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Research Article

Chemical Property of the Fly Ash Collected at an Incinerator and its Effects on Near Ambient Particles

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ABSTRACT It is crucial for understanding the characteristics of fly ash, emitted from the incinerator of municipal solid waste, to properly diagnose its impact on air quality and human health. In this study, to precisely describe the chemical property of the fly ash and its effects on near ambient particles, an intensive measurement was conducted. Fly ash was collected in dry condition from the downstream of a bag filter dust collector which is installed at an incinerator located in Iksan City, Korea. Sampling of ambient particles was carried out at both near and far away sites from an incinerator. Elemental analyses of the pretreated samples were subsequently performed by a Particle Induced X-ray Emission (PIXE) and a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Detector (EDX). Moreover, in order to estimate the residents' exposure to the fly ash and the effect of fly ash on the near ambient particles, Gaussian plume model was carried out. The high content of soluble S, Cl, K, and Ca in fly ash were detected. Small quantities of heavy elements including Zn, Br, and Pb were also detected in the water-soluble fraction. The scattering plots drawn by the ratios of Z/Zn (i.e., the ratio of mass concentration of each element (Z) to that of zinc) of ambient $PM_{2.5}$ and that of fly ash reveal a good relationship regardless of the distance from an incinerator. A ternary plot drawn by the wt% concentrations of Na, K, and Cl in the individual ambient particles and fly ash powders indicates that a small portion of the fine and coarse ambient particles was directly influenced by the fly ashes. Modeling evaluation of fly ash diffusion suggests that the air quality at the incinerator nearby areas, especially 1.5 km points, was strongly influenced by the air pollution materials emitted from an incinerator.

KEY WORDS Fly ash, Incinerator, Particle, Chemical property, Gaussian model, Health effect

1. INTRODUCTION

In numerous industrialized urban cities across the world, fixed sources, such as incinerators, power plants, and the large-scale factories aggravate urban air quality by emitting a large amount of pollutants. Above all, incineration plants of municipal solid waste give rise to serious pollution in many urban areas. At present, incineration is one of ways in most of urban cities for the treatment of municipal solid waste. Although this incinerator is an effective treatment way for waste reduction and reuse of combustion heat, it is known to emit various harmful pollutants during

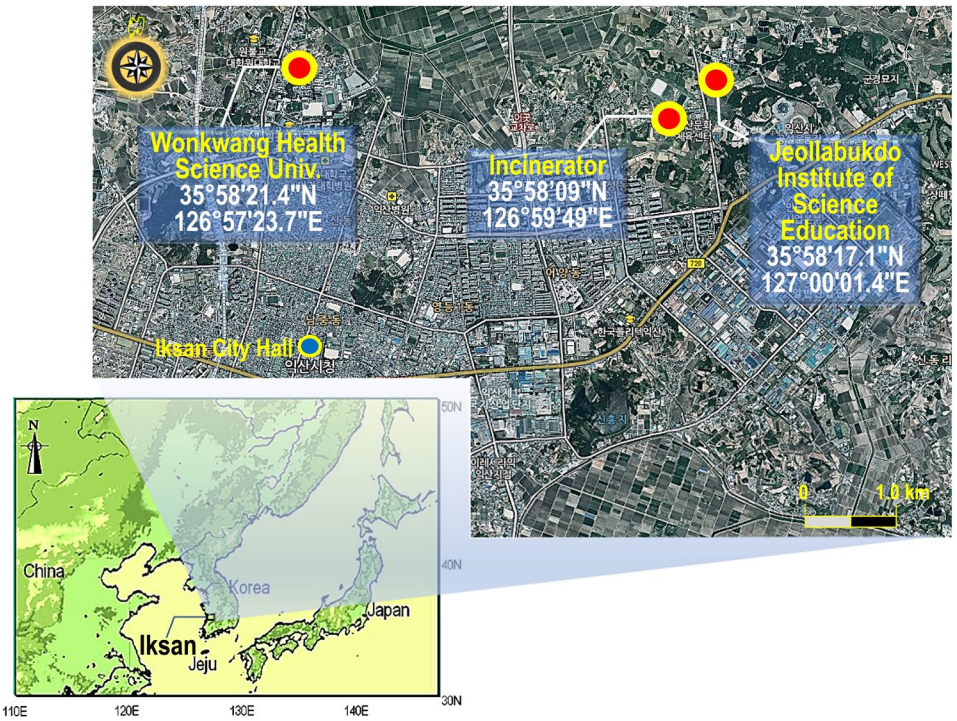


Fig. 1. Map showing the Iksan City, Korea selected as the sampling location of fly ash and ambient particle.

