Municipal Solid Waste Incineration Bottom Ash: Characterization and Kinetic Studies of Organic Matter

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Bottom ash is the main solid residue (in weight) which is produced by municipal solid waste incineration (MSWI) facilities. To be reused in public works, it has to be stored previously a few months. This material is composed primarily of a mineral matrix but also contains unburnt organic matter. The mineral content and its change in the course of aging are relatively well-known, in contrast with the organic content. So in order to detect the phenomena responsible for changes in organic matter and their effects during aging, the concentrations of the main organic compounds previously characterized, the number of microorganisms, and the release of carbon dioxide were followed kinetically (over 13 months) in model laboratory conditions (mass, particle size, humidity, temperature, aerobiosis). The results showed that the aging process led to the natural biodegradation of the organic matter available in bottom ash, composed essentially of carboxylic acids and n-alkanes (steroids and PAH’s to a lesser extent), and consequently that it would improve the bottom ash quality. Furthermore these results were confirmed by the study of aging conducted in conditions used in the industrial scale (over 12 months).

Introduction

In France, 37% of the municipal solid waste are eliminated by incineration with or without energy recovery (1). Municipal solid waste incineration (MSWI) produces large quantities of bottom ash (2.7 million tons/year) as solid residue. MSWI bottom ash is composed primarily of silica, metal oxides, silicates, chlorides, and sulfates, but also contains nonnegligible concentrations of heavy metals including Zn, Pb, Cu, Ni, Cr, and Cd, and small amounts of unburnt organic matter (2). In some European countries, bottom ash can be used in road building, but has to be stored a few months before reuse (1). Published data indicate that the aging process leads to an overall improvement in the environmental qualities of MSWI bottom ash (3–5). It has been shown that aging reduces the leaching of heavy metals and total organic carbon in parallel to a decrease of pH from highly alkaline to nearly neutral values (5). This is done by stockpiling large amounts of MSWI bottom ash in the open air, which allows some draining and evaporation. The main chemical reactions involved in the transformation of MSWI bottom ash inorganic matter are the oxidation of scrap iron (highly exothermal), the hydroxylation of metals, the carbonation of alkaline and alkaline earth metals, and the dissolution of lime and calcium sulfate (3). Few published studies (5) have dealt with changes in organic matter during aging, as well as the role of microorganisms, even though the MSWI bottom ash milieu (water, temperature, pH, organic matter) seems able to support bacterial development. The presence of metals can also preferentially favor the growth of some bacterial species. Microorganisms could thus act on the MSWI bottom ash, particularly on the organic matter via oxidation or dehydrogenation reactions of organic components (6).

Consequently, we investigated changes in organic matter related to the development of microorganisms in the milieu during aging. Two conditions of aging were tested: in conditions existing at the industrial scale (open pile of 300 tons) and in controlled conditions at the laboratory scale (aerobiosis, temperature 30 or 70 °C, 80 or 160 g samples). Laboratory simulation of aging for 13 months enabled us to kinetically follow the concentrations of target organic compounds, the number of microorganisms, and the release of carbon dioxide (at 30 °C). The latter is a significant marker of the oxidation of organic compounds by microorganisms in MSWI bottom ash during aging. Concerning aging in situ conditions, only the kinetics (for 12 months) of organic compounds could be done.

In both situations of aging, mechanisms involved in organic matter changes could be suggested. An analytical methodology was first developed to identify and quantify organic components of MSWI bottom ash, involving two extraction techniques: supercritical fluid extraction (SFE) and hot solvent extraction (Soxtec). The samples recovered were analyzed by using two state-of-the-art analytical tools: gas chromatography coupled to a mass spectrometry detector (GC-MSD) and gas chromatography with microwave-induced plasma atomic emission detection (GC-MIP-AED).

Conventional techniques were used to enumerate microorganisms in solid media: both direct counting using a fluorochrome and an indirect plate counting involving bacterial growth (7).

Experimental Section

MSWI Bottom Ash Sampling. The nature of MSWI bottom ash is closely linked to the nature of the solid waste, the type of incinerator, and the combustion conditions. We have selected one facility having a high incineration capacity and consequently producing high amounts of bottom ash.

