DOI: 10.6653/MoCICHE.201712_44(6).0008

環境中新興污染物之檢測與探索

周佩欣／國立成功大學環境工程學系 副教授

由古至今，化學物質是人類日常生活中不可或缺的一部分，例如用於治療疾病的藥物，或是添加在商品中的防腐劑、抗菌劑、防火阻燃劑等人工合成物質，不僅能保護人類健康，也提升了生活的便利程度。然而，廣泛且大量使用化學物質的生活方式，使得人類活動產生之各式廢水組成成分複雜。若污水未經妥善處理即排放至環境中，不僅會造成天然水體污染，也可能進而威脅飲用水水源之水質安全。

近年來，經由人類污水排放之新興污染物（Emerging contaminants）逐漸受到重視。新興污染物，另名為新興關切污染物（Contaminants of emerging concern），係指未受管制標準列管，但可能具有危害性的物質。其包羅萬象，如藥物與個人保健用品、管制藥品、工業用奈米物質與化學物質、抗藥性基因等皆可能被納入新興污染物的範疇 [1]。這些物質在過去可能較少於自然水體中測得，或是毒理特性尚未明朗，因此其污染問題未獲關注。然而，隨著微量分析技術的進步與毒性試驗的開發，新興污染物的環境流布與健康風險也引起注意，部分污染物也陸續被增列為法規管制對象。本文將以新興污染物中的內分泌干擾物質（Endocrine disrupting chemicals）為例，說明檢測內分泌干擾物質的分析手法，與探索環境中內分泌干擾物質的未來研究趨勢。

內分泌干擾物質的種類與環境流布

內分泌干擾物質為可藉由影響體內荷爾蒙合成、分泌、傳輸、結合、代謝等功能來擾亂生物體內分泌系統之化合物 [2]。天然的內分泌干擾物質，如動物性雌激素雌酮（Estrone, E1）與雌二醇（17β-Estradiol, E2）若大量進入環境，則可能對其他生物造成危害 [3]。合成的內分泌干擾物質包括類（抗）荷爾蒙藥物、農藥、塑膠添加劑、界面活性劑、殺菌劑等日常生活中經常接觸的化合物，其中有部分物質已因其毒性問題而被禁用或以其他物質取代，例如早期曾用來預防流產之合成類雌激素己烯雌酚，已因為具致癌性而被禁止使用 [4]。E1、E2、及口服避孕藥乙炔雌二醇（17α-Ethinylestradiol, EE2）、塑膠添加劑雙酚 A（Bisphenol A, BPA）、界面活性劑壬基酚（Nonylphenol, NP）、抗菌劑三氯沙（Triclosan, TCS）、防腐劑對羥基苯甲酸甲酯（Methyl paraben, MeP）等具內分泌干擾活性之物質為常於環境中測得之內分泌干擾物質，其於污水處理廠出流水及表面水中的濃度範圍介於數奈克至數十微克／升之間 [5-14]。雖然濃度極其微量，但已具影響水中生物健康的風險。此外，E2、EE2、BPA、NP 等物質亦曾於飲用水水源中被檢出，因此已分別被美國環保署及日本厚生勞働省列為飲用水污染物候選清單（Contaminant candidate list）與要檢討項目（Items for further study）之中 [15, 16]。

內分泌干擾物質的檢測

常見的內分泌干擾物質檢測法分為定性與定量兩種。定性法為將生物、微生物或細胞暴露於環境樣本中進行毒性測試，可量測污染物混合存在下之複合內分泌干擾活性。舉例來說，將魚體暴露於環境樣本中時，可藉由觀察存活率、第二性徵變化、產卵數、生殖腺指數、卵黃前質生成等數值變化，來評估其內分泌系統功能是否有受到干擾 [17]。然而，以活體生物進行實驗耗時長且成本高，相較之下使用微生物或細胞

之體外毒性試驗具有操作簡單並迅速之優點，故較常應用於環境樣本內分泌干擾活性之篩檢 [18, 19]。例如使用細胞株或酵母菌為載體之報導基因試驗法，其中轉殖入特定之激素受體基因、受體反應元件以及含有報導基因序列之質體，試驗機制為當內分泌干擾物質進入細胞與受體結合後，會再與質體上的反應元件反應誘發下游基因表現，分析其生成之報導基因蛋白量可推估樣本之內分泌干擾活性。常用之報導基因包括會產生 β- 半乳糖苷酶之 Lac Z 報導基因、冷光酶報導基因、與綠螢光蛋白報導基因等 [20-22]。