waste processing. Various pollutants are particulate matter (PM), gases (HCl, HF, SO_2, NO_X, and NH_3), heavy metals, and carbon compounds. Their volume and concentration are varied by the combustion technology, operating conditions, and the composition of raw waste (Amutha Rani *et al.* 2008; Achternbosch and Richers 2002). It is strictly demanded to eliminate the pollutants generated during waste processing because most of them are then emitted into atmosphere.

A large amount studies have been carried out to describe the chemical composition of the fly ash emitted from the incinerator of municipal solid waste (Amutha *et al.*, 2008; Quina *et al.*, 2008; Jiang *et al.*, 2007; Chang and Huang, 2002; Kida *et al.*, 1991). However, the relevance of chemical properties of fly ash and those of ambient PM has rarely been studied.

The chemical properties of fresh fly ash can be easily changed by several processes like gas-to-particle transformation, and growth processes of PM after discharge from the chimney. Therefore, the information concerning the chemical properties of the early fresh fly ash is required to the diagnosis of an environmental impact of fly ash emitted from the incinerator of municipal solid waste.

The aim of this study is to clarify the chemical property of the fly ash collected at an incinerator of municipal solid waste and its effects on the ambient particles near incinerator. Particularly, we performed an in-depth consideration for the trace heavy metals having a huge health hazard.

2. EXPERIMENTAL METHODS

2.1 Description of the Sampling Location of Fly Ash and Ambient Particle

Fig. 1 shows the map showing the Iksan City, Korea selected as the sampling location of fly ash and ambient particle. A large-scale industrial complex, residential region, and farmland are located within a few kilometers of an incinerator. Samplings of ambient PM were conducted at both near (Jeollabukdo Institute of Science Education (35°58′17.1″N, 127°00′01.4″E) and far away (Wonkwang Health Science University (35°58′21.4″N, 126°57′23.7″E) sites from an incinerator (35°58′09″N, 126°59′49″E) (capacity per day : 200 tons) (see Fig. 1). Near and far way sites are 0.75 and 3.60 kilometers away from an incinerator, respectively.