The facility is located near an urban area. As a result of the French customs (1), municipal solid waste include paper—cardboard (30%), fermentable matter (25%), glass (12%), fines (10%), plastics (10%), metal (6%), textiles (2%), and undefined materials (5%) (mean composition). The nature and the volume of solid waste are relatively constant from day to day.

The incinerator is one of the most common type of MSWI system in use today. It has been operated since 1989, and its rated incineration capacity is 12 tons/h. Before combustion, solid waste were not preprocessed to remove materials including ferrous or nonferrous metals and glass. They were fed into the combustion chamber via gravity and transported through the furnace via a system consisting of six rollers disposed on a slightly inclined plane. Inside the furnace, the air supply was controlled, and the gas temperature reached...
were then placed in a 1L (80 g) or 3L (160 g) jar. The size (100 mL for 80 g samples, 250 mL for 160 g). The beakers were filled with soil incubation techniques, the samples were moistened at 30 °C, grinding, and quartering. Four of these samples were submitted to analysis in order to characterize the initial state of the bottom ash, and the others were aged in standardized laboratory conditions.

**Samples Aged in Standardized Laboratory Conditions.** The granulometric heterogeneity of MSWI bottom ash was conserved in the studied samples, at the same time as reducing grain size for laboratory scale tests. By analogy with soil incubation techniques, the samples were moistened at a level equivalent to 60% of their water holding capacity, i.e., 60 mL/kg. Each sample was placed in a beaker of appropriate size (100 mL for 80 g samples, 250 mL for 160 g). The beakers were then placed in a 1 L (80 g) or 3 L (160 g) jar. The dimensions of the aging system were selected to ensure aerobic conditions (i.e., available oxygen amount and good diffusion of oxygen in the sample). The water content of the MSWI bottom ash was maintained by adding ultrapure water to the bottom of the jar. The jars were placed in constant-temperature incubators at 30 or 70 °C and opened from time to time to admit fresh air and thus maintain aerobicism throughout aging. The carbon dioxide release was followed at 30 °C. A bottle containing 0.1 N sodium hydroxide was placed inside each jar to trap carbon dioxide released from the MSWI bottom ash.

A total of 22 samples of MSWI bottom ash were aged at 30 or 70 °C for 1, 4, 9, or 13 months. Periodically, two 80 g samples of MSWI bottom ash aged in each temperature condition, and sometimes one supplementary 160 g sample, were removed from the jar and processed for analysis. The volume of sodium hydroxide for trapping carbon dioxide was removed periodically to measure carbonates and bicarbonates resulting from the atmospheric temperature, was then observed.

**Characterization of Organic Compounds.** Figure 1 illustrates the methodology for the physicochemical characterization of MSWI bottom ash. Each sample was first screened into six particle size classes, whose diameters were included in the interval indicated in millimeters. A sample of about 5 g of classes 1–5 was then prepared by manual quartering. Fraction 6 was divided into two samples. The seven samples were first extracted with supercritical carbon dioxide for 30 min, using a Hewlett-Packard (HP) Model 7680 apparatus. With the conditions of pressure (318 bar) and temperature (120 °C) chosen, the density of the supercritical fluid was relatively high (0.61 g/cm³) and was thus able to solubilize efficiently different types of compounds. This first extraction step yielded seven 1 mL extracts of double-distilled hexane (SDS, HPLC grade), which were then pooled and subjected to a silica cleanup separation. Finally, three purified SFE extracts were obtained.

The SFE residues of classes 1, 2, and 3, and the two class 6 SFE residues, were mixed, respectively, and then extracted with 100 mL of methanol (Chromanol, HPLC grade) for 2 h, using a Soxtec apparatus (Tecator). The SFE residues of classes 4 and 5 were extracted separately as above. The second extraction step yielded four 1 mL methanol extracts.

Each extract was analyzed by GC-MSD and GC-MIP-AED. Chromatographic separation was achieved on an HP Model 5890A Series II gas chromatograph (GC), equipped with a 30 m%phenyl (equivalent) polysilphenylene siloxane capillary column with a 0.22 mm i.d., and 0.25 μm film thickness (BPX5, DB-WAX, etc.).
The methodology for characterizing organic compounds in MSWI bottom ash was developed for the 80 g samples of crude MSWI bottom ash < 4 mm. It was applied to the same dilutions of the samples (200 or 160 g) aged in laboratory conditions and to samples (80 g) aged in on-site conditions.