定量法為使用高靈敏度的分析儀器量測樣本中目標內分泌干擾物質之濃度。由於環境樣本成分複雜，為降低基質效應影響並提高分析精確度，在偵測儀器前端通常會再加上層析儀器，以依據物化特性分離環境樣本中的不同污染物。液相層析儀或氣相層析儀搭配質譜偵測器為常用於環境檢測的分析利器，其分別適用於非揮發性／半揮發性物質與半揮發性／揮發性物質。層析之機制為藉由固定相管柱滯留與移動相（溶劑或氣體）帶動待測物質的能力差異來分離樣本中的複雜成分。質譜之原理則是將待測物質離子化後，使用質量分析器以電場或磁場篩選不同質量／電荷比的離子，並於質量偵測器進行分析。環境檢測上常使用串聯式質譜儀，亦即以第一個質量分析器篩選目標物質離子，並以第二個質量分析器來分離經惰性氣體碰撞後產生之碎片離子，可大幅降低偵測下限 [23]。

新興內分泌干擾物質的未來研究趨勢

使用前述之毒性測試法與質譜技術來分析環境樣本中的內分泌干擾物質時，常發現質譜儀測得之已知污染物無法完整解釋樣本中的內分泌干擾活性，顯示環境中尚存有未鑑定之內分泌干擾物質。新興內分泌干擾物質可能是毒性尚未被確認之新興污染物，也可能是來自於已知內分泌干擾物質在污水處理流程或環境中生成之衍生產物。以 BPA 為例，於硝化生物處理單元中生成之硝化 BPA 的類雌激素活性雖較 BPA 低，然而卻具有對魚體較強之基因毒性及致突變性 [24-26]。此外，研究指出暴露於 BPA 氯化衍生物中會使得雌鼠子宮重量明顯增加，活體外毒性試驗亦證實單氯與雙氯 BPA 較 BPA 有更強之類雌激素活性 [27]。

未來隨著法規的日趨嚴格與新穎處理技術的開發，經由污水排放之內分泌干擾物質或許能得到良好的控制，然而若不同時考量這些污染物於淨水、污水處理流程中，尤其是末端消毒程序中生成之衍生產物的毒性影響，將無法完整評估其可能造成之環境風險。因此，檢測內分泌干擾物質衍生產物之環境流布與宿命實為往後研究之重要課題。期待未來毒性試驗法的持續開發搭配分析儀器靈敏度之提升，能協助研究者更加完整評估與鑑定環境樣本中的主要內分泌干擾物質，以保護環境及人類健康。

參考文獻

1. Noguera-Oviedo, K. and Aga, D. S. (2016), “Lessons learned from more than two decades of research on emerging contaminants in the environment,” Journal of Hazardous Materials, Vol. 316, pp. 242-251.
2. Kavlock, R. J., Daston, G. P., DeRosa, C., Fenner-Crisp, P., Gray, L. E., Kaattari, S., Tilson, H. A. (1996), “Research needs for the risk assessment of health and environmental effects of endocrine disruptors: a report of the U.S. EPA-sponsored workshop,” Environmental Health Perspectives, Vol. 104 (Supplement 4), pp. 715-740.
3. Chang, H. S., Choo, K. H., Lee, B., Choi, S. J. (2009), “The methods of identification, analysis, and removal of endocrine disrupting compounds (EDCs) in water,” Journal of Hazardous Materials, Vol. 172, pp. 1-12.
4. Birnbaum, L. S. and Fenton, S. E. (2003), “Cancer and devel-

opmental exposure to endocrine disruptors," Environmental Health Perspectives, Vol. 111, pp. 389-394.

