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An Overview of the Effects of Heat Treatments on the Quality of Organic Wastes as a Nitrogen Fertilizer

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Additional information is available at the end of the chapter

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Abstract

Sewage sludge is often heat-dried to eliminate water and pathogens. However, heat-drying can also change the form of nitrogen (N). To improve our understanding of this phenomenon, we examined the heat-induced changes in the rate of N mineralization from soils and organic wastes. Published results revealed that the response to the heating temperature differed between soils and organic wastes. As the heating temperature increased to 200°C, the rate of N mineralization increased in soils but decreased in organic wastes. In organic wastes such as sewage sludge, the content of mineralized N tended to decrease sharply when heating temperatures increased to 150–200°C. Furthermore, our results obtained from heat-drying of sewage sludge at 180°C indicated that the rate of carbon (C) mineralization decreased with increasing heating period after the sludge temperature reached 180°C. The C in sewage sludge heated at 180°C for 120 hours after complete drying contained more humin and aromatic C than that in sludge that was heat-dried at 180°C without the additional heating period. These results suggest that the heat-drying treatment can be divided into the drying and denaturing periods and that the temperature of the sludge, not that of the reactor, affects the quality of the end-product.

Keywords: carbon, heat-drying, nitrogen mineralization, organic wastes, sewage sludge, soil, stabilization

1. Introduction

The treatment of raw organic wastes increases their potential range of beneficial uses. The most conventional treatment is composting, which is typically conducted at ambient temperatures. It is generally recognized that composted organic matter is a good soil amendment that releases inorganic nitrogen (N) relatively slowly. Besides composting, heating has become a popular method to enhance the quality of organic wastes.

To eliminate water and pathogens, sewage sludge is heat-dried by various methods such as convective drying, conductive drying, and solar drying [1]. Several researchers have also reported that heat-drying of sewage sludge can change the form of N [2]. For example, Smith and Durham [3] evaluated the content of N in five sewage sludges in paired treatments, both anaerobically digested and one additionally heat-dried for pelleting or granulation. During heat-drying, more than 75% of inorganic ammonium was lost by volatilization. However, during the aerobic incubation at 25°C for 56 days, the production of nitrate in soil amended with heat-dried sludge was similar to, or even larger than, that from the corresponding sludge without heat-drying. These results suggest that heat-drying of sewage sludge greatly increased the content of mineralizable organic N.

The occurrence of such heat-induced N transformations is not surprising, because a similar phenomenon has been seen for a variety of soils. In 1901, Daikuhara [4] reported that heating of soil samples in a pan for 20 minutes increased the content of N that could be extracted by dilute acid solutions. His forgotten research is summarized briefly in our recent paper [5].

In contrast with soils, little information is available for organic wastes. In particular, limited attention has been paid to the relationship between the heating temperature and the resulting changes in the form of N. Case et al. [6] recently reported that heat-drying of sewage sludge at temperatures ranging from 130 to 250°C significantly decreased the rate of N mineralization. Their findings differ from previous results including ours [7], which showed increased N mineralization by heat-drying.

In this chapter, we briefly review what is known about this topic by examining data from previous papers in which the heating temperature was specified. The focus is on the effect of heating on the quality of organic wastes as a source of N for crops. The content is not limited to sewage sludge but covers other organic wastes and soils. For a more comprehensive review of sewage sludge, please refer to Rigby et al. [2]. Since Daikuhara's pioneering work, there have been many relevant publications from Japan. We introduce some of these papers to make them available to the international research community and our own unpublished results.

2. Previous publications from Japan on heat-induced changes in the quality of soils and organic wastes

2.1. Soils

Around 1940, the early findings of Daikuhara [4] were re-evaluated by Mitsui [8]. A series of his experiments were carried out before and during the Pacific War (World War II), when supplies of inorganic fertilizer ran short [5]. By heat-treating two soils at several temperatures (from 65 to 400°C, for 4 hours), Mitsui found that the content of mineralized N (initial inorganic N plus mineralizable N) reached a maximum with heating around 200°C. To generalize this result, he collected 44 types of soils from paddy and upland fields throughout Japan and treated them at 130 or 200°C for 4 hours. He then evaluated the contents of inorganic N and mineralizable N by means of aerobic incubation at 26°C for 31 days.

Both forms of N were increased by the heat treatments (**Figure 1**). The average content of inorganic N was 39.8 mg kg⁻¹ (130°C) and 199.3 mg kg⁻¹ (200°C) as compared to 25.2 mg kg⁻¹ (original). The average content of mineralizable N was 89.4 mg kg⁻¹ (130°C) and 111.1 mg kg⁻¹ (200°C) as compared to 28.0 mg kg⁻¹ (original). The amount of N mineralized by heating at 200°C and subsequent incubation was positively correlated with the content of total N in the original soil ($r = 0.55^{**}$), suggesting that the soil heating effect was greater for humus-rich soils.

The findings of Mitsui [8] were extended by Sakamoto et al. [9]. They tried to reveal the origin of the N mineralized by heating and measuring the amount of N mineralized from two soils fumigated with chloroform or heated at different temperatures. Chloroform fumigation can kill most of soil microbes, so it has been used to extract the elements such as carbon (C), nitrogen (N), and phosphorus (P) in soil microbial biomass.

The amount of N mineralized from the fumigated soil was similar to that from the soil heated at 50 and 100°C, but it was much less than that from the soil heated at 150 and 200°C (**Figure 2**).

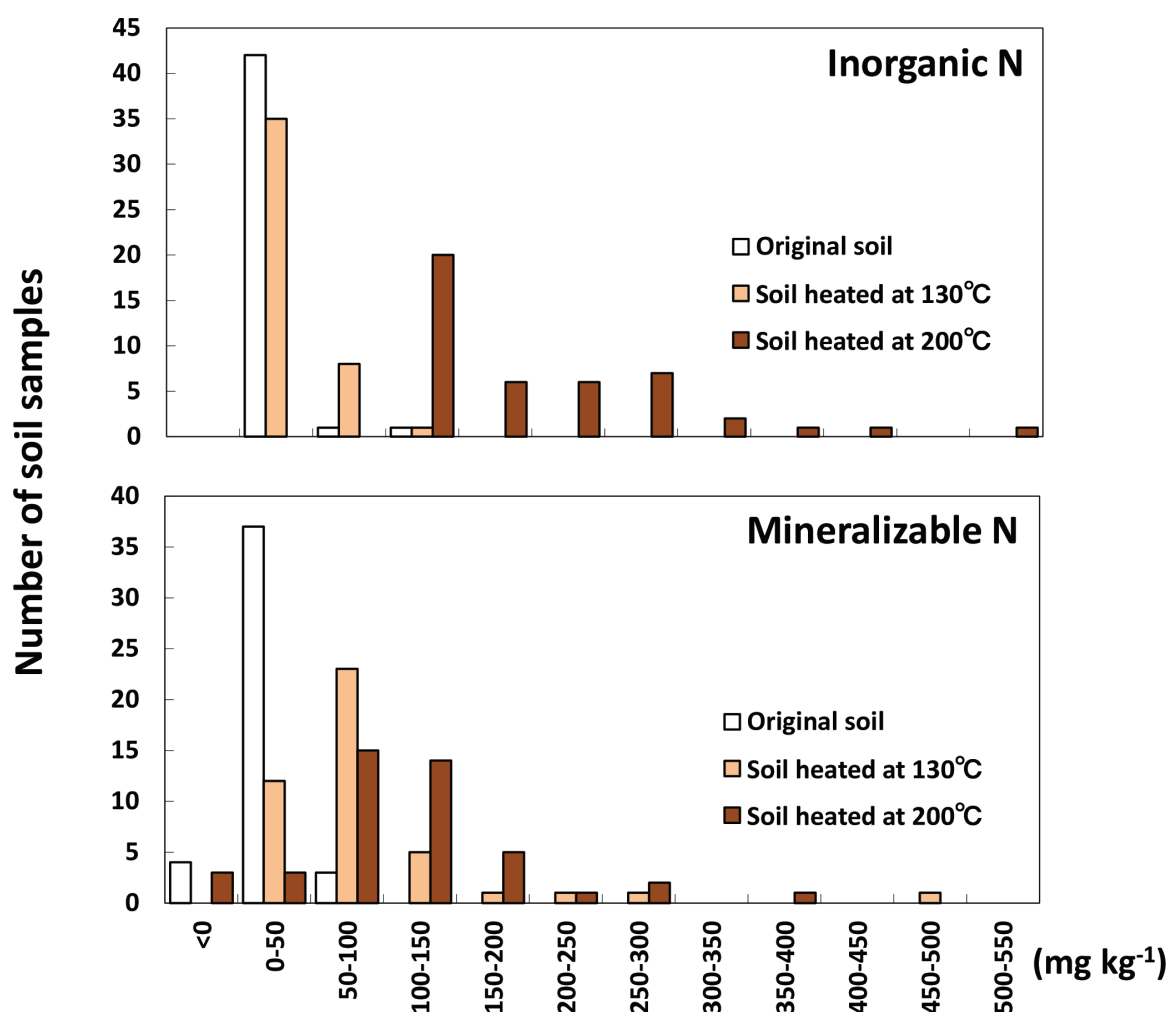


Figure 1. Frequency distributions of inorganic and mineralizable N in Japanese agricultural soils ($n = 44$) before and after heating at 130 or 200°C for 4 hours (adapted from Ref. [8]). Mineralizable N was evaluated by aerobic incubation at 26°C for 31 days.

