

Determination of nonylphenol polyethoxylates and their biodegradation products in sewage treatment plant sludge by conventional HPLC with fluorescence detector

Nguyen Viet Hung, Masafumi Tateda, Michihiko Ike and Masanori Fujita

Department of Environmental Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Sewage treatment plant (STP) treating wastewater from municipalities and industries has been shown a major source of many environmental pollutants. These pollutants usually have origin from synthetic chemicals that have been used widely for industrial, agricultural and household purposes. The synthetic chemicals, when in the aeration tank of a STP, are broken down biologically by microorganisms attached on activated sludge to form persistent biodegradation products. Many of these biodegradation products are environmental pollutants. Routes for environmental release of the pollutants are via discharges from a STP, which include treated effluent and abundant amount of sewage sludge. One group of the pollutants that are common in STP is nonylphenol polyethoxylates and their biodegradation products. Nonylphenol polyethoxylates (NPnEO) is an important group of nonionic surfactants that have been widely used in industries, agriculture and households as detergents, emulsifiers, wetting agents, dispersing agents, spermicides and pesticides etc. NPnEO and especially their biodegradation products: NP, NP1EO, NP2EO, NP1EC and NP2EC (based on definition by Ahel *et al.* (1994)) have been shown to elicit estrogenic effects (Jobling and Sumpter, 1993). In other words, they are endocrine disrupting chemicals (EDCs) that have deleterious effect on hormone system of humans and animals. Recently, the impact of EDCs in the environment is a topic of growing concern.

Sewage sludge from a STP composed mainly of activated sludge is considered one of the most complex matrixes to be analyzed for its chemical composition and concentrations of pollutants. Analytical procedures to determine concentrations of NPnEO and their biodegradation products in wastewater influent and treated effluent from STP are relatively easy, therefore, there are abundant analytical results reported. In contrast, until now there are quite few data on concentrations of NPnEO ($n > 2$) and their biodegradation products: NP1EC, NP2EC in sewage sludge, though the concentrations of the biodegradation products: NP, NP1EO and NP2EO in sewage sludge were reported by several authors (Brunner *et al.*, 1988; Lee and Peart, 1995). This fact indicated a shortage of an effective analytical procedure for determination of NPnEO ($n > 2$) and their biodegradation products: NP1EC and NP2EC in STP sewage sludge. Lee *et al.* (1997) analyzed NPnEO and NP1EC, NP2EC in sewage sludge. However, the authors applied supercritical fluid extraction method with CO₂ to extract investigated compounds from sewage sludge samples. The instrument for this extraction method is expensive and only available at specialized analytical laboratory.

In this study, an effective analytical procedure has been developed for determination of NPnEO and their biodegradation products in STP sludge. The developed analytical procedure consist of 4 steps : 1) Dry a sludge sample by vacuum freeze-drier, 2) Extract the dried sludge sample by ultrasonication extraction with methanol in 15 minutes and followed by Soxhlet extraction with dichloromethane in 8 hours, 3) Clean-up the extract from step 2 by solid phase extraction with a graphitized carbon black (GCB) cartridge, and 4) Analyze for NPnEO and NPEC compounds in the extract by a HPLC equipped with a fluorescence detector (225 nm excitation and 295 nm emission). Using the developed analytical procedure, between December, 2000 and March 2001 sludge samples taken from different STPs around Osaka and Kyoto Prefecture, Japan were analyzed for NPEO and NPEC concentrations. Recoveries for the target compounds were above 80%. Sum of NP1EO and NP2EO concentrations were found in the sludge samples at values ranging from 3.8 to 14.3 $\mu\text{g/g}$. While sum of NPnEO ($n > 2$) concentrations ranged from 1.8 to 27.5 $\mu\text{g/g}$, with the sum of NPnEO ($n > 2$), for almost all samples, was considerably less than sum of NP1EO and NP2EO in the same sample. NP1EC and NP2EC were found in the majority of total samples analyzed; and sum of their concentrations detected were in a range from 0.8 to 2.9 $\mu\text{g/g}$.

Obtained results showed that biodegradation products of nonylphenol polyethoxylates, especially NP1EO and NP2EO accumulated to really high levels of concentration in STP sewage sludge. Therefore, much attention should be paid to monitor and handle with STP sewage sludge containing these pollutants.