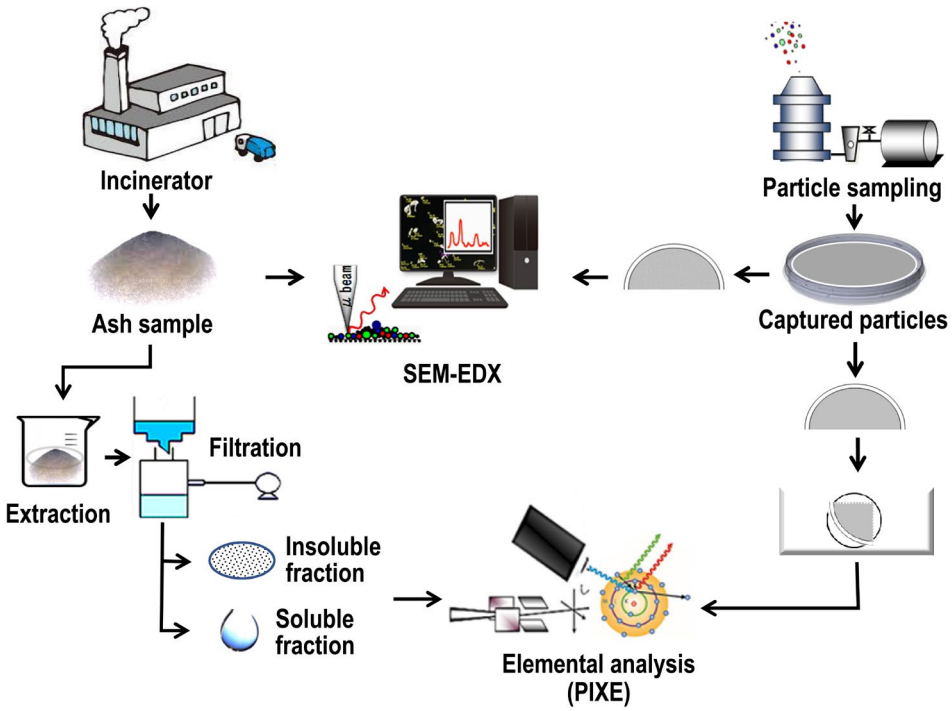


Fig. 2. Flows of pretreatment and elemental analyses of fly ash and ambient PM.

Iksan City is located in the West Central part of Korea, and it is one of modern industrial cities and home to many factories producing textiles, jewelry, and electrical products. As one of industrial complexes, the Mando Co. that is an auto parts (e.g., steering/suspension system) manufacturing plant is located near the southeastern part of an incinerator.

2.2 Sampling and Pretreatment

Fly ashes were randomly collected in dry condition from the downstream of a bag filter dust collector which removes combustion particles included in flue gas. To collect the fly ash sample representatively, three collecting points were randomly selected from the fly ash reservoir installed at incineration plant. The collected fly ash samples were then thoroughly mixed.

The field survey of PM was conducted at two different sites described above. For the sampling of PM as a function of its size, the two-stage multi nozzle cascade impactor (MCI) samplers (Tokyo Dylec Co.) were synchronously operated. The MCI sampler collected coarse ($PM_{10\text{-}2.5}$) and fine ($PM_{2.5}$) fractions of PM separately on a prefilter and a back-up filter, respectively. Each stage of the MCI sampler loaded the Nuclepore® polycarbonate filters (GE Healthcare Whatman) with 0.04 μm pore size. The details of sampler and filter arrange have been already reported elsewhere (Ma *et al.*, 2010). The sampling of ambient size-resolved PM was performed three times in each place (see Fig. 1). Single measurement was conducted for 24 hours.

During the intensive field sampling campaign, the range of wind speed was 1.03–5.69 m s^{-1}. The temperature and relative humidity were around 23.1–34.2°C and 77–91%, respectively.

After sample collection, every sample was placed in a clean sterilized petridish, which were sealed with Teflon tape and wrapped with aluminum foil. Every sample was placed in a cold storage bag during air transportation.

Fig. 2 illustrates the flows of pretreatment and elemental analyses of fly ash and ambient PM. For the laboratory analysis, fly ash samples were conditioned in a desiccator with constant temperature (20±0.5°C) and relative humidity (30%). They were then extracted using deionized water. After ultrasonic extraction, they were filtrated through a Nuclepore® filter with 0.08 μm pore size to separate into the soluble and insoluble fractions. The filtrate was considered to be soluble fraction. As illustrated in Fig. 2, the PM filters divided in half were

handled in the same manner as fly ash sample.

Meanwhile, individual particles without any pre-treatment were progressed to single particle analysis after coating with a very thin layer of platinum by a sputter coater.

2.3 Description of Analyzers

Elemental analyses of the pretreated samples were subsequently performed by the Particle Induced X-ray Emission (PIXE) installed at the Cyclotron Research Center of Iwate Medical University. As well known, it has some good advantages including an excellent sensitivity, a non-destructive technique for multielement. The details about analytical procedures by PIXE were described elsewhere (Sera *et al.*, 1999).

A Scanning Electron Microscope (SEM) (JEOL JSM-5400) equipped with an Energy Dispersive X-ray Detector (EDX) (Philips, EDAX DX-4) was employed on elemental analysis of the individual particles and individual fly ash powders. After ion coating, the samples were placed into the SEM's vacuum column (10^{-6} Torr). The randomly selected single particles and fly ash powders were analyzed at 15–20 kV working conditions. The more details on the analytical processes of SEM-EDX have been reported elsewhere (Aboraia *et al.*, 2013).