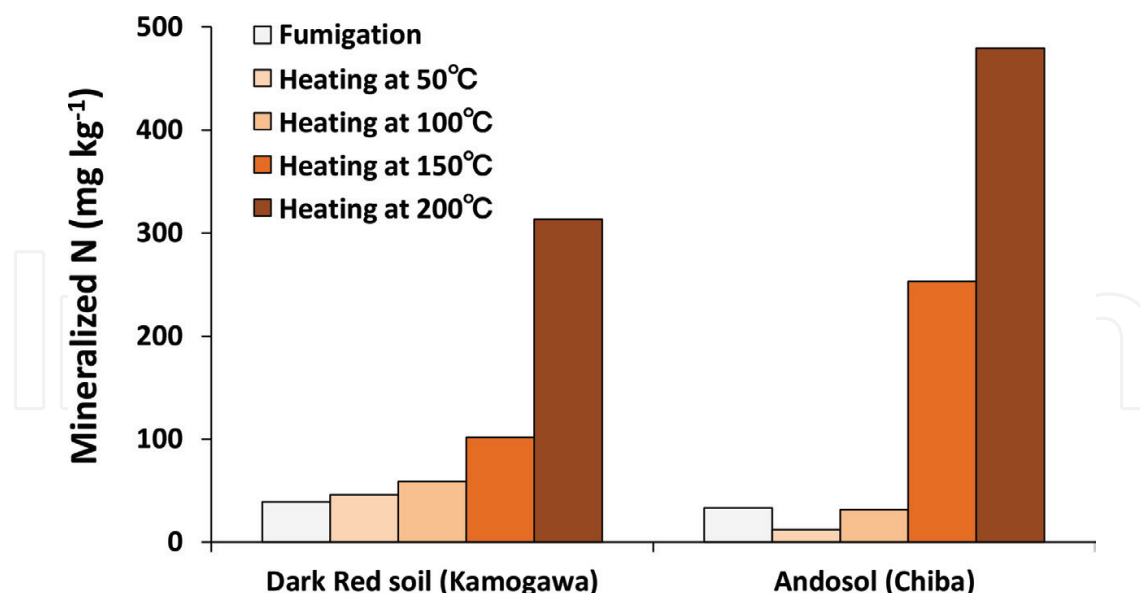


Figure 2. Amount of mineralized N in fumigated or heat-treated soils during incubation (adapted from Ref. [9]). Soils were fumigated with chloroform or heated at 50–200°C for 24 hours and then were incubated aerobically at 25°C for 20 days.

Sakamoto et al. also counted the number of microbes after the treatments by the dilution agar plate method. They found that the decrease in the number of bacteria caused by the fumigation was comparable to that by heating at 50°C, and the decrease in the number of actinomycetes and fungi by the fumigation was comparable to that caused by heating at 100°C. From these results, they concluded that the N mineralized by heating at 50 and 100°C derived mainly from the microbial biomass fraction, whereas the N mineralized at temperatures above 100°C derived mainly from the nonbiomass fraction.

2.2. Rapeseed oil cake and sewage sludge

In addition to soils, organic wastes have been heat-treated before recycling for use as fertilizer. In 1932, Yoshimura et al. [10] reported why the rate of N mineralization from rapeseed oil cake (the residue that remains after oil extraction) imported from China was lower than that from oil cake produced in Japan. At that time, rapeseed oil cake was produced by roasting, crushing, steam-heating, and squeezing. Because the Chinese rapeseed oil cakes were darker, they hypothesized that the rapeseed was roasted for a longer period and thus at a higher temperature and evaluated the relationship between the roasting conditions and the rate of N mineralization.

Yoshimura et al. found that the rate of N mineralization decreased with increasing roasting period and temperature. **Figure 3** clearly shows that the rate of extraction of N with 50 mM NaOH and the growth of tobacco decreased as the roasting temperature increased from 150 to 170°C [11]. The growth of tobacco supplied with rapeseed oil cakes imported from China was smaller than that with the domestic cakes. These results contrast with those of soils. Probably because of the uniqueness, we found no evidence that their paper had been cited until we rediscovered it recently [12].

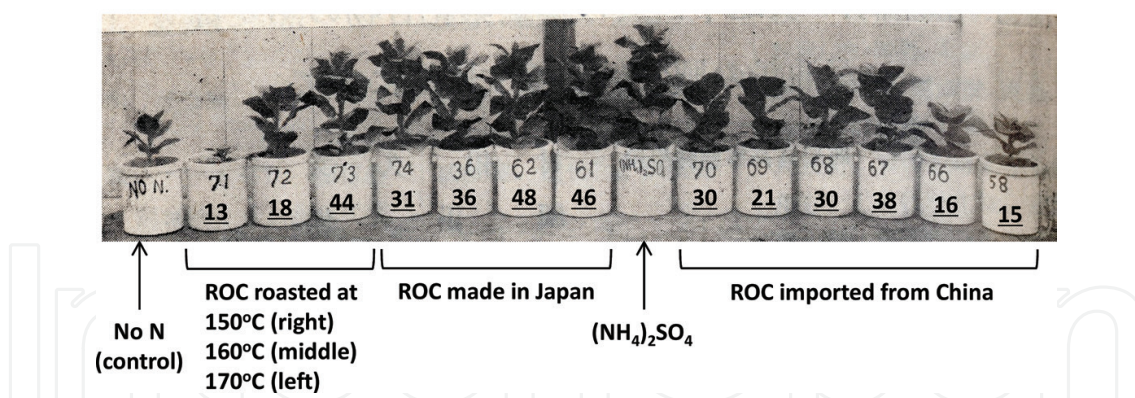


Figure 3. Effects of the application of rapeseed oil cake (ROC) on the growth of tobacco (reprinted from Ref. [11]). Rapeseed oil cake or $(\text{NH}_4)_2\text{SO}_4$ was applied at 1.5 gN pot^{-1} . Underlined values indicate the percentage of total N in the ROC that was extractable with 50 mM NaOH.

Yoshida [13] confirmed and extended those findings in 1970s. We are not sure if he was aware of Yoshimura's results, as he did not cite them. But whether by chance or not the materials that he selected were rapeseed oil cake and food sludge. Food sludge was dewatered by centrifugation, and both materials were dried at $90\text{--}95^\circ\text{C}$ and crushed. They were then heat-treated at 150°C for 2 hours, 165°C for 1 hour, 175°C for 1 hour, or 200°C for 0.5 hour. These materials were subjected to the aerobic incubation at 30°C for 50 days, and the content of mineralized N produced during the incubation was evaluated.

When rapeseed oil cake was heat-dried at 175°C for 1 hour or at 200°C for 0.5 hour, the rate of N mineralization became much lower than that of the control (**Figure 4**). The results were similar for food sludge, indicating that the decrease of N mineralization caused by high temperatures was not limited to rapeseed oil cake. The influence of heating at 175°C was quite different from that of heating at 165°C for both materials. This difference suggests that there is a threshold temperature between 165 and 175°C after which the rate of N mineralization decreases with increasing temperature.

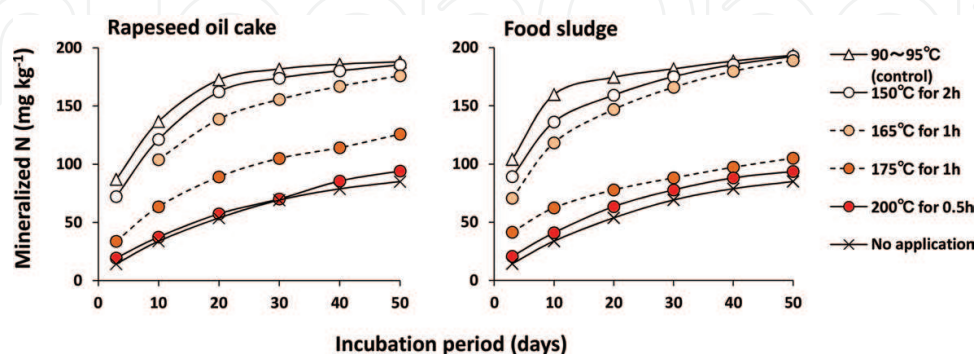


Figure 4. Patterns of N mineralization from a sandy loam soil to which rapeseed oil cake and food sludge treated at different temperatures were applied at a rate of 0.2 gN kg^{-1} soil (created by the authors from the data in Ref. [13]). Aerobic incubation was carried out at 30°C for 50 days. "No application" represents the original soil without application.

In the same year, Kurihara and Watanabe [14] reported that heat-drying of sewage sludge at 130°C for 1 hour could increase the rate of N mineralization by around 30%. In their experiment, mineralizable N was evaluated by the aerobic incubation at 29°C for 35 days. Their result is similar to the findings of Smith and Durham [3]. In addition to heat-drying, Kurihara and Watanabe reported that freeze-drying of sewage sludge decreased the rate of N mineralization by around 30%.

