Hazardous organic matters in municipal sewage sludge in Taiwan

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Abstract Application of municipal sewage sludge to agricultural land has attracted significant attention in recent years because it conserves abundant nutrients and hydrocarbons that can be used as a soil amendment. The presence of hazardous organic matters (HOMs) in sewage sludge limits the feasibility of reuse of sewage sludge. The purpose of this study was to investigate the types and the concentrations of HOMs in municipal sewage sludge in Taiwan. An efficient SFE/GC/MS method was used to determine HOMs in sludge samples. The results indicated that di-(2-ethylhexyl) phthalate (DEHP) was persistently found in both aerobically and anaerobically digested sludges. 4-nonylphenol (4-NP) was only found in anaerobically digested sludges. Both DEHP and 4-NP have been characterized as endocrine disrupting chemicals (EDCs) or environmental endocrine disruptors (EEDs). It suggested that sludges containing high levels of DEHP and 4-NP need further treatment and reduction of possible impacts on the environment before their reuse as soil fertilizers.

Keywords 4-nonylphenol; di-(2-ethylhexyl) phthalate; sewage sludge; supercritical fluid extraction

Introduction
Due to the dramatic increases in water consumption and the use of human-made chemicals in recent years, various types of hazardous organic matters (HOMs) are found in sewage and some of them are difficult to remove during treatment at a conventional sewage treatment plant (STP). Because of inappropriate treatment, most HOM accumulates in the sewage sludges or discharges into the environment with the effluent of STPs (Field et al., 1995). Among these HOMs, lipophilic/hydrophobic substances readily accumulate in sewage sludges (Schnaak et al., 1997). However, some persistent organic compounds are still found in sludges after the treatment (aerobic or anaerobic digestion) and disposal of sludge (Banat et al., 1999; Lin et al., 1999; Cheng et al., 2000). The fate of these HOMs following sewage sludge disposal has recently become a significant environmental issue.

Sewage sludge often conserves abundant nutrients and hydrocarbons, and it can be further used as soil fertilizer. Land application of sewage sludge has become a popular and an environmental-friendly disposal method because it transforms the best-available parts of sludge into resources for agriculture use (Eljarrat et al., 1997). However, the elevated concentrations of HOM presented in sewage sludges limit the land application of sludge. According to the survey of municipal sewage sludge samples by the Danish Environmental Protection Agency, the cut-off values of polycyclic aromatic hydrocarbons (PAHs), linear alkylbenzene sulphonates (LASs), nonylphenol and -ethoxylates (NPEs) and di-(2-ethylhexyl) phthalate (DEHP) have been decided for sludge samples applied to arable lands in 1997 and 2000, respectively (Table 1) (Madsen et al., 1997). Because of the estrogen-like and carcinogenic effects, it is noteworthy that 4-nonylphenol (4-NP) and DEHP have been characterized in the category of the endocrine disrupting chemicals (EDCs) or environmental endocrine disruptors (EEDs) in many countries (Kuch and Ballschmiter, 2000).

Sewage sludge is a highly complex matrix with multi-porous property. Conventional extraction methods cannot efficiently concentrate the HOMs from the sludge samples because of the insufficient contact between solvent and the HOMs (Barnabas et al., 1994).
In addition, being labor-intensive, solvent consuming and time wasting are the common disadvantages of conventional solvent extraction methods (Field et al., 1998). A solvent-free and high efficiency supercritical fluid extraction (SFE) method is one of alternatives to conventional extraction methods for analysis of HOM present in the municipal sewage sludge (Cheng et al., 2000).

It is very important to obtain basic information about concentrations of these HOMs in sludge in order to assess the environmental impact of specific sludge disposal practices (Rogers, 1996). The purposes of this study are to investigate the concentrations of 4-NP and DEHP presented in the different types of municipal sewage sludges collected from three STPs in northern Taiwan. A comparison between results obtained in this study and other studies is also discussed.

