Adsorption of EDCs on Reclaimed Water-Irrigated Soils: A Comparative Analysis of a Branched Nonylphenol, Nonylphenol and Bisphenol A

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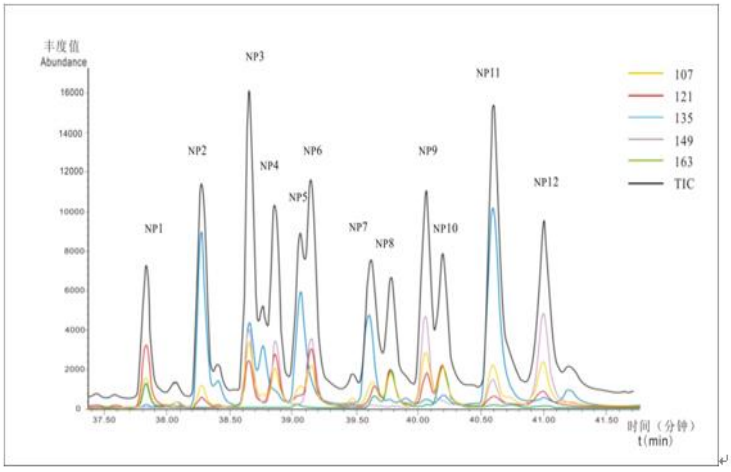
Supplementary Material

S1: Separation of NP isomers

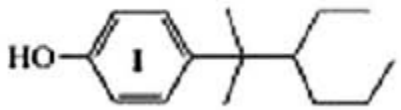
The following are the isomers of technical 4-NP isomer mixtures. There are hundreds of isomers in the mixtures, and there are 12 main isomers.



(Wang et al.,2013)

Wang SY., Liu F, Liu YL., Chen L. 2013. Determination of 12 isomers of p-nonylphenol in groundwater by gas chromatography-mass spectrometry. Chinese Journal of Analytical Chemistry,11(41) 1699- 1703

The structure of 4-NP7 (abbreviation NP7) is as below. Although the nomenclature in different publications is different, but the structure is the same (Kim et al., 2005; Saito et al., 2007; Uchiyama et al., 2008; Katase et al., 2008).



4-(3-ethyl-2-methylhexan-2-yl) phenol

Kim, YS., Katase,T., Horii, Y., Yamashita, N., Makino, M., Uchiyama, T., Fujimoto, Y., Inou. T. 2005. Estrogen equivalent concentration of individual isomer-specific 4-nonylphenol in Ariake sea water, Japan. Marine Pollution Bulletin. 51: 850–856.

Saito H, Uchiyama T, Makino M, Katase T, Fujimoto Y, Hashizume D. Optical resolution and absolute configuration of branched 4-nonylphenol isomers and their estrogenic activities. 2007. J Health Sci;53(2):177–84.

Uchiyama T, Makino M, Saito H, Katase T, Fujimoto Y. 2008. Syntheses and estrogenic activity of 4-nonylphenol isomers. Chemosphere, 73(1):S60–5.

Katase T, Okuda K, Kim YS, Eun H, Takada H, Uchiyama T, et al. 2008. Estrogen equivalent concentration of 13 branched para-nonylphenols in three technical mixtures by isomer-specific determination using their synthetic standards in SIM mode with GC–MS and two new diasteromeric isomers. Chemosphere;70(11):1961–72.

S2: Detection of dissolved organic matter (DOM)

The soil sample was air dried and passed a 0.25mm sieve. 0.05g-0.5g soil was accurately weighed and was put into a hard test tube. Then add 10.00mL 0.4mol/L potassium dichromate sulfuric acid from the automatic zero setting burette, shake well and insert a glass funnel into each tube mouth. Insert the test tubes into the wire cage one by one, and then sink the wire cage into the furnace for heating to 185 ℃ ~ 190 ℃ in oil bath pot, so that the liquid level in the tube is lower than the oil level. It is required that the oil bath temperature drop to 170 ℃ ~ 180 ℃. When the solution in the tube boils, start

timing. After 5min, lift the wire cage out of the oil bath pot, cool for a while and wipe off the oil (wax) outside the tube. Transfer the decocting solution and soil residue in the test tube into 250mL triangular flask without damage, and use water to wash the test tube and small funnel, and mix the washing solution into the triangular flask, so that the total volume of the solution in the triangular flask is controlled within 50mL-60mL. Add 3 drops of phenanthrene, the remaining K_2CrO_7 was titrated with ferrous sulfate standard solution as the indicator. The discoloration process of the solution was orange yellow, blue green and brown red.

S3: The extraction of NP and BPA

This method takes USEPA 3550c as a reference. NP and BPA were extracted by small volume extraction agent after centrifuged. 1 g of NaCl was added into the supernatant, adjust pH to 2 with HCL, 4 mL of methylene chloride was added, then shock the solution for half an hour to mix them completely, and then centrifuged, at last transfer the separated methylene chloride solvent to a new vessel using a bath tube, repeat three times and combined the extracted solution, then anhydrous Na_2SO_4 was added to remove residual water, concentrated to 1 mL and put in a 2mL-Little brown bottle and stored at 4℃.

USEPA. SW-846 Test Method 3550C: Ultrasonic Extraction. https://www.epa.gov/hw-sw846/sw-846-test-method-3550c-ultrasonic-extraction.

S4: Statistical analysis of the effect of temperature on the adsorption of NP and NP7

Adsorption efficiency of NP7 and NP to soil was calculated when adsorption equilibrium respectively at 5℃, 25℃ and 35℃ at each treatment, which is showed below.

Table1 The adsorption efficiency of NP and NP_7 to soil at adsorption equilibrium time for each treatment

	NP			NP_7		
	5℃	25℃	35℃	5℃	25℃	35℃
200ug/L	81.94%	80.87%	67.00%	85.95%	83.23%	73.25%
500 ug/L	78.95%	61.94%	68.25%	83.38%	80.10%	72.49%
1000 ug/L	68.82%	61.02%	63.47%	71.11%	75.12%	68.77%
1500 ug/L	68.74%	63.76%	62.44%	73.38%	75.12%	69.47%
2000 ug/L	65.07%	62.43%	57.02%	75.42%	70.02%	70.56%
3000 ug/L	67.23%	65.14%	65.63%	74.26%	68.77%	68.21%
4000 ug/L	69.86%	66.89%	65.50%	79.35%	70.98%	70.98%

Table2 Statistical analysis of the effect of temperature on NP and NP_7

Temperature		Average[a]	Mean value of standard error	t	df	*p*
5℃	NP	77.55%	0.02081	1.9	12	0.082
	NP7	71.52%	0.02398			
25℃	NP	74.76%	0.0203	2.661	12	0.021
	NP7	66.01%	0.0259			
35℃	NP	70.53%	0.00708	4.028	12	0.002
	NP7	64.19%	0.01407			

Note: a indicate the average adsorption efficiency.

From table 2, we concluded that the difference of the temperature effect on the adsorption of NP7 and NP at 5℃ was not significant($p>0.05$); while the difference of the temperature effect at 25℃ was significant($p<0.05$); the difference of the temperature effect at 35℃ was significant($p<0.05$) as well; What's more, the difference was more significant at 35℃ than 25℃. It indicated that with the temperature increasing, the difference between the effect of temperature on NP7 and NP was more significant.