3. Heat-induced changes in mineralized N in sewage sludge

We have also examined the effect of heating of sewage sludge on the rate of N mineralization [7] and the growth of komatsuna (*Brassica campestris* L. var. *rapa*), a leafy vegetable [15]. We introduce our results in this section. For heating of sewage sludge, we used a pilot-scale conductive dryer ([16]; Krosaki Harima, K-10, Fukuoka, Japan). Sewage sludge in the reactor is heated indirectly by means of a surrounding oil heater in which the temperature can be regulated up to 200°C (Figure 5). During the treatment, the sludge is also mixed and crushed by a rotary stirrer to homogenize and granulate the products.

Dewatered sewage sludge collected from a wastewater treatment plant in Shimane Prefecture, Japan, was used in the experiment. We compared two heat treatments such as dry-heating of air-dried sludge (AD) and heat-drying of moist sludge without a preliminary air-drying step (HD). Using these treatments, we prepared four types of materials: AD dry-heated at 120°C

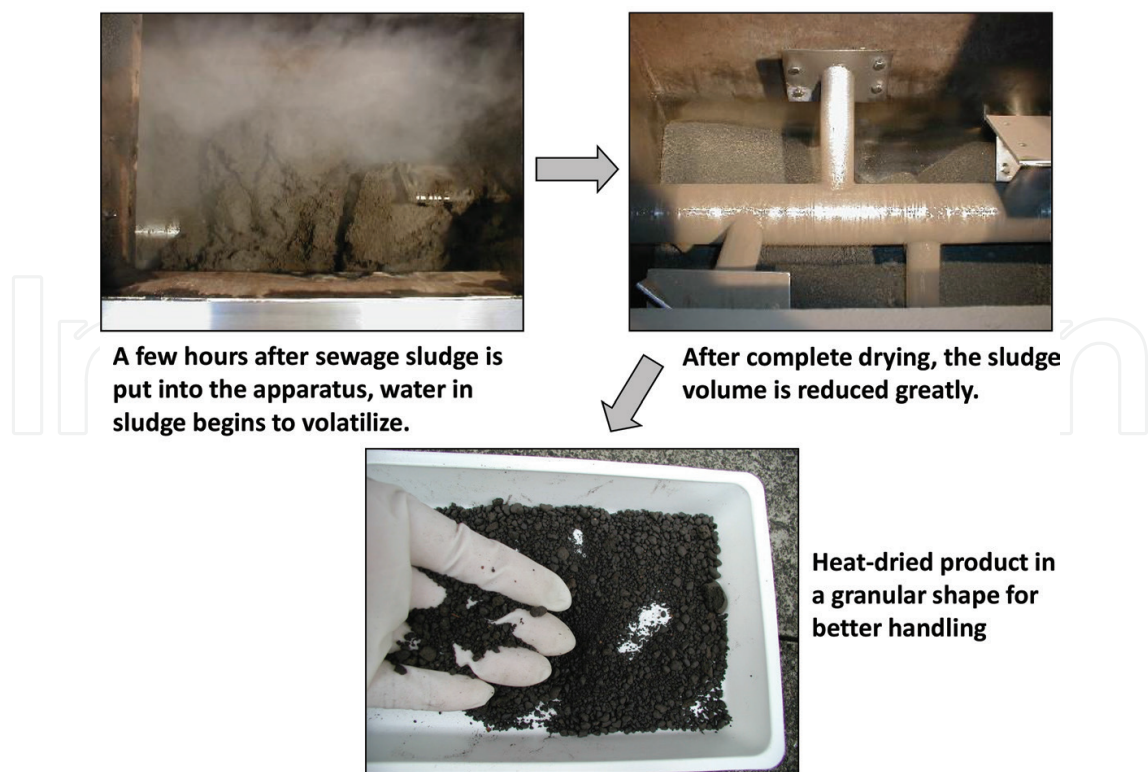


Figure 5. Reactor used in the pilot-scale conductive dryer system in our previous research [7, 16].

(AD-120), AD dry-heated at 180°C (AD-180), moist sludge heat-dried at 120°C (HD-120), and moist sludge heat-dried at 180°C (HD-180). Dry-heating requires an air-drying pretreatment and is not practical in terms of time and cost. We nonetheless used it to evaluate the effect of heating on the sludge properties more directly by comparing AD-120 and AD-180 with AD. The heating period was fixed at 16 hours.

These materials were mixed with three soils (an Andosol, a Fluvisol and an Arenosol) at a rate of 1% w/w, and the soils were aerobically incubated at 30°C for 84 days. Regardless of the soil type, the rate of N mineralization was increased significantly by heating of the air-dried sludge at 120°C and it was decreased significantly by heating of the air-dried sludge at 180°C (Figure 6). The conventional treatment based on heat-drying of moist sludge at 120 or 180°C exerted similar but less pronounced effects. These heat-induced changes were attributed to the transformation of sludge organic N, because volatilization of N during the heating treatments was negligible [7].

Using the same combination of sludges and soils, we carried out two successive pot experiments. Komatsuna, a popular test vegetable in Japan, was grown after a basal application of sludges at a rate of 20 Mg ha⁻¹ (dry matter base). Sludge application was carried out only once before the start of the first experiment.

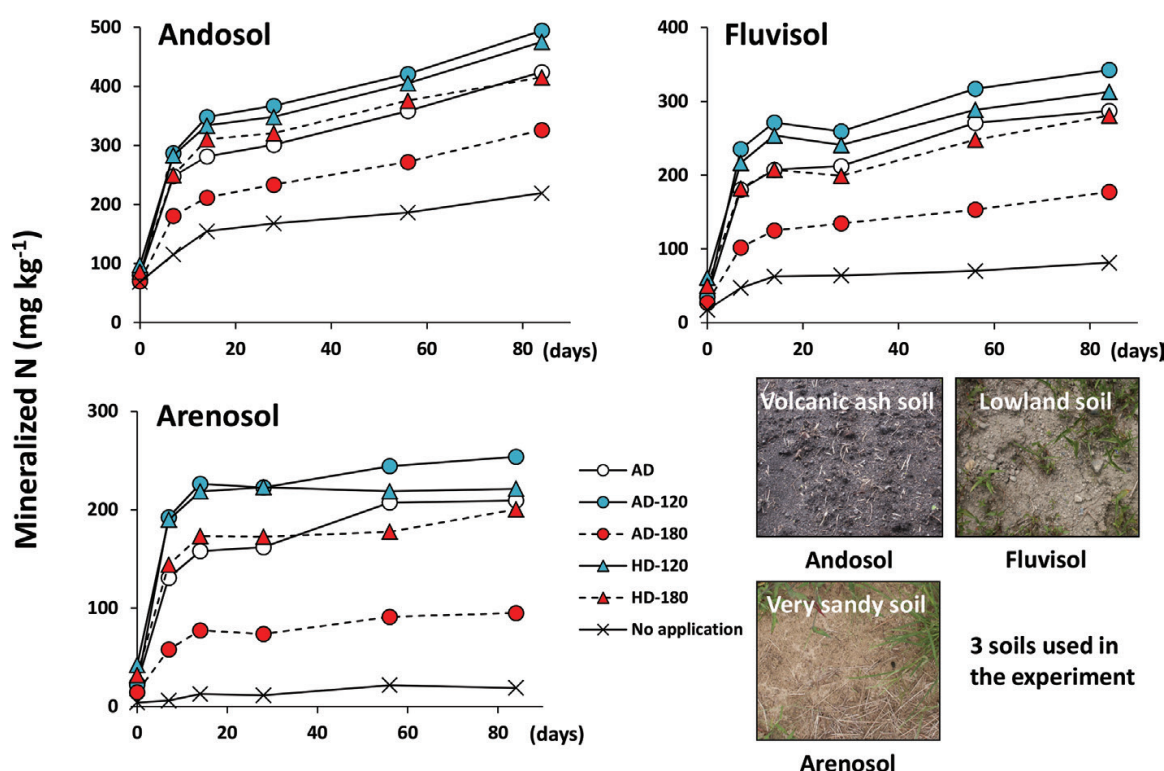


Figure 6. Patterns of N mineralization from three soil types amended with heat-treated sewage sludge (adapted from Ref. [7]). The heat treatment was followed by aerobic incubation at 30°C for 84 days. AD: air-drying, AD-120: dry-heating at 120°C, AD-180: dry-heating at 180°C, HD-120: heat-drying at 120°C, and HD-180: heat-drying at 180°C. Each treatment was duplicated.

In the first experiment, the amount of N uptake by the plants increased significantly by heating air-dried sludge at 120°C and decreased significantly by heating at 180°C, when the sludge was applied to the Fluvisol or Arenosol (**Figure 7**). Heat-drying of the sludge at 120 or 180°C also increased N uptake significantly. In the Andosol, on the other hand, N uptake was not so much influenced by the rate of N mineralization from sewage sludge as that observed in the other two soils (**Figure 6**). Because both Andosol and sewage sludge (which contained ferrous polysulfate as a coagulant) adsorbed P in soil solution (data not shown), we considered that the beneficial effect of N supply from sewage sludge on plant growth was offset by the limited supply of P [15].

The second pot experiment was carried out without an additional sludge application after complete removal of the plants from the first experiment. The plant growth in the second experiment became smaller than that in the first one, and the difference among the treatments decreased (**Figure 8**). The supply of N from the sludge did not last long. Thus, at least for the komatsuna plants used in our experiment, frequent application of sludge is required to sustain plant growth. However, it will also lead to the accumulation of sludge-derived N and P in soil, because less than 40 and 15% of the sludge N and P, respectively, were apparently recovered by two harvests of the plants [15]. From these results, we concluded that heated sludges can act as an effective organic N fertilizer, provided that they are applied to a suitable type of soil and that the short-term effects on soil productivity are balanced with the long-term effects on environmental quality.