Materials and methods

Chemicals

DEHP (99%), methanol (99.8%) and hexane (99.35%) were obtained from RDH Chemicals (Germany), RDH, and Fisons (UK), respectively. 4-NP (90%) was obtained from Tokyo Chemicals (Japan). Sodium sulfate was obtained from SHOWA (99%) (Japan). SFE-grade carbon dioxide (99.999%) was purchased from Air Products (Nepean, Canada).

Sludges

Sludge samples (aerobically and anaerobically digested sludges) were collected from three different STPs (Min-Shen, De-Hwa and Ba-Li) in northern Taiwan. The sludge samples were air-dried for two weeks, ground and homogenized by passing through a 30-mesh sieve for further analyses. This was done with the aim of minimizing the risk of nonhomogeneity of sludge samples and to obtain the maximum solubility of analyte in the supercritical fluid extraction (Lin et al., 1999).

Supercritical fluid extraction

The extraction of 4-NP and DEHP from sludge samples was performed by a high efficiency supercritical fluid extractor (HP 7680T). The optimal extraction conditions for 4-NP and DEHP are shown in Table 2.

Analyses

A HP-1800A GCD system (Hewlett-Packard) was used for all determinations of 4-NP and DEHP in this study. Separation was performed using a 30 m × 0.25 mm I.D. HP-1 capillary column (J&W Scientific, Folsom, CA, USA). Helium with a flow rate of 1.0 ml/min was used as the carrier gas. A seven-point calibration curve obtained in the preliminary study was used to quantify the analyte concentrations. The mass spectrometer was operated at 70

<table>
<thead>
<tr>
<th>Organic substances</th>
<th>Limit value valid from July 1 1997 (mg/kg sludge dry weight)</th>
<th>Limit values valid from July 1 2000 (mg/kg sludge dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear alkylbenzenesulphonates (LAS)</td>
<td>2,600</td>
<td>1,300</td>
</tr>
<tr>
<td>Sum of 11 PAHs</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Nonylphenol and -ethoxylates (NPE)</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Di-(2-ethylhexyl) phthalate (DEHP)</td>
<td>100</td>
<td>50</td>
</tr>
</tbody>
</table>

a acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzofluoranthenes (b+j+k), benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene

b nonylphenol and nonylphenoxyethoxylates with 1-2 ethoxy-group
eV and scanned from 30 to 425 u at 1 scan/s. The instrument detection limits (IDL) for analyses of 4-NP and DEHP were 0.88 mg/l and 0.12 mg/l, respectively. The method detection limits (MDL) for analyses of 4-NP and DEHP in sludges by SFE/GC/MS were 1.82 mg/kg and 1.84 mg/kg, respectively.

### Results and discussion

#### HOMs in sewage sludges

Sludge samples collected from three municipal STPs (Min-Shen, De-Hwa and Ba-Li) in this study were extracted by SFE and determined by GCD. The total ion current (TIC) profiles of organics extracted from different sewage sludges are shown in Figure 1 and Figure 2. It was found that the peak with the retention time of 23.96 min indicated the presence of DEHP in the aerobically digested sludge of Min-Shen STP (Figure 1). The peak with the retention time of 35.42 min in Figure 2 also indicated the presence of DEHP in the anaerobically digested sludge of De-Hwa STP. Due to different chromatographic conditions in Figure 1 and Figure 2, the retention time of DEHP was not the same (no isomers were found). In addition, ten isomers of NPE appeared in the retention time between 21.11 and 22.40 min and 4-NP was included.

<table>
<thead>
<tr>
<th>Sample (g)</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Dynamic/static CO₂ flow rate (ml/m)</th>
<th>Modifier (ml methanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NP</td>
<td>0.2</td>
<td>97</td>
<td>2/30</td>
<td>3.0</td>
</tr>
<tr>
<td>DEHP</td>
<td>0.2</td>
<td>202</td>
<td>1/20</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Figure 1** The TIC chromatograms obtained in the GCD analysis of DEHP in the aerobically digested sludge Min-Shen STP

