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Behaviour of Fossil and Biogenic Carbon in Sewage Sludge Treatment Processes and Their Impacts on Greenhouse Gas Emissions

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The newly revised guidance from the 2019 Intergovernmental Panel on Climate Change (IPCC) encourages assessment of fossil carbon in wastewater treatment plants (WWTPs). In this study, liquid scintillation counting was used to measure the fossil and biogenic carbon in solid wastewater samples obtained from two WWTPs, one with (WWTP A) and one without (WWTP B) a digestion process. The results were compared with those obtained from accelerator mass spectrometry measurements. Greenhouse gas (GHG) emissions under two IPCC scenarios were also compared, an earlier version and a revised version without and with consideration of fossil CO_2. The results showed that fossil carbon accounted for 3 – 10 % of the total carbon in mixed sludge. Mixed sludge contributed 50 – 75 % of the fossil carbon total input, with 100 % of the biogenic carbon total input in sewage sludge treatment processes. In the digestion process of WWTP A, the fossil carbon contribution from biogas was nearly 0 %, about 15 % in digested sludge. Only a small amount of fossil carbon decomposes during the anaerobic digestion process. The calculated GHG emissions based on the IPCC's earlier and revised scenarios differed by 1,100 ~ 1,800 kg CO_2-eq/d, accounting for 36 – 65 % of the GHG emissions in sewage sludge treatment processes. The effect of fossil carbon on GHG emissions in sewage sludge treatment cannot be ignored and should be studied further.

1. Introduction

Quantifying GHG emissions from wastewater treatment processes is important for carbon neutral operations, and considerable effort has been applied to monitoring and modelling such emissions. GHG mainly originate from sources of fossil carbon (petrol, coal, etc.), but not biogenic carbon (wood, biodiesel, etc.). Burning fossil fuel results in the emission of carbon that has been stored for up to millions of years in the ground, while burning wood emits carbon that is part of the biogenic carbon cycle. The Intergovernmental Panel on Climate Change (IPCC) assumed that all CO_2 emissions in the wastewater treatment process were biogenic and recommended against their inclusion in the 2006 GHG inventory (Eggleston et al., 2006). Subsequent studies have indicated that wastewater contains substantial amounts of fossil carbon thought to be derived from petroleum products. In 2019, the IPCC revised their guidance to encourage assessment of fossil carbon in WWTPs (Bartram et al., 2019). Further studies are expected to improve the accuracy of emission estimates from non-biological sources associated with wastewater treatment operations and wastewater discharge (Bartram et., 2019).

As reported by Law et al. (2013), fossil carbon is widely present throughout the wastewater treatment process, but mainly comes from the influent, some likely to become oxidized into CO_2 during the biological treatment process and some remaining in the sludge. Studies have reported that the fossil carbon remaining in sludge occupies over half of the total input of fossil carbon (Law et al., 2013). Dewatered sludge contains 10~25 % fossil carbon (Tseng et al., 2016). When sewage sludge is incinerated, some of the fossil carbon in the sludge is transformed into fossil CO_2, which increases GHG emissions. For example, during 150 t/d of sewage sludge incineration, GHG emissions by accounting for fossil CO_2 is 8 – 9 t CO_2-eq/d higher than not counting it (~20 t

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CO_2-eq/d) (Kang et al., 2019). This implies an underestimation of GHG emissions. At present, there has been no systematic research on fossil carbon, especially in sewage sludge treatment processes including anaerobic digestion and incineration. The measurement of fossil carbon in WWTPs is important to improve the quality and evaluation of WWTP GHG emission data.

In this study, the fossil and biogenic carbon behaviour in sewage sludge treatment processes was investigated, providing data to allow for accurate evaluations of their impact on GHG emissions. The liquid scintillation counting (LSC) method was used to analyze the fossil and biogenic carbon contributions. Two WWTPs were examined, one with (WWTP A) and one without (WWTP B) a digestion process, to clarify the differences in characteristics between samples. The data for two seasons (autumn and winter) was examined to establish any seasonal differences. The earlier and revised scenarios presented by the IPCC were examined to show the necessity of accounting for fossil CO_2 as a GHG.