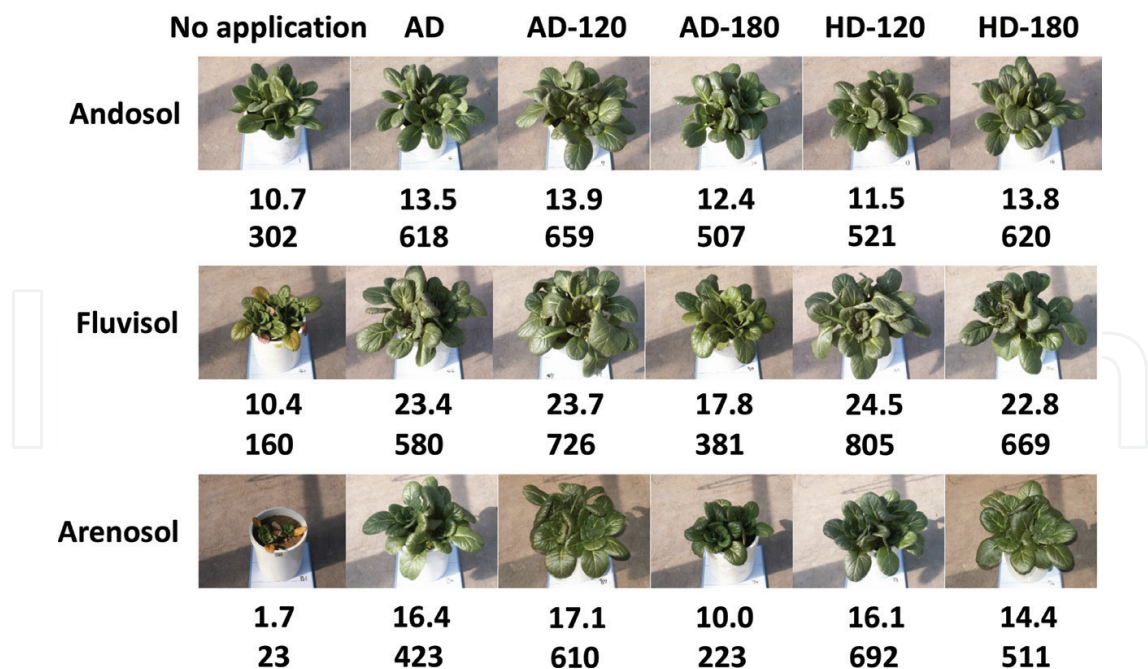


Figure 7. Effect of the application of heat-treated sewage sludge on the growth of a leafy vegetable (komatsuna) grown in three types of soils (adapted from Ref. [15]). This first experiment was carried out for 88 days in the winter. AD: air-drying, AD-120: dry-heating at 120°C, AD-180: dry-heating at 180°C, HD-120: heat-drying at 120°C, and HD-180: heat-drying at 180°C. Upper and lower values indicate the dry matter weight (g pot⁻¹, *n* = 3) and N uptake (mg pot⁻¹, *n* = 3), respectively. All pictures were taken from the same angle.

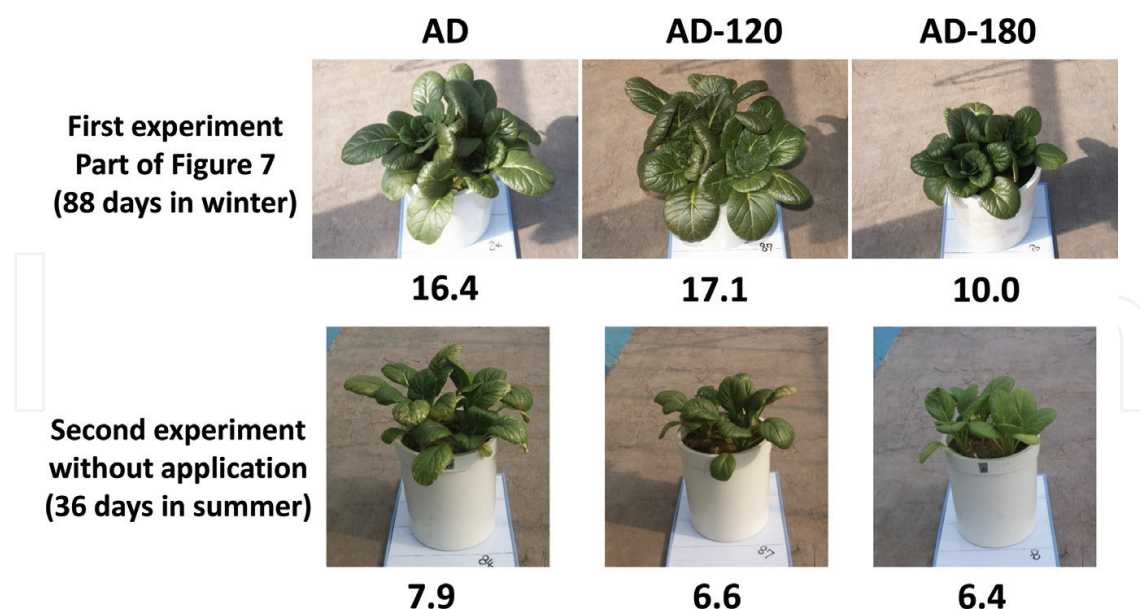


Figure 8. Sustainability of the effects of an initial application of sewage sludge on the growth of a leafy vegetable (komatsuna) grown in an Arenosol (adapted from Ref. [15]). The second experiment was carried out without sludge application. AD: air-drying, AD-120: dry-heating at 120°C and AD-180: dry-heating at 180°C. Values are the dry matter weight (g pot⁻¹, $n = 3$).

Case et al. [6] re-evaluated previous results, including ours. On the hypothesis that the effect of heat-drying on N mineralization from sewage sludge would differ among heating temperatures, they heat-dried anaerobically digested sewage sludge at different temperatures (70, 130, 190, or 250°C) until the water content reached less than 5%. Heat-drying treatment was carried out with a laboratory oven (laboratory-drying), and the product was abbreviated as LD. The sludge materials were applied to a sandy loam soil (Luvisol) and incubated aerobically at 15°C for 160 days. During the incubation, the production of exchangeable ammonium, nitrate, and carbon dioxide (CO₂) was monitored.

The production of nitrate during the whole incubation period was largest for the original sewage sludge (Original), followed by LD-70, LD-130 > LD-190 > LD-250 (**Figure 9**). Thus, nitrate production decreased with increasing temperature from 130 to 250°C. Because the content of exchangeable ammonium was almost zero at 80 days after the incubation (data not shown), the amount of nitrate produced after day 80 can be regarded as the amount of mineralized N (initial inorganic N plus mineralizable N).

The overall production of CO₂ was also largest in Original, LD-70, and LD-130, followed by LD-190 and LD-250 (data not shown). But the initial rate of CO₂ emission from Original was lower than that from LD-70 and LD-130, indicating that microbial decomposition of LD-70 and LD-130 occurred more rapidly. From these results, Case et al. concluded that heat-drying temperature significantly influenced the rate of N mineralization from sewage sludge but that heat-drying did not improve the rate of N mineralization at any temperatures they examined. They also emphasized that the heat-drying treatment in the laboratory produced different results from the treatment in a large-scale wastewater treatment plant (**Figure 9**) and the heat-drying temperature is one of the several factors that potentially affect the rate of N mineralization.

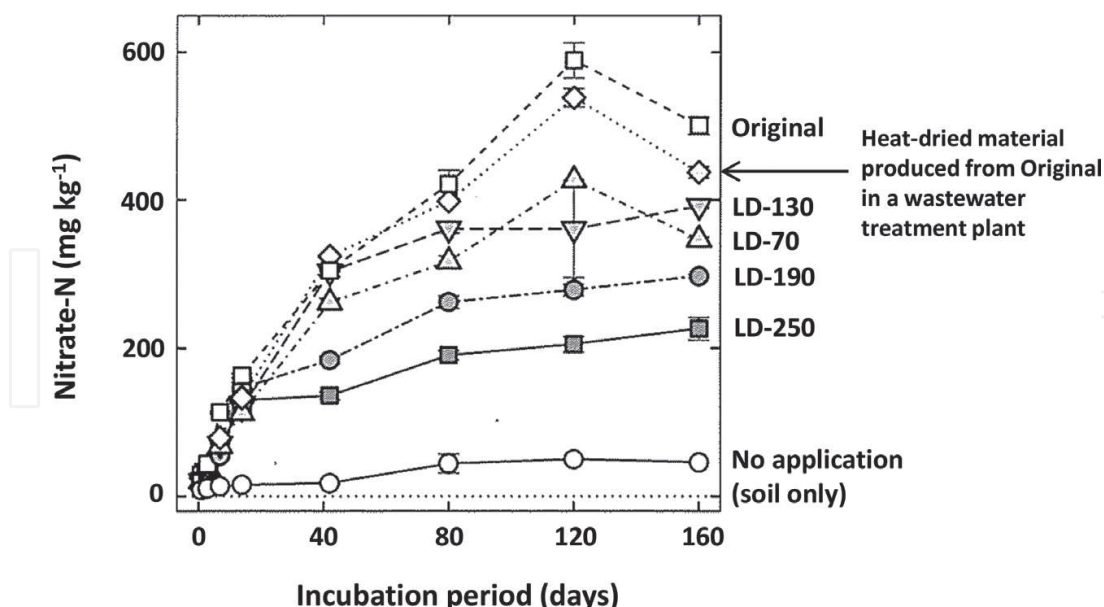


Figure 9. Patterns of nitrate production from a sandy loam soil (a Luvisol) amended with heat-treated sewage sludge at 2% (w/w). Aerobic (pF 2) incubation was carried out at 15°C for 160 days. Anaerobically digested sewage sludge (Original) was heated in a laboratory oven at 70, 130, 190, or 250°C until the water content was less than 5% (LD-70, LD-130, LD-190, and LD-250, respectively). Reproduced with permission from Case et al. [6], *Environ. Sci. Pollut. Res.*, Springer International Publishing AG.