Enumeration of Microorganisms. A subsample of about 10 g was taken from the 80 and 160 g samples of MSWI bottom ash, for the enumeration of microorganisms. The direct counting method was based on staining bacteria with a DNA intercalating agent, acridine orange (AO), that fluoresces green when excited by UV radiation (8). Serial dilutions of the sample were done in 8% sodium chloride. One milliliter of each dilution was stained with 100 μl of AO solution (0.1%). Over a 2 min time period. Then the stained suspension was filtered on a polycarbonate membrane filters (Nucleopore, Costar) before mounting on a glass slide. Enumeration was carried out with an inverse epifluorescence microscope (Zeiss Universal) by counting at least 100 bacterial cells on each slide.

The indirect counting method involved the plate growth of microorganisms on an unselective agar nutrient (Trypticase Soy Agar at 4 g/L) containing cycloheximide to inhibit fungi development. The number of colonies is directly related to the number of bacteria cultured during a 5 day incubation period at 30 °C.

Microorganisms were enumerated in two different samples of crude MSWI bottom ash and in all the samples aged in the laboratory (mentioned above), including two additional assays from 17 months of aging at 30 °C.

Results and Discussion

In all MSWI bottom ash samples (crude or aged), each organic compound identified was quantified. To define the concentration of each organic compound for one state of aging (initial or in the course of laboratory aging), we have taken into account the mean of the results obtained with different samples (2, 3, or 4) but having the same age (explaining the often elevated relative standard deviations). The same was true for the results of enumeration of microorganisms.

The principal organic compounds present initially in the extractable matter from MSWI bottom ash were carboxylic acids (total concentration 73 μg/g), n-alkanes (14.1 ± 1.6 μg/g), steroids (24.1 ± 0.2 μg/g), phthalates (about 6 μg/g), and PAH’s (from 130 to 210 ng/g).

The acid concentration profile determined in crude MSWI bottom ash (Figure 2a) shows that there was a predominance of compounds containing an even number of carbon atoms, especially C16 and C18 (palmitic and oleic acids). The short chain acids, from 6 to 10 carbon atoms, account for a much lower proportion of the total quantity of acids.

The concentration profile of n-alkanes in MSWI bottom ash (Figure 2b) shows a bimodal distribution with a short mode of C14–C20 and a pseudo-normal distribution from C21 to C36. This profile presents some analogies with that of a petroleum paraffin series, such as heavy diesel fuel, whose distillation range is between 254 °C (bp of C14) and 496 °C (bp of C36). In light of these results, MSWI bottom ash could be so compared to natural products as oils.

Six steroids were identified and quantified: 4,6-cholestadien-3β-ol, cholesterol, β-sitosterol (both major compounds), cholestane, ergosterol, and stigmasterol. These compounds are considered as excellent biomarkers.

Seven phthalates were also identified in extracts of crude MSWI bottom ash. Dibutyl phthalate and bis(2-ethylhexyl) phthalate were the major compounds. The concentrations of the other phthalates identified [dimethyl, diethyl, bis(2-methylpropyl), nonyldecyl, decyldecyl] were lower than 1 ng/g. These toxic compounds are relatively stable chemically andresistant to biodegradation, contrary to steroids.

Highly toxic, PAH’s are usually generated when organic matter is treated in conditions of pyrolysis, i.e., incomplete combustion or combustion without oxygen, explaining their presence in MSWI bottom ash. The most commonly found types [from naphthalene to dibenz[a,h]acridine] were identi-
fied in MSWI bottom ash, including phenanthrene (27%), fluoranthene (21%), and pyrene (17%). Their total concentration in the MSWI bottom ash studied was relatively low.

As a result, all carboxylic acids, n-alkanes, steroids, phthalates, and PAHs determined initially were selected as target compounds for kinetic studies.