2. Materials and methods

2.1 Sampling

To study the behaviour of fossil and biogenic carbon in sludge treatment processes, samples of mixed sludge (primary sludge + waste-activated sludge), digested sludge, biogas, polymer for dewatering, dewatered sludge, effluent, incineration auxiliary fuel (heavy oil), incinerated ash, incinerated gas, and scrubbing wastewater were obtained from WWTP A and WWTP B in Japan in autumn and winter (Figure 1). In WWTP A, 470 m^3/day of mixed sludge was subjected to a combination of mesophilic anaerobic digestion, dewatering, and incineration processes. For incineration, 83 % of biogas is used for incineration as auxiliary fuel. The digested sludge was dewatered using a belt press after adding polymer, and the dewatered sludge was then combusted in a fluidized bed incinerator. Acid in the flue gas was removed with a wet scrubbing tower using caustic soda. Effluent from the water line was used to wash the belt press and dilute the polymer and caustic soda. By contrast, in WWTP B, 320 m^3/d of mixed sludge was treated by dewatering and incineration processes, similar to the system used for WWTP A; however, WWTP B had no digestion process.

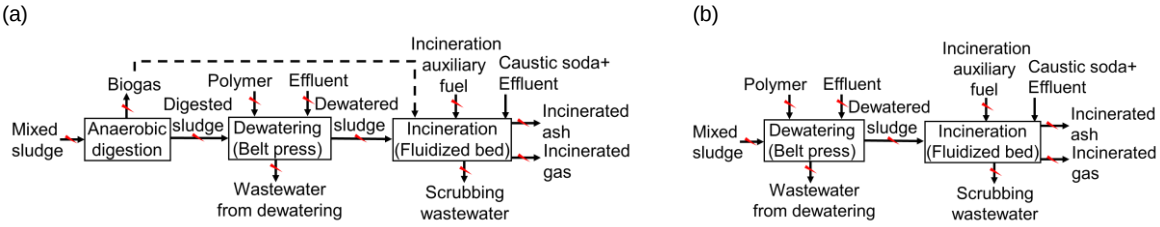


Figure 1: Sewage sludge treatment processes and sampling points (↘) in (a) wastewater treatment plant (WWTP) A and (b) WWTP B

2.2 Fundamental feature analysis

For liquid and solid samples, the total solids content (TS) included both suspended solids and dissolved solids, which were measured using a weighing method following filtration or centrifugation (Sall et al., 2006). Volatile total solids were measured after heating wastewater to 600 °C for 1 h in a thermostatically controlled muffle oven (Sall et al., 2006). Fixed total solids were the residue remaining after heating. Total carbon (TC) and total organic carbon (TOC) of all samples were determined, and inorganic carbon was calculated from the difference between TC and TOC (Sall et al., 2006). A TOC Analyser (TOC-V_{CSH}; Shimadzu Co., Ltd, Kyoto, Japan) was used directly for the wastewater samples. Sludge and ash samples were first treated with a solid sample combustor (SSM-5000A; Shimadzu Co., Ltd). For gas samples, biogas from WWTP A was measured using an Agilent 490 Micro GC system (GL Sciences Inc., Osaka, Japan) to estimate N_2, CH_4, and CO_2 contents. Incinerated gas was measured using a Graphtec GL240 system (Graphtec Corp./Shimadzu Co., Ltd., Kyoto, Japan) to estimate CO, CO_2, and O_2 contents.

2.3 ^{14}C Analytical Methods

^{14}C in samples was analyzed by LSC and accelerator mass spectrometry (AMS) following a standard method ASTM D6866-18 (Li et al., 2020). In LSC, the photomultiplier tube detects low-energy β-rays emitted by ^{14}C, enabling direct measurement of the biogenic carbon concentration in the samples (Edler, 2009). Before the LSC measurement, a combustion pretreatment was carried out. The combustion system is shown in Figure 2. To remove the natural air containing CO_2 from the quartz tube, a 21 vol% O_2/79 vol% N_2 pure gas (flow rate:

70 mL/min) flowed into the quartz tube for 45 min. A sample containing 1.43 g of carbon was placed on a quartz boat and burned at 550 °C for 1 h. The temperature was raised to 700 °C for 1.5 h. Produced CO was transformed into CO_2 by copper oxide at 900 °C. The gas passed through an empty bottle, allowing the temperature to fall. A $KMnO_4$ solution (100 mL at 0.5 w/v%) was used to remove SO_2, silica gel was used to remove moisture, 35 mL of Carbo-Sorb E (PerkinElmer Co., Ltd., Waltham, MA, USA) was used to absorb the generated CO_2, and a $Ba(OH)_2$ solution (0.15 mol/L) was used to check if all CO_2 was captured by Carbo-Sorb E. After combustion, 10 mL of the absorbed CO_2 Carbo-Sorb E was mixed with 10 mL of Permafluor E+ (PerkinElmer Co., Ltd.) in a 20-mL glass counting vial (PerkinElmer Co., Ltd.). The mixture was analyzed using LSC (Tri-Carb 2700; PerkinElmer Co., Ltd.) for 200 min, in triplicate. The TS in the wastewater and gas samples was too low to analyze the ^{14}C content of these samples by LSC. The samples were analyzed by Beta Analytic Testing Laboratory (Miami, FL, USA) for ^{14}C analysis using AMS, which is more sensitive and has better precision than LSC (< 1 % versus < 9 %) (Edler, 2009). AMS accelerates ions to high kinetic energies before mass analysis. Among mass spectrometric methods, it has the benefit of being able to separate rare isotopes from an abundant mass. Only mixed sludge samples were used to compare AMS with LSC.

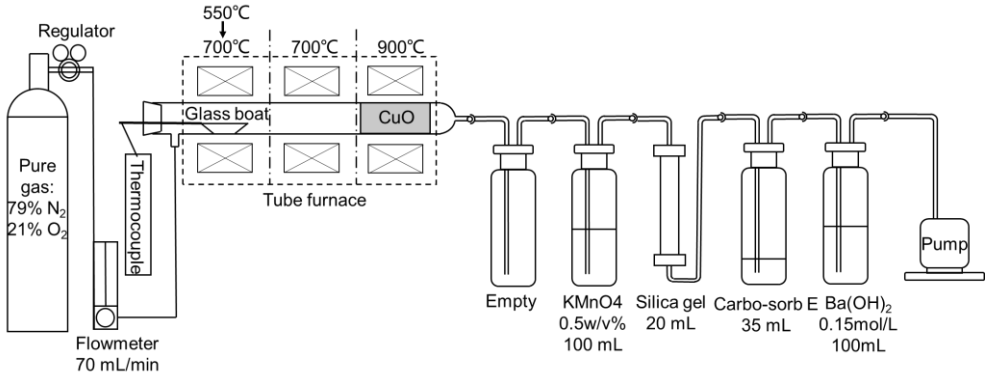


Figure 2: Scheme of the pre-combustion system for liquid scintillation counting.

3. Results and discussions

3.1 Calibration curve for LSC

The biogenic carbon contribution from two samples, G2020 (grass collected from Kyoto University Katsura Campus, Kyoto, Japan at 7.7.2020) and PPW (polypropylene, PPW-5J; Seishin Enterprise Co., Tokyo, Japan), were measured using AMS. The results showed that the carbon contents in G2020 and PPW were mostly biogenic carbon and fossil carbon. As such, mixing of the G2020 and PPW constituents was used to simulate samples with different fossil/biogenic carbon proportions to create a calibration curve for LSC (Figure 3).

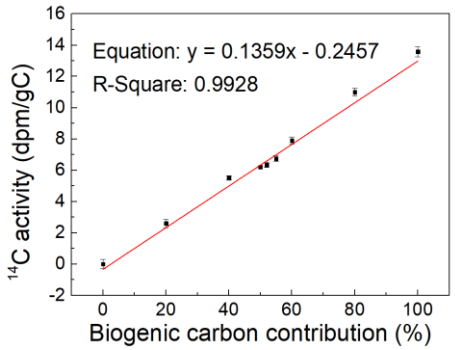


Figure 3: Calibration curve for the liquid scintillation counting method

The calibration curve followed a linear relationship, which was used to calculate the biogenic carbon contribution in sludge samples, as following Eq(1):