In addition to Case et al. [6], the positive ([17]; 60°C for 13 hours) or negative ([18]; 250°C until reaching constant weight) effects of heat-drying on the amount of mineralized N in sewage sludge have been reported by comparing dewatered sludge with sewage sludge heat-dried at a single temperature. Maki et al. [19] also found that the content of chemically extractable organic N in cow dung manure was decreased by heating at temperatures from 80 to 180°C for 2 hours in a laboratory oven. As summarized by Rigby et al. [2] and Case et al. [6], several researchers have reported N mineralization from heat-dried sludge without specifying the heating conditions. According to the literature review by Rigby et al. [2], the percentage of mineralizable N to total organic N in heat-dried sewage sludge ranged from 26 to 71% (40% in average). This value was similar to aerobically digested sewage sludge whose value ranged from 32 to 58% (47% in average).

4. Summary of the heating effects on mineralized N in organic wastes

By compiling the abovementioned reports, we plotted the heat-induced changes of mineralized N (initial inorganic N plus mineralizable N) in organic wastes as a function of the heating temperature (Figure 10). It should be noted that only a rough comparison of these results among the studies is possible, because the materials used as a control, the heating conditions and the incubation conditions differed.

Nevertheless, the figure suggests certain trends. First, the response to the heating temperature differed between soils and organic wastes. As the heating temperature increased from around

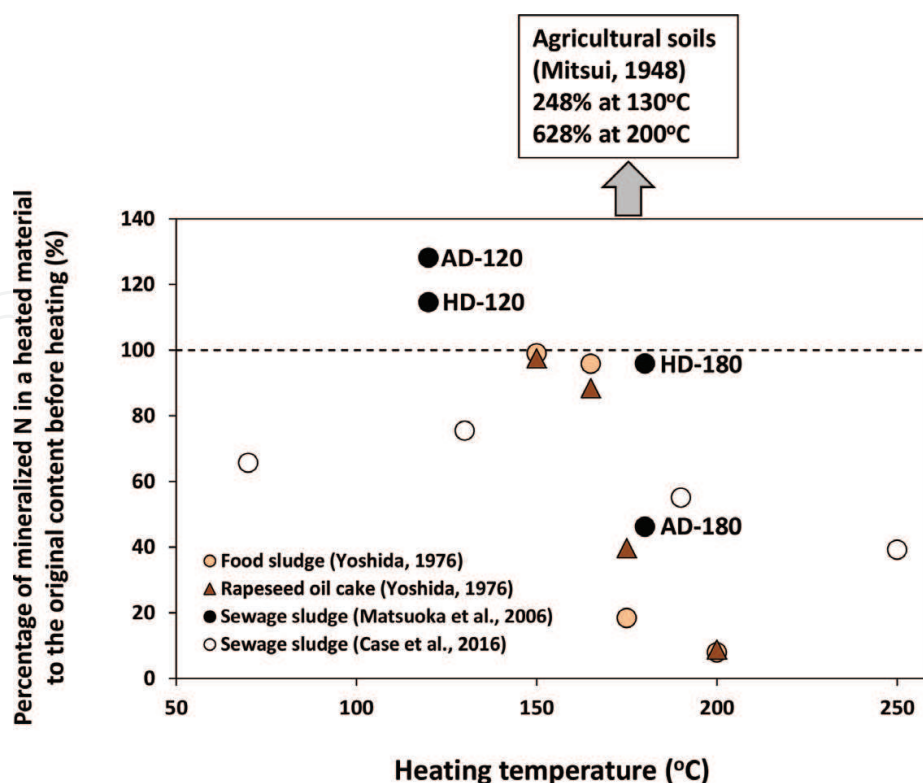


Figure 10. Relationship between temperature at which organic wastes were heated and heat-induced changes in mineralized N (initial inorganic N plus mineralizable N). The data from Mitsui [8] represent the average value obtained from 44 soils. Our data [7] also represent the average value obtained from three soils (Figure 6).

120 to 200°C, N mineralization increased in soil but decreased in organic wastes. The reason for the difference remains to be elucidated. Second, the content of mineralized N in organic wastes decreased sharply by heating at 150–200°C except for Case et al. [6] who reported a more gradual decrease. The reason for this difference is also uncertain. The release of CO₂ from the sludge of Case et al. during the incubation decreased slightly with heating at 130°C, but decreased sharply with heating at 190°C [6], which indicates that the threshold temperature for the stabilization of sludge C did exist between 130 and 190°C. On the other hand, we could not estimate the suitable temperature to increase N mineralization from organic wastes due to the insufficient number of available data. Lastly, the heating effect on N mineralization was influenced by both the heating temperature and by the initial water content of the sewage sludge. A typical example can be found in the difference between our samples at 180°C (AD-180 and HD-180).

We will have a closer look at the last point. **Figure 11** shows the temporal changes in the water content and the temperature of sewage sludge during the production of AD-180 and HD-180. Samples were heated for 16 hours with the reactor temperature set at 180°C. For both materials, the heat-drying process can be divided into two periods: the drying period (sludge < 100°C), in which most of the heat is consumed to dry the sludge, and the denaturing period (sludge > 100°C). Because of the difference in the initial water content, it took about 5 hours for AD-180 to reach 180°C, and about 14 hours for HD-180. As a result, HD-180 stayed at 180°C for only 2–3 hours. This clearly indicates that the temperature of sewage sludge during the heat-drying

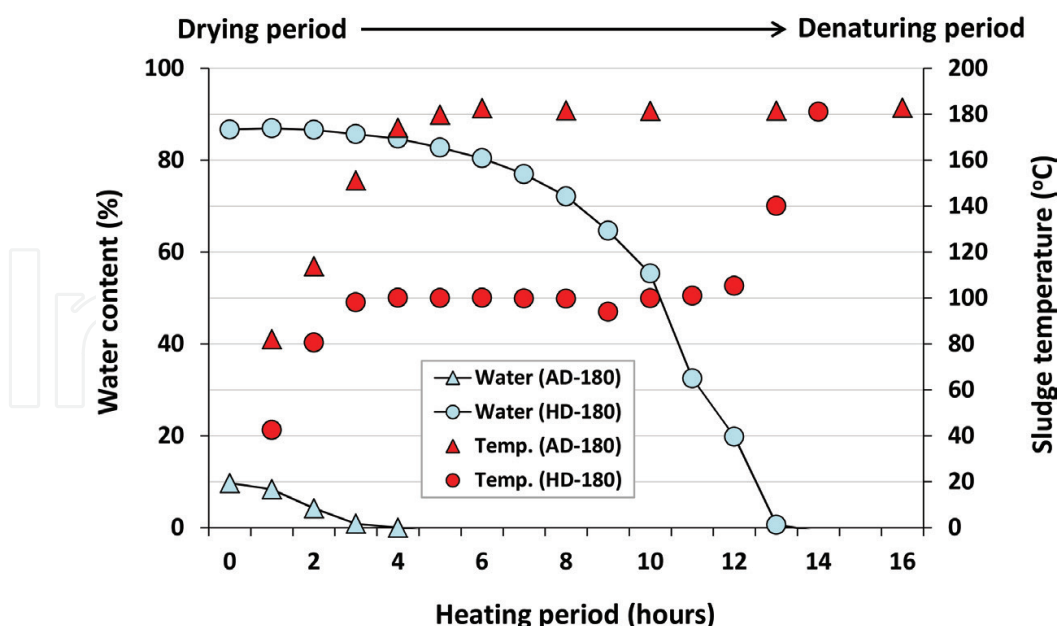


Figure 11. Changes in the water content and the temperature of sewage sludge during heating at 180°C with (AD-180) or without (HD-180) air-drying as a pretreatment (adapted from Ref. [7]). The heating treatment was carried out for 16 hours in the pilot-scale conductive dryer illustrated in Figure 5.

treatment rather than the temperature of the reactor is a most important factor that affects the availability of N in the heat-dried products. In the case of heat-drying of sewage sludge at temperatures higher than 150°C, it is plausible that the presence and the length of the denaturing period are key factors that determine whether the rate of N mineralization decreases or not.

Different from our samples treated beyond the drying period, the water content of the heat-dried sewage sludge produced at wastewater treatment plants varies from less than 10% [3, 6, 20] to more than 60% [21]. If sewage sludge was heat-dried homogeneously and the content of water in the end-product was relatively high, we can assume that the sludge temperature during the heat-drying treatment did not exceed 100°C.