At time zero, the MSWI bottom ash contained (6.01 ± 0.17) \times 10^7 colony forming units (cfu) per gram of dry material that were viable in the conditions chosen, among the (1.07 ± 0.04) \times 10^7 cells/g of dry MSWI bottom ash counted by AO microscopy. The greatest increase in the number of microorganisms living in the MSWI bottom ash and viable in vitro was during the first month of the aging process at 30°C (Figure 3). Microorganisms continued to develop until about 5 months. This was reflected by the considerable release of carbon dioxide, significant of the capacity of microorganisms to use organic carbon available in MSWI bottom ash. At 4 months, the number of microorganisms that could be cultured nearly reached the total number of AO counted cells present in MSWI bottom ash. All bacteria present were thus viable and could be grown in a medium other than MSWI bottom ash. The number of microorganisms that could be cultured gradually decreased from 5 to 17 months of aging. This decrease was initially very low (between 4 and 9 months), accelerating during the last 4 months. In parallel, the total number of cells increased slightly, suggesting that microorganisms could survive in the MSWI bottom ash, because they were adapted to this material but no longer to the nutrient broth. After 17 months, the number of microorganisms that could be cultured stabilized around 10^7 cfu/g of dry bottom ash. During this period of regression of the number of viable bacteria, carbon dioxide release continued and tended toward a plateau that was reached after about 11 months. The quantities of carbon dioxide produced by surviving microorganisms in MSWI bottom ash were much lower at the end of aging. This low microbial respiration could be due to the exhaustion of available carbon sources in MSWI bottom ash.

Fewer data could be obtained when the aging process was run at 70°C (enumeration of viable bacteria and trapping of carbon dioxide released could not be done at this temperature). It is nevertheless probable that bacteria also developed in the MSWI bottom ash during aging at 70°C.

This temperature does not totally inhibit microbial development in a milieu, but it can result in an initial latency period during which the microorganisms must adapt to the imposed temperature before developing. In a given, direct enumeration of microorganisms in samples aged at 70°C for 9 months showed a nonpersistent development, probably thermophilic bacteria. Many of thermophiles have an optimum growth temperature between 50 and 60°C, but some of them indeed grow at temperatures well above 90°C (9).

The biodegradation of organic matter down to the final stage of totally inorganic was observed for different types of organic compounds. The phenomenon was particularly intense for aliphatic compounds, carboxylic acids, and n-alkanes. In general, these compounds are preferentially degraded in comparison to aromatic compounds (10). Similarly, microorganisms metabolize preferentially lower molecular weight compounds (10–11). Laboratory aging led to a rapid degradation of carboxylic acids in MSWI bottom ash (Figure 4), regardless of chain length. During standardized aging at 30°C, degradation of acids occurred primarily during the first month (60% degradation). When laboratory aging was conducted at 70°C, the slower development of microorganisms at this temperature resulted in a slower initial decomposition of carboxylic acids. Nevertheless, during the first 4 months of aging at 70°C, acid degradation was 66%. Fatty acid metabolism by most microorganisms involves a sequence of reactions (6) (dehydrogenation, hydration, dehydrogenation of alcohol), called β-oxidation. The biodegradation of acids occurred principally up to 4 months of aging, and the phenomenon continued up to 9 months (overall degradation about 85%). Between 9 and 13 months of aging at 30 and 70°C, there was an increase in unsaturated C18 (linoleic), C16 (hexadecenoic), and C14 (tetradecenoic) acids in parallel to a decrease in oleic acid (C18), and saturated C16 (hexadecanoic) and C14 (tetradecanoic) species. A large number of microorganisms, however, are able to dehydrogenate fatty acids; e.g., Tricholoma grammamowraud transforms oleic acid to linoleic acid (6).

Aging in on-site conditions also led to an overall degradation of acids (80–90%) in MSWI bottom ash. The decreasing acid concentration between 0 and 7 months could be partially due to the leaching by rainwater from MSWI bottom ash in the pile. The results at 12 months might suggest an increase in the acid concentration at the end of aging.

At both temperatures (Figure 5), the biodegradation of n-alkanes during the first month of standardized aging
resulted in the formation of short-chain n-alkanes (C14 and C16), as a result of microbial oxidation of n-alkanes having longer alkyl chains (C32). After 1 month, n-alkanes degradation occurred without distinction of chain length. The microbial oxidation process (α or β) of n-alkanes was thus more intense between 1 and 4 months (degradation rate about 50%). A large number of microorganisms can use n-alkanes as substrate, in particular zymogenic bacteria belonging to the genus Pseudomonas (10). It is highly probable that these ubiquitous bacteria were present in MSWI bottom ash. Changes in n-alkanes between 4 and 13 months of aging were not significant because of the standard deviations observed.