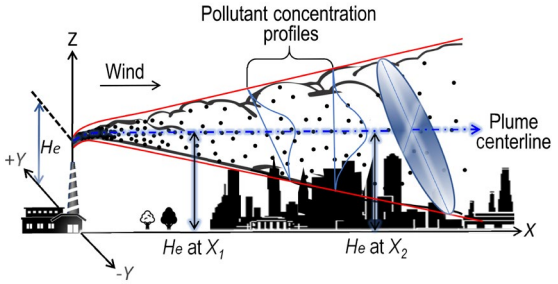
2.4 Schematic Representation of Gaussian Plume Coordinate

In order to estimate the residents' exposure to the fly ash emitted from an incinerator and the effect of fly ash on the near ambient particles of the downwind region, a modeling study on fly ash dispersion was carried out by the Gaussian plume model. Fig. 3 illustrates the dispersion of pollutants emitted from an incinerator and the schematic representation of a plume coordinate system for the Gaussian plume equation. The basic concept of this dispersion model is to calculate air pollutant concentration in the vicinity of an incinerator. The well-known Gaussian model formulation is as follows:

$$C_{fly\ ash}(x,y,z) = \frac{Q}{2\pi \cdot u \cdot \sigma_y \cdot \sigma_z} exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left[exp\left(-\frac{(Z-H_e)^2}{2\sigma_z^2}\right) + exp\left(-\frac{(Z+H_e)^2}{2\sigma_z^2}\right)\right]$$

where:

$C_{fly\ ash}$ (x, y, z) = fly ash concentration (μg m^{-3}) as a function of downwind *x*, *y*, *z* position



X = downwind distance from plume source (m)
$X_{1,2}$ = downwind distance from plume source to $X_{1,2}$ points (m)
Y = horizontal plume distribution
Z = vertical plume distribution
He = effective height of plume rise (159.4 m)

Fig. 3. Schematic representation of a plume coordinate system for the Gaussian plume equation.

Q = average emission rate of pollutant (g s^{-1})
u = average wind speed (m s^{-1})
σ_z = dispersion width in the z direction (m)
σ_y = dispersion width in the y direction (m)
H_e = effective height of plume rise (m)

In this study, Q, u, and H_e were 0.02 g s^{-1}, 7.7 m s^{-1}, and 159.35 m, respectively. Meanwhile, σ_z and σ_y can be decided by follow equations. The value of Q was the actual measurement data monitored by the incineration plant itself.

$$\sigma_y = ax^{0.894}$$

$$\sigma_z = cx^d + f$$

In above equations, *a*, *c*, *d*, and *f* can be also decided according to atmospheric stability and the downwind distance (i.e., *x*). In this study, atmospheric stability was decided on the class-C of (i.e., weak unstable) by the average surface wind speed (up to 5–6 m/s) and clear weather of the measurement period (corresponds to clear summer day with sun higher than 60 degree angle above the horizon). Finally, fly ash concentration was calculated at x distance (up to 5 km) from plume source (i.e., $C_{fly\ ash}$ (5.0,0,0)).

3. RESULTS AND DISCUSSION

3.1 Chemical Property of Fly Ash

It is expected that the chemical nature of fly ash is dependent on both the waste composition and boiler conditions. Fig. 4 shows the elemental concentration of