Biogenic carbon contribution (%) = [^{14}C activity (dpm/g C) + 0.2457] / 0.1359 (1)

The fossil carbon contribution can then be calculated as following Eq(2):

Fossil carbon contribution (%) = 100 % - Biogenic carbon contribution (%) (2)

To study the limit of detection and quantification for biogenic carbon, blank samples were combusted several times. According to the method of Uemoto (2010), the limit of detection was 3.3 %, and the limit of quantification was 6.5 %. In this study, when the detected biogenic carbon contribution of the sample was less than 3.3 %, biogenic carbon was not detected (i.e., assumed to be zero); above 6.5 %, the value was considered to be a reliable measure.

3.2 Fossil carbon contribution in sewage sludge treatment processes

Table 1 shows the fossil carbon contribution in all samples. The experiment was repeated twice and the results were shown as average with variance. The LSC and AMS methods showed a difference of less than 5 %, demonstrating the accuracy of LSC. Overall, mixed sludge was the main contributor (input) of carbon in the sludge treatment processes. There were no seasonal differences in fossil carbon contributions for either of the WWTPs; seasonality was not a factor with regard to the composition of biogenic and fossil carbon in this study. Using AMS, Tseng (2016) found that the fossil carbon contributions in primary sludge and waste-activated sludge were about 1 % and 15 %, in agreement with the range of 3.3 – 6.2 % for mixed sludge in this study. Law (2013) concluded that the fossil carbon contribution in WWTPs was related to industrial wastewater. In the present study, industrial wastewater accounted for 10 % and 12 % of the influent in WWTP A and B. The fossil carbon contribution of mixed sludge in WWTP B was slightly higher than that of WWTP A. The fossil carbon contribution of biogas was 0.9 – 1.1 % in this study, similar to the range of 1.6 – 2.7 % in earlier studies (Law et al., 2013; Tseng et al., 2016). The fossil carbon contribution in mixed sludge in this study was higher than that in biogas and lower than that in digested sludge, indicating that the digestion process mainly decomposes biogenic carbon and generates biogas rich in biogenic carbon.

Table 1: Fossil carbon contribution in samples (%)

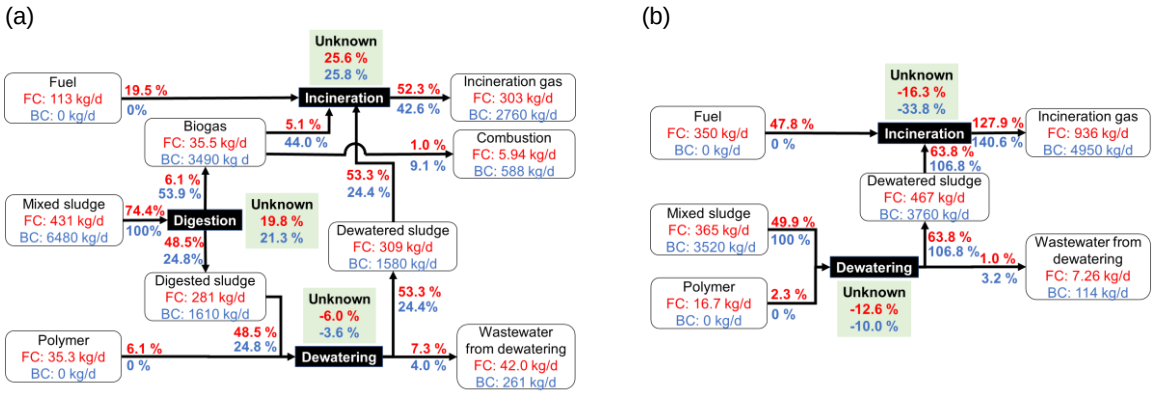
Season	Plant	WWTP A		WWTP B	
	Method	LSC	AMS	LSC	AMS
Autumn	Mixed sludge	5.2 ± 0.2	3.9 ± 0.3	9.3 ± 0.9	6.2 ± 0.3
Winter		7.6 ± 1.7	3.3 ± 0.3	9.5 ± 1.0	5.1 ± 0.3
Autumn	Digested sludge	14.8 ± 0.8	N.A.	N.A.	N.A.
Winter		15.0 ± 1.1	N.A.	N.A.	N.A.
Autumn	Dewatered sludge	16.4 ± 0.8	N.A.	11.5 ± 1.6	N.A.
Winter		16.4 ± 0.4	N.A.	10.6 ± 2.0	N.A.
Autumn	Wastewater from dewatering	15.6 ± 1.3	N.A.	N.A.	6.2 ± 0.4
Winter		N.A.	11.8 ± 0.3	N.A.	5.9 ± 0.3
Autumn	Biogas	N.A.	1.1 ± 0.1	N.A.	N.A.
Winter		N.A.	0.9 ± 0.2	N.A.	N.A.
Autumn	Incinerated gas	N.A.	9.1 ± 0.1	N.A.	15.9 ± 0.0
Both	Polymer	97.7 ± 0.1*	N.A.	94.1 ± 0.3*	N.A.
Both	Heavy oil	97.5 ± 0.3*	N.A.	98.6 ± 0.4*	N.A.