**Figure 2** The TIC chromatograms obtained in the GCD analysis of 4-NP in the aerobically digested sludge De-Hwa STP
The concentrations of 4-NP and DEHP found in sewage sludges obtained from three STPs in northern Taiwan are shown in Table 3. The results clearly demonstrated that both 4-NP and DEHP were found in anaerobically digested sludge from De-Hwa STP. However, 4-NP was only found in anaerobic sludges. Ahel et al. (1996) revealed that NPnEO becomes NP1EO, NP2EO, NP1EC and NP2EC during biological activated sludge treatment and NP1EO and NP2EO were then transformed into 4-NP under anaerobic digestion of sludge. This is the reason why 4-NP is only found in anaerobic sludges. However, DEHP can be present in both aerobic and anaerobic sludges. DEHP is not readily biodegraded during the biological treatment processes of STP. It can only be degraded slowly under aerobic conditions and can hardly be biodegraded under anaerobic conditions (Irvine et al., 1993; Madsen et al., 1999; Cheng et al., 2000).

According to the results listed in Table 3, it is significant that the concentrations of 4-NP and DEHP in sewage sludges of these three STPs all exceeded the safety values of sludge applied to agricultural lands suggested by the Danish EPA (Table 1). Therefore, these sludges need further treatment to avoid possible environmental impact before land application of the sludges.

Comparing the results with other studies
In addition to comparing the results obtained in this study, it is necessary to make a comparison between this study and other studies on the levels of 4-NP and DEHP found in sewage sludges. Table 4 shows the concentrations of 4-NP and DEHP gathered in this study and other studies. It was found that the concentrations of 4-NP in sewage sludges in different countries are similar and the concentration distribution of DEHP varies widely. It should be emphasized that the data obtained in this study or the studies in other countries will be useful to build a database of hazardous organic diversity in sewage sludges.

Conclusions
The SFE/GC/MS method developed in this study was found suitable for determination of HOMs in sewage sludges. The results obtained from this study reflect that hazardous organic matters (4-NP and DEHP) are present in the municipal sewage sludges of STPs in northern Taiwan. It was found that 4-NP mainly occurs in anaerobic sludges. DEHP can be

### Table 3 The concentrations of 4-NP and DEHP in three municipal sewage sludges

<table>
<thead>
<tr>
<th>Sewage treatment plants (STP)</th>
<th>Type of sludge</th>
<th>DEHP (mg/kg dw)</th>
<th>4-NP (mg/kg dw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min-Shen</td>
<td>Aerobically digested</td>
<td>142.86 (0.15%)^a</td>
<td>ND</td>
</tr>
<tr>
<td>De-Hwa</td>
<td>Anaerobically digested</td>
<td>153.15 (1.26%)</td>
<td>243.89 (0.86)</td>
</tr>
<tr>
<td>Ba-Li</td>
<td>Anaerobically digested</td>
<td>105.16 (2.11%)</td>
<td>266.96 (1.94)</td>
</tr>
</tbody>
</table>

^a standard deviation (RSD) values, n = 3

### Table 4 Comparison of the 4-NP and DEHP concentrations present in different sewage sludges

<table>
<thead>
<tr>
<th>Country</th>
<th>4-NP (mg/kg dw)</th>
<th>DEHP (mg/kg dw)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taiwan</td>
<td>244–267</td>
<td>105–153</td>
<td>This study</td>
</tr>
<tr>
<td>Canada</td>
<td>137–470</td>
<td>–</td>
<td>Lee and Peart (1995)</td>
</tr>
<tr>
<td>Germany</td>
<td>–</td>
<td>170</td>
<td>Schnaak et al. (1997)</td>
</tr>
<tr>
<td>USA</td>
<td>–</td>
<td>136–578</td>
<td>Staples et al. (1997)</td>
</tr>
</tbody>
</table>
determined in both aerobic and anaerobic sludges of STPs. However, the concentrations of 4-NP and DEHP significantly exceeded the ceiling values for sludge land application suggested by the Danish EPA. It is remarkable that there is a requirement for further treatment of such sludge if the sewage sludge will be applied to enhance the fertility of the agricultural soils. The most important goal of this study is to assist and contribute sufficient data to the government to establish the suitable regulations or legislation on limits of HOMs in sewage sludges.

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References