In the on-site experiment, the concentration profile of n-alkanes in MSWI bottom ash samples aged for 7 months differed from the results obtained in the laboratory experiment. There were higher concentrations of short n-alkanes, and there were nonnegligible levels of methylated n-alkanes. Formed short n-alkanes could result from microbial metabolism, but the contamination of the samples or the pile of MSWI bottom ash, due to the proximity to highways, is more probable. Nevertheless, the results at 12 months showed the degradation of n-alkanes during aging (between 50% and 60%), with no relationship to chain length.

In addition to the transformation of aliphatic organic compounds, laboratory aging also caused the transformation of steroids initially present in MSWI bottom ash. At 70 °C, there was a rapid degradation (in 4 months) of all steroids (80%), in particular the three major compounds, 4,6-cholestadien-3-β-ol, cholesterol, and β-sitosterol. At 30 °C, the aging process caused the transformation of 4,6-cholestadien-3-β-ol and β-sitosterol, with no substantial decrease in the total steroid concentration. The mechanisms involved could be microbial dehydrogenation or hydroxylation reactions (6). Steroids were not assayed in bottom ash aged outdoors because of the abundance of sources of contamination in proximity to the pile.

PAH's initially present in MSWI bottom ash were also transformed during laboratory aging (at 30 and 70 °C), primarily during the first 4 months. During this period, the relative concentrations of the major compounds (phenanthrene, fluoranthene, and pyrene) decreased first, while that of naphthalene increased. This may have resulted from the degradation of high molecular weight PAH's by microorganisms in MSWI bottom ash, with the formation of naphthalene, probably due to inhibition of the mechanism before microbial catabolism (12). Then the relative concentration of naphthalene decreased between 1 and 4 months, perhaps due to its volatilization, causing a decrease in its concentration and an increase in the relative concentration of phenanthrene, fluoranthene, and pyrene in MSWI bottom ash. It may also have been partially degraded by microorganisms.

The kinetic changes in phthalate concentrations, especially that of bis(2-ethylhexyl) phthalate (Figure 6), revealed no significant changes in these compounds during simulated or on-site aging, suggesting that phthalates remain unchanged during the aging process. Phthalates initially present in MSWI bottom ash are probably not a sufficient and available source of carbon for microorganisms in comparison to carboxylic acids and n-alkanes, which in addition are more easily degraded than aromatic compounds.

To conclude, changes in the organic matter of MSWI bottom ash during aging are governed primarily by biotic mechanisms. The first 4 months led to the biodegradation of organic matter available in MSWI bottom ash, composed essentially of carboxylic acids and n-alkanes (steroids and PAH's to a lesser extent). This organic matter was completely transformed to inorganic substances, with the principal metabolite detected being carbon dioxide. After 4 months, residual organic matter changed little, since microorganisms (no mobility) exhausted available organic substrates (energy sources) and so activity decreased. Chemical reactions also probably took place during aging in light of the presence of metal catalysts, freeradicals, and temperature effects in MSWI bottom ash. The results of the present work suggest that these phenomena are not very pronounced.

Overall, aging in on-site conditions confirmed the data obtained in model conditions. In light of the well-designed and operated facility, these results should be furthermore representative of the evolution of a widespread (in France at least) quality of MSWI bottom ash.

The kinetic and mechanistic studies revealed the presence of biogeochemical tracers such as carboxylic acids, n-alkanes, and steroids, and stable tracers, e.g., phthalates. By analogy with fossil mixtures in which observed alterations of organic compounds are significant of the extent of biodegradation of the mixture (13), the degree of degradation of organic compounds (biomarkers) would be significant of the degree of MSWI bottom ash aging.

Thanks to its own material properties (including especially its moisture content and temperature effects), aging would
naturally improve the MSWI bottom ash quality by reducing its organic content and for extent its polluting character.

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Supporting Information Available
Two figures showing the evolution of carboxylic acid and n-alkane contents in MSWI bottom ash, during aging in on-site conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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