*These data are considered to be 0, as they are below the limit of detection and quantification of biogenic carbon. AMS: accelerator mass spectrometry; LSC: liquid scintillation counting; N.A.: not analyzed; WWTP: wastewater treatment plant.

Dewatered sludge (after digestion) has been reported to contain 15.5 – 22.6 % fossil carbon (Tseng et al., 2016; Kang et al., 2019), similar to the same amount found at WWTP A (~16 %). Polymer added for dewatering is mainly produced from fossil carbon (99.6 %; Law et al., 2013); here, the polymer was 100 % fossil carbon. Heavy oil was used as an auxiliary fuel in both WWTPs to support complete and continuous combustion of dewatered sludge; carbon in heavy oil is completely fossil carbon. Digestion mainly degrades biogenic carbon, as opposed to fossil carbon, which remains in the sludge. For the dewatering process, fossil carbon does not have a preferential path, because the biogenic and fossil carbon contributions in wastewater from dewatering, i.e., the sludge before and after dewatering, are the same. Notably, only heavy oil (fossil carbon) was used as an auxiliary fuel in the sludge incineration process at WWTP B. WWTP A also used biogas (biogenic carbon) from the sludge anaerobic digestion process. The fossil carbon contribution in the incineration gas of WWTP A was lower than that of WWTP B.

3.3 Fossil and biogenic carbon behaviour

In WWTP A and B, the amounts of fossil and biogenic carbon were relatively stable between autumn and winter. Seasonal variation did not affect the behaviour of fossil and biogenic carbon. Figure 4 shows the mass flows of fossil and biogenic carbon calculated from the contributions and flow rate of each media for the two WWTPs, along with the annual average. For both WWTPs, all biogenic carbon originated from the mixed sludge. For the total input of fossil carbon, including that from mixed sludge, polymer, and auxiliary fuel, the mixed sludge provided 74.4 % and 49.9 % of the fossil carbon for WWTPs A and B. The rest of the fossil carbon came from the polymer and fuel (6 % and 19 % for WWTP A and 2 % and 48 % for WWTP B). The high proportion of generated biogas (83 %) in WWTP A used as auxiliary fuel reduced the reliance on heavy oil. WWTP B consumed more heavy oil; the fossil carbon from WWTP B was significantly higher. In WWTP A, which used a digestion process, 6.1 % of the fossil carbon was transformed into biogas, while 48.5 % remained in the digested sludge. The digestion process mainly decomposes biogenic carbon; nearly all of the fossil carbon and one third of the biogenic carbon (i.e., the sum of biogas and digested sludge) remained in the digested sludge. Similar to these findings, Law et al. (2013) found that 12 % of fossil carbon with 54 % of biogenic carbon was degraded in an anaerobic digestion process. The two types of carbon in the dewatering process showed similar behaviour in both WWTPs, with almost all of the carbon transferred to the dewatered sludge. Auxiliary fuel contributed a large amount of fossil carbon. During the incineration process, carbon from the dewatered sludge, fuel, and biogas was completely transformed into CO_2. Theoretically, there is no difference between output and input due to conservation of matter. Actual result indicates the difference-"unknow" exists. The unknown is caused by the fluctuation of sludge feature due to the changing influent quality in the actual WWTPs and ranged from −33.8 % to 25.8 %.



