

Management of Chemical Substances in Biosolids

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1. Introduction

Thousands of chemical substances are used in industrial factories, agriculture/aquaculture farms, hospitals and households. Some or most of them are discharged into sewage and flow into wastewater treatment plants.

Chemical substances recognized as environmental pollution recently and not legally regulated for environmental protection, such as endocrine disruptors (EDs), pharmaceuticals and personal care products (PPCPs), are of great concerns for their occurrence and fate in wastewater treatment process because it often happens that sewage is the primary pathway of those substances entering into the environment.

Hydrophobic chemical substances tend to be partitioned in biosolids. When they remained unchanged or retained chemical activity, utilization (especially land application) of those biosolids may cause adverse effect on human health and environment by exposure.

(In FY2002 the total amount of sewage sludge generated was 2,105 kt of dry solids (DS) and around 14% of this amount (293 kt-DS) was recycled for agricultural use.)

2. Objectives

Our research aims to understand the occurrence of chemical substances in biosolids and their fate in biosolids treatment/utilization process. We will develop management method of chemical substances in biosolids, if necessary.

3. Research methods and results

We studied the occurrence and the fate of three categories of chemical substances in biosolids. The categories and research results are as follows;

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(1) Endocrine disrupting chemicals (EDs)

Nonylphenols (NPs), nonylphenol ethoxylates (NPnEOs) and nonylphenol polyethoxycarboxylates (NPnECs) were analyzed by LC/MS/MS.

Biosolids composts from 17 cities in Japan contained detectable level of NPs, NPnEOs and NPnECs.

Anaerobically digested sludge composts contained high concentration of NPs.

NP1-2EO and NP1-2EC were the major contributor to the NPnEOs and NPnECs in composts, respectively.

Ethoxylates chains of NPnEOs and NPnECs were shortened in biosolids composts

NPs biodegradation decreased under high temperature condition(70 ° C)

High temperature operation may suppress the NP degrading microbial activities in the composting plant.

Degradation pathways of NP2EO-NP2EC- (NP1EC)-degradation or NP1EO-NP1EC-degradation played major roles in the aerobic degradation of NPnEOs and NPnECs that remained in biosolids.

(2) Estrogens

Estrone (E1), 17- β estradiol(E2), estriol (E3), ethynylestradiol (EE2) and their conjugates (both glucronated and sulfated) were analyzed by LC/MS/MS.

Biosolids composts from 17 cities in Japan contained almost no detectable level of Estrogens.

(3) Pharmaceuticals and Personal Care Products (PPCPs)

We conducted a screening research based on several statistics of PPCPs production, use and discharge in Japan to develop a priority PPCPs list in biosolids.

We have also developed measurement methods of important PPCPs in biosolids and have been conducting field survey to understand the occurrence and the fate of them.

4. Conclusions

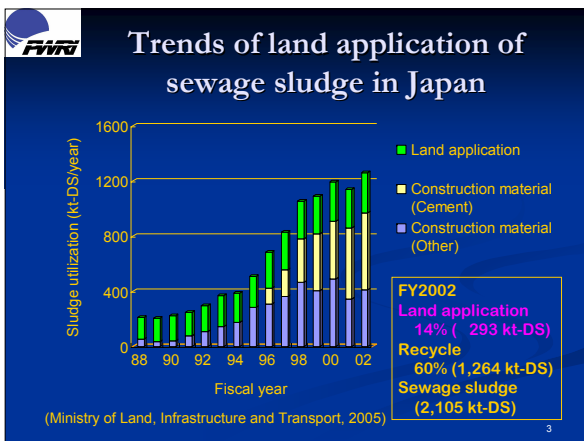
Most of endocrine disrupting chemicals in biosolids were degraded when composted for land application. But they were found in some biosolids composts and need to be studied for effective degradation methods in biosolids utilization/treatment process. PPCPs research is currently in progress and the necessity of development of management methods in biosolids will be discussed in the future.

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Background

- Thousands of chemical substances flow into wastewater treatment plants.
- Sewage is often the primary pathway of new environmental pollutants, such as endocrine disruptors (EDs), pharmaceuticals and personal care products (PPCPs), to the environment.
- Hydrophobic species of these chemicals may move to biosolids. Some hydrophilic species also have tendencies to be absorbed in activated sludge.
- Utilization (land application) of these biosolids may cause adverse effect on human health and environment by exposure.