5. Servos, M., Bennie, D. T., Burnison, B. K., Jurkovic, A., McInnis, R., Neheli, T., Schnell, A., Seto, P., Smyth, S. A., Ternes, T. A. (2005), "Distribution of estrogens, 17β-estradiol and estrone in Canadian municipal wastewater treatment plants," Science of the Total Environment, Vol. 336, pp. 144-170.
6. Viglino, L., Aboulfadl, K., Prevost, M., Sauve, S. (2008), "Analysis of natural and synthetic estrogenic endocrine disruptors in environmental waters using online preconcentration coupled with LC-APPI-MS/MS," Talanta, Vol. 76, pp. 1088-1096.
7. Cargouet, M., Perdiz, D., Mouatassim-Souali, A., Tamisier-Karolak, S., Levi Y. (2004), "Assessment of river contamination by estrogenic compounds in Paris area (France)," Science of the Total Environment, Vol. 324, pp. 55-66.
8. Vulliet, E., Wiest, L., Baudot, R., Grenier-Loustalot., M.-F. (2008), "Multi-residue analysis of steroids at sub-ng/L levels in surface and ground-waters using liquid chromatography coupled to tandem mass spectrometry," Journal of Chromatography A, Vol. 1210, pp. 84-91.
9. Gorga, M., Petrovic, M., Barcelo, D. (2013), "Multi-residue analytical method for the determination of endocrine disruptors and related compounds in river and waste water using dual column liquid chromatography switching system coupled to mass spectrometry. Journal of Chromatography A, Vol. 1295, pp. 57-66.
10. Yu, Y., Wu, L. S., Chang, A. C. (2013), "Seasonal variation of endocrine disrupting compounds, pharmaceuticals and personal care products in wastewater treatment plants," Science of the Total Environment, Vol. 442, pp. 310-316
11. Bertanza, G., Pedrazzani, R., Dal Grande, M., Papa, M., Zambarda, V., Montani, C., Steimberg, N., Mazzoleni, G., Di Lorenzo, D. (2011), "Effect of biological and chemical oxidation on the removal of estrogenic compounds (NP and BPA) from wastewater: an integrated assessment procedure," Water Research, Vol. 45, pp. 2473-2484
12. Lishman, L., Smyth, S. A., Sarafin, K., Kleywegt, S., Toito, J., Peart, T., Lee, B., Servos, M., Beland, M., Seto, P. (2006), "Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada," Science of the Total Environment, Vol. 367, pp. 544-558.
13. Yu, Y., Huang, Q., Wang, Z., Zhang, K., Tang, C., Cui, J., Feng, J., Peng, X. (2011), "Occurrence and behavior of pharmaceuticals, steroid hormones, and endocrine-disrupting personal care products in wastewater and the recipient river water of the Pearl River Delta, South China," Journal of Environmental Monitoring, Vol. 13, pp. 871-878.
14. Kasprzyk-Hordern, B., Dinsdale, R. M., Guwy, A. J. (2009), "The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters," Water Research, Vol. 43, pp. 363-380.
15. United States Environmental Protection Agency (USEPA), http://water.epa.gov/drink/contaminants/
16. Ministry of Health, Labour and Welfare, Japan, http://www.mhlw.go.jp/
17. Naderi, M., Wong, M. Y., Gholami, F. (2014), "Developmental exposure of zebrafish (Danio rerio) to bisphenol-S impairs subsequent reproduction potential and hormonal balance in adults," Aquatic Toxicology, Vol. 148, pp. 195-203.
18. Kawanishi, M., Takamura-Enya, T., Ermawati, R., Shimohara, C., Sakamoto, M., Matsukawa, K., Matsuda, T., Murahashi, T., Matsui, S., Wakabayashi, K., Watanabe, T., Tashiro, Y., Yagi, T. (2004), "Detection of genistein as an estrogenic contaminant of river water in Osaka," Environmental Science & Technology, Vol. 38, pp. 6424-6429.
19. Giesy, J. P., Hilscherova, K., Jones, P. D., Kannan, K., Machala, M. (2002), "Cell bioassays for detection of aryl hydrocarbon receptor (AhR) and estrogen receptor (ER) mediated activity in environmental samples," Marine Pollution Bulletin, Vol. 45, pp. 3-16.
20. Legler, J., van de Brink, C. E., Brouwer, A., Murk, A. J., van de Saag, P. T., Vethaak, A. D., van de Burg, B. (1999), "Development of a stably transfected estrogen receptor-mediated luciferase reporter gene assay in the human T47D breast cancer cell line," Toxicological Science, Vol. 48, pp. 55-66.
21. Houtman, C. J., Sterk, S. S., van de Heijning, M. P. M., Brouwer, A., Stephany, R. W., van der Burg, B., Sonneveld, E. (2009), "Detection of anabolic androgenic steroid abuse in doping control using mammalian reporter gene bioassays," Analytica Chimica Acta, Vol. 637, pp. 247-258.
22. Nagy, S. R., Sanborn, J. R., Hammock, B. D., Denison, M. S. (2001), "Development of a green fluorescent protein-based cell bioassay for the rapid and inexpensive detection and Characterization of ah receptor agonists," Toxicological Science, Vol. 65, pp. 200-210.
23. 台灣質譜學會（2016），「質譜分析技術原理與應用」，全華圖書，台北。
24. Masuda, S., Terashima, Y., Sano, A., Kuruto, R., Sugiyama, Y., Shimoi, K., Tanji, K., Yoshioka, H., Terao, Y., Kinae, N. (2005), "Changes in the mutagenic and estrogenic activities of bisphenol A upon treatment with nitrite," Mutation Research-Genetic Toxicology and Environmental Mutagenesis, Vol. 585, pp. 137-146.
25. Toyoizumi, T., Deguchi, Y., Masuda, S., Kinae, N. (2008), "Genotoxicity and estrogenic activity of 3,3'-dinitrobisphenol A in goldfish," Bioscience, Biotechnology, and Biochemistry, Vol. 72, pp. 2118-2123.
26. Sun, Q., Li, Y., Chou, P-H., Peng, P-Y., Yu, C-P. (2012), "Transformation of bisphenol A and alkylphenols by ammonia-oxidizing bacteria through nitration," Environmental Science & Technology, Vol. 46, pp. 4442-4448.
27. Takemura, H., Ma, J., Sayama, K., Terao, Y., Zhu, B. T., Shimoi, K. (2005), "In vitro and in vivo estrogenic activity of chlorinated derivatives of bisphenol A," Toxicology, Vol. 207, pp. 215-221.