydroxydodecanoic acid	505-95-3	$C_{18}H_{36}O_3$, MW= 216.1725	4.87	
12-oxochenodeoxycholic acid	2458-08-4	$C_{24}H_{38}O_5$, MW= 406.2719	4.44	
2-hexyldecanoic acid	25354-97-6	$C_{16}H_{32}O_2$, MW= 256.2402	11.05	
cyclohexanecarboxylic acid	98-89-5	$C_7H_{12}O_2$, MW= 128.0837	3.31	
1-Methyl-1-cyclohexane carboxylic acid	1123-25-7	$C_8H_{14}O_2$, MW= 142.0994	4.18	
trans-4-tert-butylcyclohexanecarboxylic acid(*cis*- and *trans*-mixture)	943-29-3	$C_{10}H_{18}O_2$ (cis- and trans-), MW= 170.1307	5.05; 5.23	
trans-4-tert-butylcyclohexanecarboxylic acid	5962-88-9	$C_{11}H_{20}O_2$-butyl, MW= 184.1463	5.34	
cyclohexane pentanoic acid	943-29-3	$C_{11}H_{20}O_2$, MW= 184.1463	5.84	

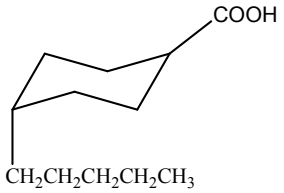
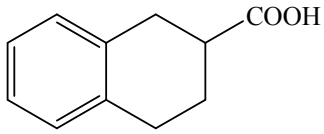
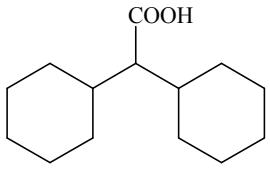
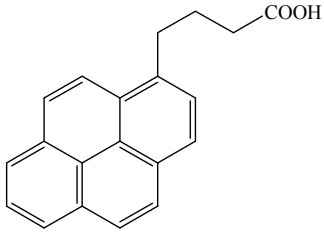
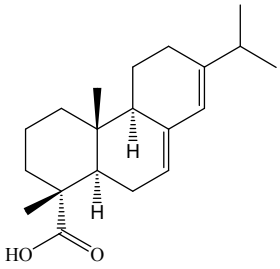
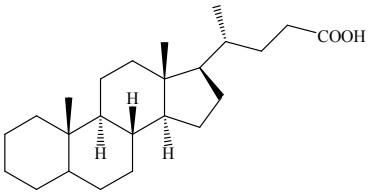
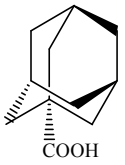
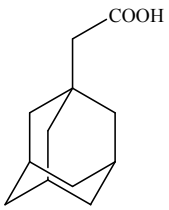
trans-4-pentylcyclohexane carboxylic acid	38289-29-1	$C_{12}H_{22}O_2$, MW= 198.1620	7.00	
1,2,3,4-tetrahydro-2-naphthoic acid	53440-12-3	$C_{11}H_{12}O_2$, MW= 176.0837	3.97	
2,2-dicyclohexylacetic acid	52034-92-1	$C_{14}H_{24}O_2$, MW= 224.1776	7.88	
1-pyrenebutyric acid	3443-45-6	$C_{20}H_{16}O_2$, MW= 288.1150	6.25	
abietic acid	514-10-3	$C_{20}H_{30}O_2$, MW= 302.2246	10.98	
5-beta-cholanic acid	546-18-9	$C_{24}H_{40}O_2$, MW= 360.3028	12.95	
1-adamantane carboxylic acid	828-51-3	$C_{11}H_{16}O_2$, MW= 180.1150	4.70	
1-adamantaneacetic acid	4942-47-6	$C_{12}H_{18}O_2$, MW= 194.1307	4.98	

Table S2. Concentrations of detected PAHs and alkyl-PAHs in the tap water samples (ng/L) collected during the Lanzhou the “4.11” tap water pollution event and the non-pollution period.

	Pollution period					Non-pollution period				
	HG	CG	QLH	AN	XG	HG	CG	QLH	AN	XG
phenanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
fluoranthene	5.5 ± 2.2	6 ± 1	10.5 ± 11.6	10.2 ± 9.5	4.3 ± 3.9	1.6 ± 1.3	2 ± 0.7	2.9 ± 1.6	1.4 ± 0.6	3.7 ± 2.5
pyrene	2.7 ± 1.1	2.3 ± 0.6	5.4 ± 5.9	4.9 ± 5.2	2.6 ± 3.8	ND	ND	ND	ND	ND
chrysene	0.2 ± 0.1	0.4 ± 0.3	0.5 ± 0.8	0.4 ± 0.6	0.4 ± 0.7	0.1 ± 0.2	0.2 ± 0.3	0.1 ± 0.2	0.1 ± 0.2	3.2 ± 9.1
benzo[a]anthracene	2.3 ± 0.8	2.4 ± 2.3	1.6 ± 0.9	1.7 ± 1.2	1.4 ± 2.4	0.6 ± 0.3	0.8 ± 0.4	0.9 ± 0.6	0.9 ± 1.4	5.6 ± 14.4
benzo[b]fluoranthene	0.5 ± 0.3	0.6 ± 0.3	0.4 ± 0.2	0.3 ± 0.3	0.2 ± 0.2	0.3 ± 0.3	0.5 ± 0.5	0.2 ± 0.2	0.2 ± 0.2	1.9 ± 5.2
benzo[k]fluoranthene	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.3	0.1 ± 0.1	0.1 ± 0.1	1 ± 2.3
benzo[a]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
indene benzene pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzo[ghi]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-methylphenanthrene	1.8 ± 0.3	1.5 ± 0.5	1.7 ± 0.8	1.8 ± 1.2	ND	ND	ND	ND	ND	ND
9-methylphenanthrene	1.9 ± 0.7	1.4 ± 1.2	1.7 ± 1.3	1.3 ± 1.2	1 ± 1	ND	ND	ND	ND	ND
methylpyrene	0.2 ± 0.1	0.3 ± 0.2	0.4 ± 0.4	0.2 ± 0.1	0.3 ± 0.4	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.2	0.3 ± 0.4
4-methyldibenzothiophene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-methylindene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-methylphenanthrene	2.2 ± 0.5	1.8 ± 0.8	1.9 ± 0.8	1.9 ± 1.4	ND	ND	ND	ND	ND	ND
2-methylphenanthrene	ND	2.7 ± 1.5	3.4 ± 1.5	2.9 ± 1.7	ND	ND	ND	ND	ND	ND
4-methylphenanthrene	0.8 ± 0.2	0.8 ± 0.6	1 ± 0.8	0.8 ± 0.7	0.4 ± 0.4	ND	ND	ND	ND	ND

ND: not detected.

Reference

1. Zhao, Y.; Hong, B.; Fan, Y. Q.; Wen, M.; Han, X. Accurate analysis of polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs homologs in crude oil for improving the gas chromatography/mass spectrometry performance. *Ecotox. Environ. Safe*, **2014**, *100*, 242-250.