5. Heat-induced stabilization of C in sewage sludge

5.1. Preliminary experiments

We carried out additional experiments to better understand why N mineralization was decreased significantly by dry-heating at 180°C (Figure 6). Since N mineralization is a part of the biological decomposition of organic C, we focused on the chemical form of the C. The heat-induced denaturation of C in sewage sludge (stabilization in the case of AD-180) was evaluated by using biological and chemical methods as follows; aerobic incubation, chemical extraction, and ^{13}C -NMR.

To extend the stabilization period, sewage sludge was heated at 180°C for a much longer period than in our previous experiment. Dewatered sewage sludge made from human waste

was sampled from a wastewater treatment plant in Chiba Prefecture, Japan. The sludge was air-dried at room temperature or heat-dried at 180°C by the conductive dryer in **Figure 5**. The air-dried sludge without heating (AD) contained C and N at 36 and 5.6%, respectively. The sludge was heated for 14 hours until its temperature reached 180°C, or it was continued for an additional 24 hours (a total of 38 hours) or 120 hours (a total of 134 hours). The heat-dried materials treated at 180°C for the additional 0, 24, or 120 hours are referred to as HD-180 (0 hour), HD-180 (24 hours), or HD-180 (120 hours), respectively.

The difference between HD-180 (0 hour) and other two HD-180 materials is originated solely from the dry-heating process at 180°C. The total C content was about 37% in all HD-180 materials. However, the rate of C mineralization decreased significantly with increasing dry-heating period (**Figure 12**). The percentage of total C that was mineralized during the 35-days incubation was 12.5% in HD-180 (0 hour), which was slightly lower than AD (13.1%). It decreased to 5.8% in HD-180 (24 hours) and to 4.1% for HD-180 (120 hours). These results indicate that the stabilization of C occurred mainly during the initial 24 hours of the dry-heating period and proceeded slowly thereafter.

The color of the heat-dried sewage sludge was also quite different from that of the air-dried sludge. For example, HD-180 (30 hours) was darker than AD (**Figure 13**). This suggests that the stabilization of C and N in sewage sludge was concomitant with the Maillard reaction, which is a series of nonenzymatic browning reactions occurring when virtually all foods are heated [22]. This reaction starts from the condensation of the carbonyl group of a reducing sugar with a free amino group of an amino acid [22]. The color of powdered materials can be measured easily and precisely with a color sensor [23]. Thus, the color of the end-products can be a useful proxy for the temperature of the sludge throughout the heat-drying treatment.

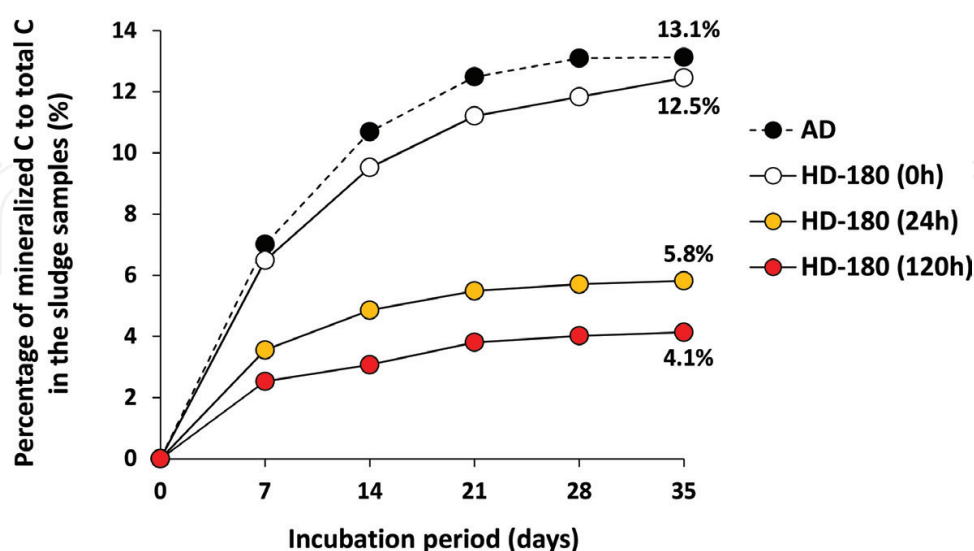


Figure 12. Average percentage of sludge C mineralized during aerobic incubation at 30°C for 35 days. The sludge materials were applied to an Acrisol from Shimane University at Honjo at 1% (v/v), and the soil was incubated at a moisture content of 60% of maximum water holding capacity. Each treatment was triplicated.

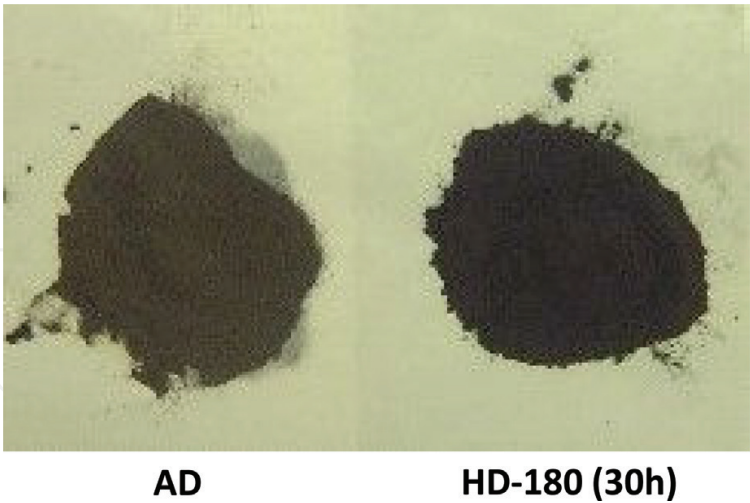


Figure 13. Color differences between two samples of finely ground sewage sludge. AD: air-drying, HD-180 (30h): heat-drying at 180°C with a stabilization period of 30 hours.

5.2. Fractionation of organic matter by chemical extraction

Based on these preliminary observations, we analyzed the composition of organic matter in three samples, i.e., AD, HD-180 (0 hour), and HD-180 (120 hours). The samples were crushed with an agate mortar to pass a 70-mesh sieve with an opening of 0.212 mm for the following analyses. Analyses were performed without replicates.

We used an extraction method known as Nagoya method [24], which is based on the different solubilities of organic matter fractions in alkaline and acid solutions. This method was originally designed to classify humic substances in soils, and we applied it to sewage sludge. **Figure 14** shows the procedures for separating humic substances into fulvic acid, humic acid, and humin fractions.

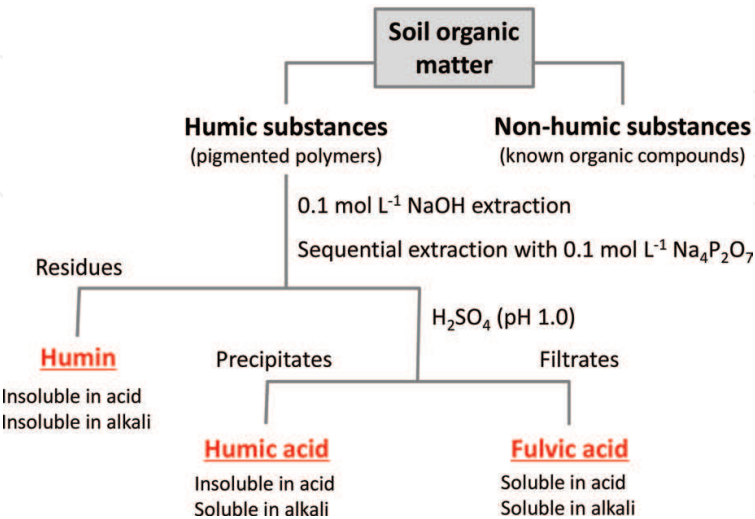


Figure 14. Procedures for the fractionation of soil organic matter into fulvic acid, humic acid, and humin according to the Nagoya method [24].

Figure 15 shows the relative contents of the fractions in our samples. The results of Collard et al. [20] were added to the figure, which were obtained from heat-drying of sewage sludge at 85 and 120°C. However, only a rough comparison between two datasets is possible, because Collard et al. used a slightly different extraction method (the IHSS method) and also removed lipids with a mixture of dichloromethane and methanol before extracting humic substances. In contrast, we did not remove nonhumic substances beforehand (the original method), so our extractable fractions (fulvic and humic acids) may have been overestimated as a result of contamination of nonhumic substances such as lipids and carbohydrates. Here we pay attention to the percentage of humin as an index of the stability of sludge C, since the humin fraction was considered to be least affected by such contamination.

The percentage of humin in the original sludge without heating suggested that our sample was less stabilized than that of Collard et al. In our samples, the heat-drying at 180°C greatly increased the percentage of humin; 12% in AD, 37% in HD-180 (0 hour), and 50% in HD-180 (120 hours). In the samples of Collard et al. [20], on the other hand, heat-drying at 120°C decreased the percentage of humin; 59% in Original, 59% in HD-85, and 30% in HD-120. These results indicate that the stability of sludge C was unaffected by heat-drying at 85°C, decreased at 120°C and increased at 180°C. The effects of heating on the stability of C differed between 120 and 180°C, which agreed with our results of N mineralization [7].