Objectives

- Understand the occurrence of chemical substances in biosolids
- Understand the fate of chemical substances in biosolids treatment/utilization process
- Develop management method of chemical substances in biosolids, if necessary

Chemical substances

- Endocrine disrupting chemicals
- Estrogens
- Pharmaceuticals and Personal Care Products (PPCPs)

Chemical substances in biosolids

(1) Endocrine disrupting chemicals (EDs)

An example of nonylphenols (NPs)

Oc1ccc(C9H19)cc1

4-Nonylphenol

An example of nonylphenol polyethoxylates (NPEOs)

HOCH2CH2OCH2CH2O-C6H4-C9H19

4-nonylphenol diethoxylate

Nonylphenol polyethoxycarboxylates (NPECs)

Chemical substances in biosolids

(2) Estrogens (EDs)

Oc1ccc2c3c4c1O[C@H]4[C@@H](O)CC[C@]32

17 β estradiol (E2)

Oc1ccc2c3c4c1O[C@H]4[C@@H](O)CC[C@]32O

Estrone (E1)

Oc1ccc2c3c4c1O[C@H]4[C@@H](O)CC[C@]32

Estriol (E3)

Oc1ccc2c3c4c1O[C@H]4[C@@H](O)CC[C@]32C#C

Ethinylestradiol (EE2)

Chemical substances in biosolids

(3) Pharmaceuticals and Personal Care Products (PPCPs)

Human

O=C(O)c1ccc(Nc2ccc3c(c2)nc4c3ncn4)cc1

Metenamic acid 61-68-7

CN1C=NC2=C1C(=O)N(C)C2=O

Theophylline 58-55-9

OC12CCC3C(C1)CC[C@]3(O)CC2

Ursodeoxycholic acid 128-13-2

Veterinary

CC1=C(C(=O)N)C(=O)C2=C(C1)C(=O)C=C(C2)N

Chlortetracycline 57-62-5

CC1=C(C(=O)N)C(=O)C2=C(C1)C(=O)C=C(C2)N

Oxytetracycline 79-57-2

**(1) Endocrine disrupting chemicals (EDs)
Nonylphenolic compounds**

- NPs
- NPnEOs
- NPnECs

- Occurrence
- Fate

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NPCs degradation pathway

Raw sludge: NPnEOs + NPnECs, Anaerobically digested sludge: NPs

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**Occurrence of NPCs
in biosolids composts in Japan**

- Raw sludge 7
- Anaerobically digested sludge 5
- Mixed material 5

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**NPCs in biosolids composts
in Japan (n=17, LC/MS/MS)**

NPCs	37.9 ± 25.7	(5.6-90.7)
NPs	21.1 ± 20.5	(4.3-72.6)
NPnEOs	7.6 ± 7.8	(1.1-28.9)
NPnECs	9.2 ± 8.7	(0.2-26.2)

NPnEOs < 1.0 mg/kg-dry for NP6-15EOs,
NPnECs < 1.0 mg/kg-dry for NP5-10ECs

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**Anaerobically digested sludge
composts contained higher NPs**

$p = 0.0074 < 0.01$, Mann-Whitney's U test

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**NPs are dominant in anaerobically
digested sludge composts**