*Red: Fossil carbon (FC); Blue: Biogenic Carbon (BC)

Figure 4: Illustration of fossil carbon and biogenic carbon behaviour in (a) wastewater treatment plant (WWTP) A and (b) WWTP B

3.4 Impact of fossil carbon on GHG emissions

Based on the fossil carbon behaviour of WWTPs A and B, two scenarios were compared to evaluate GHG emissions from the two WWTPs. The earlier IPCC scenario included CH_4 and N_2O, which can be calculated as described in a previous study (Oshita et al., 2014) that investigated the diffusion CH_4 and N_2O from sludge treatment systems. The revised scenario of the IPCC includes not only CH_4 and N_2O but also the fossil carbon in dewatered sludge. For each WWTP, because the GHG emissions for the two seasons were similar, the average of the two seasons was analyzed. For WWTP A, the earlier IPCC scenario and the revised scenario GHG emission results were 1,986 kg CO_2-eq/d (1,513 kg CO_2-eq/d of CH_4 and 473 kg CO_2-eq/d of N_2O) and 3,119 kg CO_2-eq/d (1,133 kg CO_2-eq/d of fossil carbon) (Table 2).

The value of the revised scenario was 57 % higher than that of the earlier IPCC guideline, as fossil carbon occupied about 36 % of the GHG emission. Similarly, GHG emissions for WWTP B were 973 kg CO_2-eq/day (92 kg CO_2-eq/d of CH_4 and 681 kg CO_2-eq/d of N_2O) and 2,776 kg CO_2-eq/d (1,803 kg CO_2-eq/d of fossil carbon) according to the earlier and revised scenarios. The value of the revised scenario was 185 % higher than that of the earlier scenario, as fossil carbon occupied about 65 % of the GHG emission. Fossil carbon in sludge has a substantial impact on GHG emissions, occupying 36~65 % of GHG emissions from sewage sludge treatment processes. Compared with WWTP B, fossil carbon occupied a smaller proportion in WWTP A, because most of the CH_4 produced in the digestion process of WWTP A was accounted for in the IPCC's

scenario; that for WWTP B was not, and total fossil carbon of input sludge in WWTP B is higher than WWTP A.

Table 2: Total greenhouse gas emissions (kg CO_2-eq/d)

Name	WWTP A	WWTP B
CH_4	1,513	92
N_2O	473	681
Fossil carbon	1,133	1,803

4. Conclusions

A LSC method was established, including pre-treatment and a calibration curve, to measure the fossil and biogenic carbon in solid WWTP samples. Compared with AMS, LSC results differed by less than 5 %, supporting the accuracy of the LSC method. Using the LSC method, fossil and biogenic carbon contribution and behaviour analyses were performed. The results showed that fossil carbon accounted for 3–10 % of the TC in mixed sludge. Mixed sludge provided 50–75 % of the fossil carbon total input, with 100 % biogenic carbon total input, in sewage sludge treatment processes. In the digestion process of WWTP A, the fossil carbon contribution from biogas was nearly 0 %, but was about 15 % from digested sludge. Compared to total biogenic carbon (50 %), little fossil carbon (5 %) decomposed during anaerobic digestion. The dewatered sludge retained almost all of its fossil and biogenic carbon in the sludge before dewatering, indicating that the dewatering process does not alter the fossil carbon distribution. In this study, no seasonal variation between autumn and winter in fossil carbon distribution and behaviour was observed. The GHG emission results based on the IPCC's earlier and revised scenarios were compared, which revealed a difference between the two of 1,100~1,800 kg CO_2-eq/d, accounting for 36–65 % of the GHG emissions in the sewage sludge treatment processes. The effect of fossil carbon on GHG emissions in sewage sludge treatment cannot be ignored and must be investigated further.

Acknowledgments

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