Comparing among our samples, however, the rate of C mineralization from AD and HD-180 (0 hour) was not so much different as the percentage of humin (**Figures 12 and 15**). This indicates that the increase of the percentage of humin was not proportional to the decrease of C mineralization during the incubation. In our previous study [7], the chemical forms of organic N in heat-treated materials were also evaluated by sequential extraction. Although organic N in AD-180 was most recalcitrant to chemical extractions, the results could not quantitatively explain the very low rate of N mineralization. These results suggest that mineralization of sludge

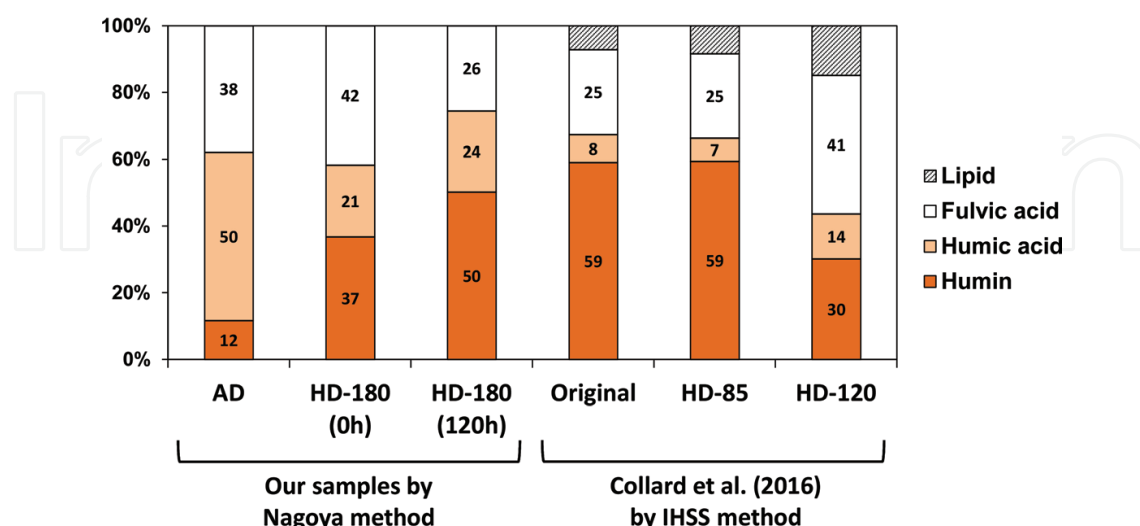


Figure 15. Relative percentages of fulvic acid, humic acid, and humin in sewage sludge samples. The percentage of lipid is also presented for the results of Collard et al. [20] after adaptation by the authors. In their paper, the activated sludge (Original) was heat-dried at 85°C (HD-85) and then pelleted at 120°C (HD-120).

C and N was determined not only by its chemical solubility but also by other physical factors such as microbial accessibility.

5.3. Analysis of the functional groups of C by ^{13}C -NMR

We also analyzed the C forms in AD, HD-180 (0 hour), and HD-180 (120 hours) by the solid-state ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectroscopy. The ^{13}C -NMR method provides estimates of the relative percentages of the main functional groups of C. The analytical procedures and machine conditions were the same as those described by Hiradate et al. [25]. When our samples were analyzed without any pretreatment, the ^{13}C -NMR spectra were divided into the four regions. According to Hiradate et al. [25], these regions were assigned to the functional groups as follows (**Figure 16**); alkyl C (0–45 ppm), O-alkyl C (45–110 ppm), aromatic C (110–165 ppm), and carbonyl C (165–210 ppm).

In AD, the percentage of alkyl C plus O-alkyl C exceeded 60%. Fernández et al. [26] also reported the predominance of these functional groups (75%) in sewage sludge heat-dried at 70–80°C. During the drying period from AD to HD-180 (0 hour), the percentage of alkyl

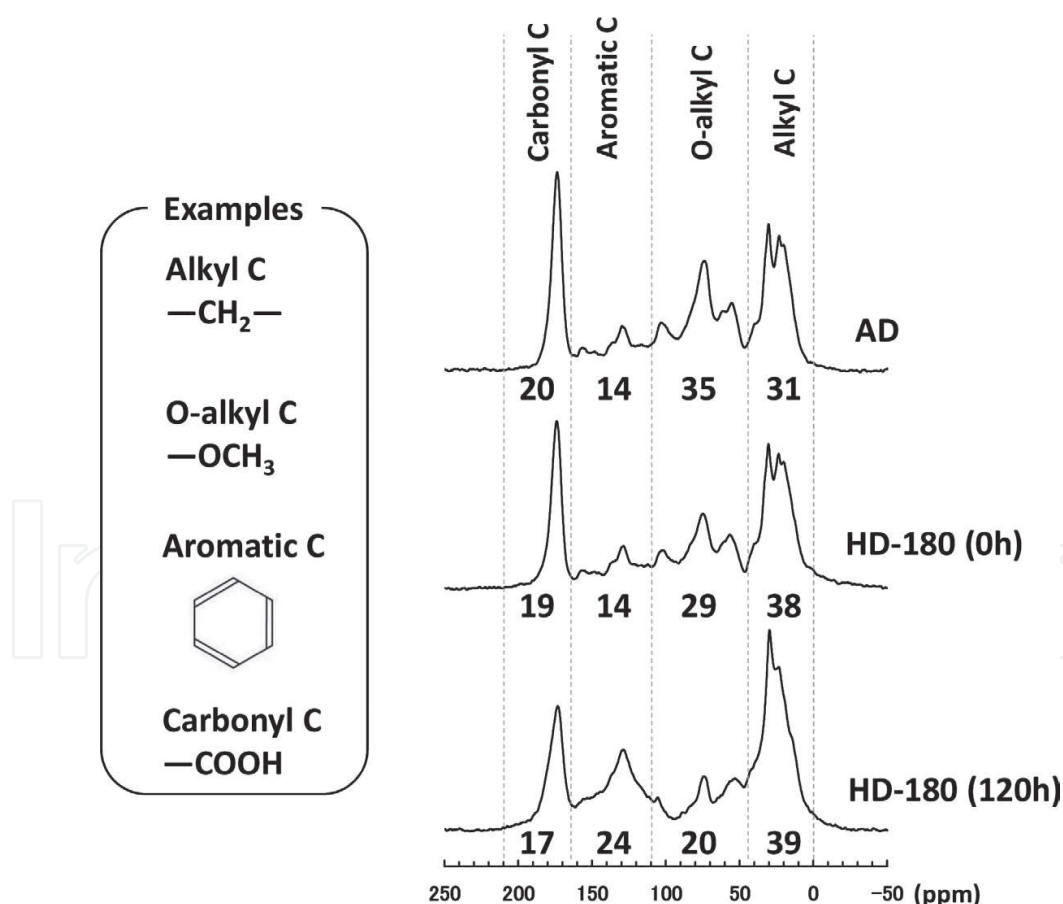


Figure 16. Solid-state ^{13}C -NMR (CP/MAS-TOSS, 75.45 MHz) spectra of sewage sludge samples. The ^{13}C -NMR spectrum was divided into the four chemical shift regions: 0–45 ppm (alkyl C), 45–110 ppm (O-alkyl C), 110–165 ppm (aromatic C), and 165–210 ppm (carbonyl C). The values in the spectra indicate the relative percentage of each type of C calculated by integrating the signal intensity.

C increased from 31 to 38%, whereas that of O-alkyl C decreased from 35 to 29%. During the stabilization period caused by dry-heating for 120 hours, the percentage of aromatic C increased from 14 to 24%, whereas that of O-alkyl C decreased from 29 to 20%. The proportion of carbonyl C was relatively constant throughout the treatments.

The transformation of C during the treatments at 180°C could be detected by applying the ^{13}C -NMR method to our crude samples. The transformation occurred not only during the stabilization period but also during the initial drying period, but the functional groups affected by the transformation differed between the periods. These results indicate that the reactions in the drying period differed from those in the stabilization period. A slight decrease of carbonyl C from 19 to 17% during the stabilization period implied the occurrence of the Maillard reaction. However, it is uncertain to what extent the changes observed in the ^{13}C -NMR spectra were responsible for the different rates of mineralization of C between HD-180 (0 hour) and HD-180 (120 hours). The higher proportion of aromatic C in HD-180 (120 hours) may have contributed to the lower rate of C mineralization, because the aromatic polymers in plant residues and microbial products are regarded as more recalcitrant to biological decomposition [27].

Similar to our results, the heating of Susuki (*Miscanthus sinensis* A.) leaves at 250°C for 1 hour in a laboratory oven increased the percentage of aromatic C from 17 to 66% and decreased that of O-alkyl C from 70 to 15% [28]. Heating at 250°C burned the leaves. On the other hand, the ^{13}C -NMR spectrum of the 200°C-heated samples remained unchanged from that of the untreated control. Heating of the leaves at 200°C for 1 hour did not cause burning but turned them brown possibly owing to the Maillard reaction.