$p = 0.042 < 0.05$, Mann-Whitney's U test

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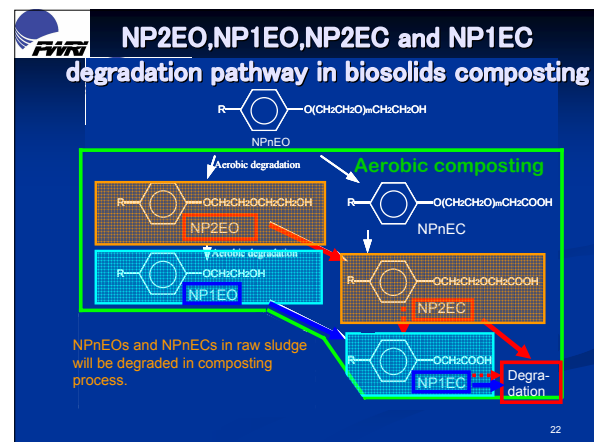
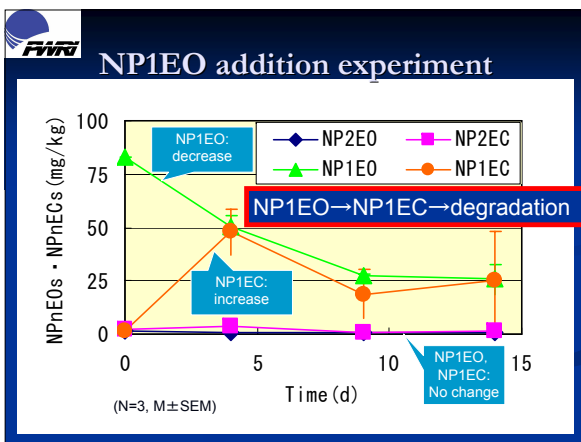
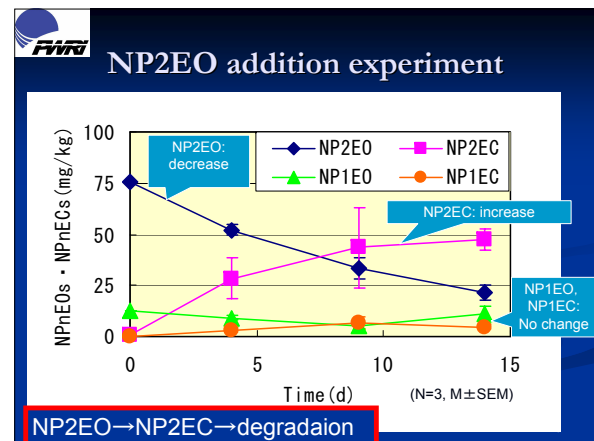
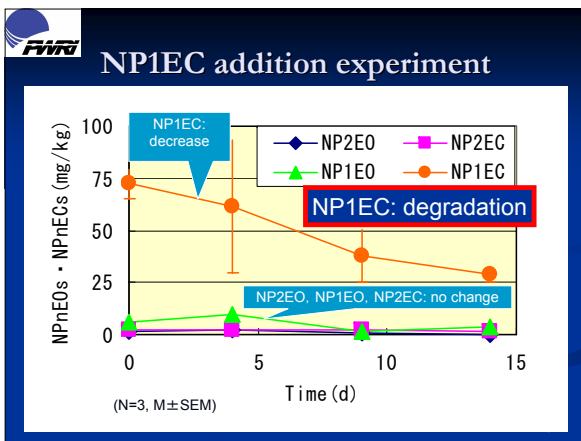
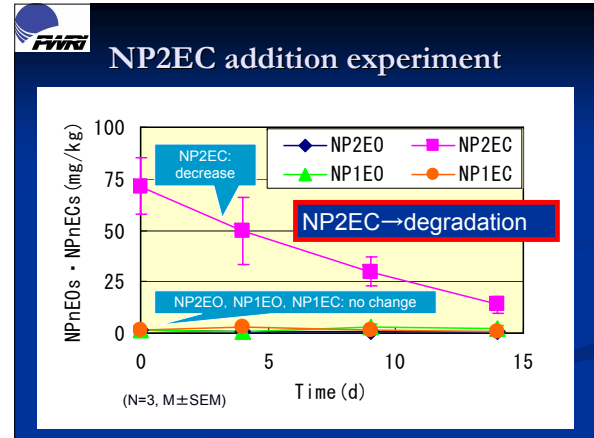
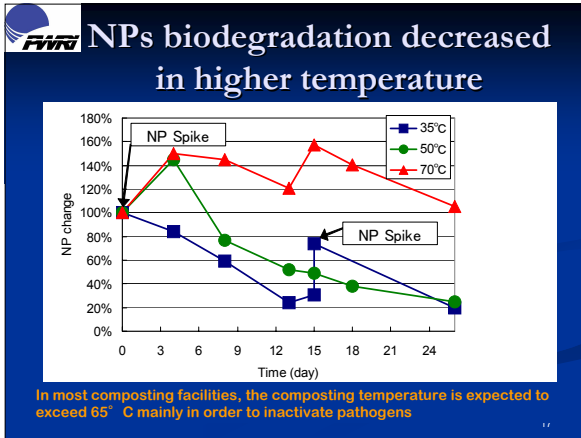
**Fate of NPCs in biosolids
composting process**

- Fate of NPs in anaerobically digested sludge composting process
- Fate of NPnEOs and NPnECs in raw sludge composting process

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Compost experiment apparatus

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- ### Conclusion (1)
- Biosolids composts from 17 cities in Japan contained detectable level of NPs, NPnEOs and NPnECs
 - Anaerobically digested sludge composts contained high concentration of NPs
 - NP1-2EO and NP1-2EC were the major contributor to the NPnEOs and NPnECs in composts, respectively

- ### Conclusion (2)
- Ethoxylate chains of NPnEOs and NPnECs were shortened in biosolids composts
 - NPs biodegradation decreased under high temperature condition (70 °C)
 - High temperature operation may suppress the NP degrading microbial activities in the composting plant



Conclusion (3)

- Degradation pathways of NP2EO-NP2EC-(NP1EC)-degradation or NP1EO-NP1EC-degradation played major roles in the aerobic degradation of NPnEOs and NPnECs that remained in biosolids.

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(2) Estrogens (EDs)

- 17- β estradiols(E2)
 - Estrone (E1)
 - Estríol (E3)
 - Ethynlestradiol (EE2)
 - Conjugates (G,S)
- Sewage sludge composts from 17 cities in Japan contained almost no detectable level of Estrogens. E2-diS (β estradiols-3,17-disulfate) was found slightly (0-2.7 mg/kg).

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(3) Pharmaceuticals and Personal Care Products (PPCPs)

- Screening
- Research

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