As for sewage sludge, Fernández et al. [29] compared the properties of heat-dried sewage sludge with those of composted sludge. Sewage sludge that was heat-dried at the maximum sludge temperature of 75°C contained more fulvic acid than sewage sludge composted in windrows for 3 months. The solid-state ^{13}C -NMR spectroscopy indicated that the humic acid fraction of the heat-dried sludge contained more alkyl C and less aromatic C than that of the composted sludge. These results indicated that heat-drying of sewage sludge at 75°C (sludge temperature) did not increase the stability of C as much as did windrow composting. In their study, the heat-drying was carried out by indirect convection with air heated between 380 and 450°C. The temperature of the sludge during the treatment (<75°C) was therefore much lower than the hot air supplied for drying. This reemphasizes the importance of the temperature of sewage sludge during the drying period as a factor that affects the quality of the end-product.

6. Conclusions

By reviewing literature, we suggested that the heat-induced changes in N mineralization differ between soils and organic wastes. As the heating temperature increased to 200°C, the rate of N mineralization increased in soils but decreased in organic wastes. The rate of N mineralization from organic wastes tended to decrease sharply when heating temperatures increased

to 150–200°C. Since the materials examined, heating conditions and analytical methods differed among the researchers, our findings may have been biased by these artifacts. More comparative studies are required to confirm these findings and reveal the processes involved. Furthermore, the results obtained from heat-dried sewage sludge indicated that the solid-state ^{13}C -NMR spectroscopy can be a powerful tool to characterize the heat-induced stabilization of sludge C in addition to the incubation and extraction methods that have been used by soil scientists.

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References

- [1] Bennamoun, L., Arlabosse, P., Léonard, A. (2013) Review on fundamental aspect of application of drying process to wastewater sludge. *Renew. Sust. Energ. Rev.* **28**, 29-43. DOI: 10.1016/j.rser.2013.07.043
- [2] Rigby, H., Clarke, B. O., Pritchard, D. L., Meehan, B., Beshah, F., Smith, S. R., Porter, N. A. (2016) A critical review of nitrogen mineralization in biosolids-amended soil, associated fertilizer value for crop production and potential for emissions to the environment. *Sci. Total Environ.* **541**, 1310-1338. DOI: 10.1016/j.scitotenv.2015.08.089
- [3] Smith, S. R., Durham, E. (2002) Nitrogen release and fertilizer value of thermally-dried biosolids. *Water Environ. J.* **16**, 121-126. DOI: 10.1111/j.1747-6593.2002.tb00382.x

- [4] Daikuhara, G. (1901) Studies on heated soil fertilizer. *The Bulletin of the Imp. Agri. Exp. Stat. Jpn.* **20**, 1-46. (In Japanese).
- [5] Moritsuka, N., Matsuoka, K. (2016) An overview of the studies on biochar fertilizer carried out at the beginning of the twentieth century in Japan. In Larramendy, M and Soloneski, S., editors. *Organic Fertilizers – From Basic Concepts to Applied Outcomes*. pp. 203-221, InTech, Croatia. DOI: 10.5772/62526
- [6] Case, S. D. C., Gómez-Muñoz, B., Magid, J., Jensen, L.S. (2016) Increasing thermal drying temperature of biosolids reduced nitrogen mineralization and soil N₂O emissions. *Environ. Sci. Pollut. Res.* **23**, 14383-14392. DOI: 10.1007/s11356-016-6607-3
- [7] Matsuoka, K., Moritsuka, N., Masunaga, T., Matsui, K., Wakatsuki, T. (2006) Effect of heating treatments on nitrogen mineralization from sewage sludge. *Soil Sci. Plant Nutr.* **52**, 519-527. DOI: 10.1111/j.1747-0765.2006.00061.x
- [8] Mitsui, S. (1948) Studies on the effect of soil heating. *Nat. Agri. Exp. Stat. Tokyo Bull.* **62**, 1-48. (In Japanese with an English summary).
- [9] Sakamoto, K., Yoshida, T., Satoh, M. (1992) Comparison of carbon and nitrogen mineralization between fumigation and heating treatments. *Soil Sci. Plant Nutr.* **38**, 133-140. DOI: 10.1080/00380768.1992.10416960
- [10] Yoshimura, K., Murata, H., Takase, Y. (1932) Studies on the fertilizer values of rapeseed oil cakes produced in Japan and China (part 1). *Jpn. J. Soil Sci. Plant Nutr.* **6**, 283-300. (In Japanese).
- [11] Murata, K., Sonoda, T. (1934) Influence of thermal changes of nitrogenous compounds in oil-cake during the production on the fertilizer values. *Jpn. J. Soil Sci. Plant Nutr.* **8**, 37-38. (In Japanese).
- [12] Moritsuka, N., Matsuoka, K. (2008) Past and present studies on the agronomic effects of soil heating. *Jpn. J. Soil Sci. Plant Nutr.* **79**, 505-510. (In Japanese).
- [13] Yoshida, T. (1976) Utilization of activated wastewater sludge as fertilizers (2). Effect of treating conditions on fertilizer values. *J. Water Waste.* **18**, 419-426 (In Japanese).
- [14] Kurihara, K., Watanabe, M. (1976) Factors affecting the N mineralization of activated sludges. *Ann. Rep. Div. Fert. Chem. Nat. Inst. Agri. Sci.* **189**, 2-15. (In Japanese).
- [15] Moritsuka, N., Matsuoka, K., Matsumoto, S., Masunaga, T., Matsui, K., Wakatsuki, T. (2006) Effects of the application of heated sewage sludge on soil nutrient supply to plants. *Soil Sci. Plant Nutr.*, **52**, 528-539. DOI: 10.1111/j.1747-0765.2006.00062.x
- [16] Matsui, K., Shibata, K. (2002) Recycling of sewage sludge in agriculture by using sludge thermal treatment. *J. Jpn Waste Manage. Assoc.* **55**, 292-296 (In Japanese).
- [17] Silva-Leal, J., Torres-Lozada, P., Cardoza, Y. J. (2013) Thermal drying and alkaline treatment of biosolids: effects on nitrogen mineralization. *Clean Soil Air Water.* **41**, 298-303. DOI: 10.1002/clen.201100681

- [18] Corrêa, R. S., White, R. E., Weatherley, A. J. (2012) Effects of sewage sludge stabilization on organic-N mineralization in two soils. *Soil Use Manage.* **28**, 12-18. DOI: 10.1111/j.1475-2743.2012.00387.x
- [19] Maki, H., Kono, S., Nagai, K. (2009) Change in nutrient content and solubility by carbonization or heat treatment of cattle manure. *Jpn. J. Soil Sci. Plant Nutr.* **80**, 257-262. (In Japanese with an English summary).
- [20] Collard, M., Teychené, B., Lemée, L. (in press) Comparison of three different wastewater sludge and their respective drying processes: Solar, thermal and reed beds – Impact on organic characteristics. *J. Env. Manage.* DOI: 10.1016/j.jenvman.2016.05.070
- [21] Yoshida, H., Nielsen, M. P., Scheutz, C., Jensen, L. S., Christensen, T. H., Nielsen, S., Bruun, S. (2015) Effects of sewage sludge stabilization on fertilizer value and greenhouse gas emissions after soil application. *Acta Agri. Scand. B.* **65**, 506-516. DOI: 10.1080/09064710.2015.1027730
- [22] Ames, J. M. (1990) Control of the Maillard reaction in food systems. *Trends Food Sci. Technol.* **1**, 150-154. DOI: 10.1016/0924-2244(90)90113-D
- [23] Moritsuka, N., Matsuoka, K., Katsura, K., Sano, S., Yanai, J. (2014) Soil color analysis for statistically estimating total carbon, total nitrogen and active iron contents in Japanese agricultural soils. *Soil Sci. Plant Nutr.* **60**, 475-485. DOI: 10.1080/00380768.2014.906295
- [24] Kumada, K., Sato, O., Ohsumi, Y., Ohta, S. (1967) Humus composition of mountain soils in Central Japan with special reference to the distribution of P type humic acid. *Soil Sci. Plant Nutr.* **13**, 151-158. DOI: 10.1080/00380768.1967.10431990
- [25] Hiradate, S., Nakadai, T., Shindo, H., Yoneyama, T. (2004) Carbon source of humic substances in some Japanese volcanic ash soils determined by carbon stable isotopic ratio, $\delta^{13}\text{C}$. *Geoderma*, **119**, 133-141. DOI:10.1016/S0016-7061(03)00257-X
- [26] Fernández, J. M., Plaza, C., Polo, A., Plante, A. (2012) Use of thermal analysis techniques (TG-DSC) for the characterization of diverse organic municipal wastes streams to predict biological stability prior to land application. *Waste Manage.* **32**, 158-164. DOI:10.1016/S0016-7061(03)00257-X
- [27] Lützow, M. V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H. (2006) Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review. *Euro. J. Soil Sci.* **57**, 426-445. DOI: 10.1111/j.1365-2389.2006.00809.x
- [28] Honma, H., Hiradate, S., Shindo, H. (1999) Analysis of the burning process of Susuki (*Miscanthus sinensis* A.) plants by ^{13}C -NMR, FT-IR and XRD. *Jpn. J. Soil Sci. Plant Nutr.* **70**, 277-282. (In Japanese with an English summary).
- [29] Fernández, J. M., Hockaday, W. C., Plaza, C., Polo, A., Hatcher, P. (2008) Effects of long-term soil amendment with sewage sludges on soil humic acid thermal and molecular properties. *Chemosphere.* **73**, 1838-1844. Doi:10.1016/j.chemosphere.2008.08.001