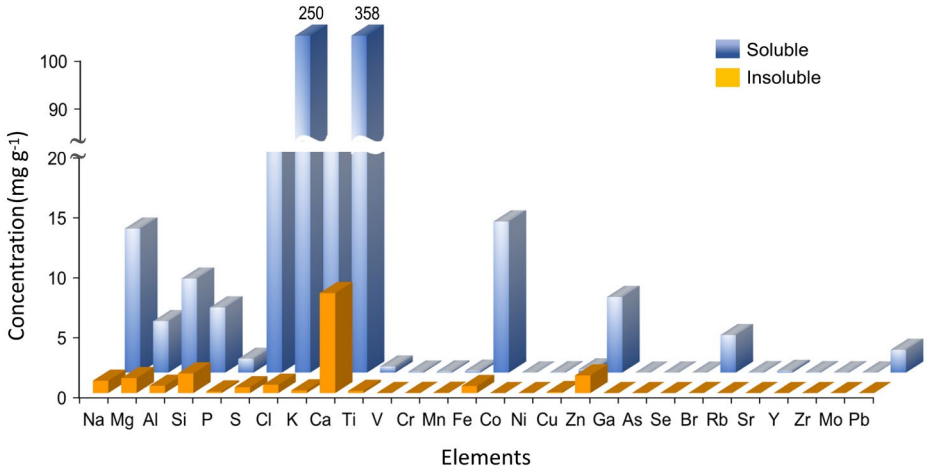


Fig. 4. Elemental concentration of water-soluble and insoluble fractions of fly ash.

the water-soluble and insoluble fractions of fly ash. The elements in water-soluble tend to have an overwhelmingly higher concentration than those of water-insoluble through entire elements. One of the main peculiarities is a significant enrichment of soluble S, Cl, K, and Ca. The high content of soluble Cl and S in the fly ash from municipal solid waste incinerators have been reported in other studies (Colangelo *et al.*, 2012; Wang *et al.*, 2006). High concentration Ca might be also derived from the lime solution injected into the scrubber to remove acidic flue gases. A previous study reported that Ca accounted for 19.37 to 39.90% of the fly ashes collected from urban waste incinerators in China (Jiang *et al.*, 2007).

As the next enrich element, Na, Al, and Fe were detected in both soluble and insoluble fractions, respectively. In addition, several toxic components such as Zn, Br, and Pb also show a meaningful concentration in water-soluble fraction. Among them, Zn showed considerable concentrations in both water-soluble (6.31 mg g^{-1}) and insoluble (1.48 mg g^{-1}). Although, the quantity was very small, Cr (0.09 mg g^{-1}), Mn (0.16 mg g^{-1}), Ni (0.03 mg g^{-1}), As (0.01 mg g^{-1}), Mo (0.02 mg g^{-1}), Co (0.01 mg g^{-1}), and Sr (0.15 mg g^{-1}) were also detected from the water-soluble fraction. Even if the levels of these elements are substantially lower than those of major components, there is a big interest in whether health effects are caused from long-term exposure to low-levels of these hazard metals (Chillrud *et al.*, 2005).

The reason of a relatively high concentration of Na along with Cl might be the inflow of food waste. Hyks and Astrup (2009) specified the elemental components of the waste incinerator bottom ash and reported that the input of road salts and PVC caused high Cl amount, impregnated wood resulted in high content of As, automotive shredder residues induced Cu, Mo, Ni, and Zn and batteries increased the content of Co, S and Sr. The vinyl rolls used for the compressed storage of raw waste before incineration might also cause Cl-enrichment in fly ash. Furthermore, Zhu *et al.* (2008) studied chloride forms and its amount in the fly ash collected in a bag filter with the injection of calcium hydroxide for acid gas removal. In their study, the fly ash contained 35% chlorine as NaCl, 11% as KCl, 37% as $CaCl_2$, 13% as Friedel's salt ($Ca_2Al(OH)_6(Cl,OH)\cdot 2H_2O$), and the remaining 4% as CaClOH. Moreover, in this study, owing to geographical features (i.e., adjacent to the sea) of incinerator location, it is easily considered that sea-slats will have any influence on the elemental composition of raw waste during field load.

Meanwhile, Keppert *et al.* (2012) indicated that the chemical composition of fly ashes depends on their separation temperature from the flue gas line. According to their study, most heavy metals including As and Pb increase with decreasing separation temperature.

3.2 Effects on Ambient Particles

Fig. 5 shows correlationships between the Z/Zn (i.e., the ratio of mass concentration of each element (Z) to that of zinc) of ambient $PM_{2.5}$ collected at both near (top) and faraway (bottom) sites from an incinerator and that of fly ash. Several enriched elements (i.e., Cl, Ca, Al, and Si) having excessively high Z/Zn ratio were excluded from Fig. 5. As shown in scattering plots, although R level is slightly higher at near site (0.94) than that of far-

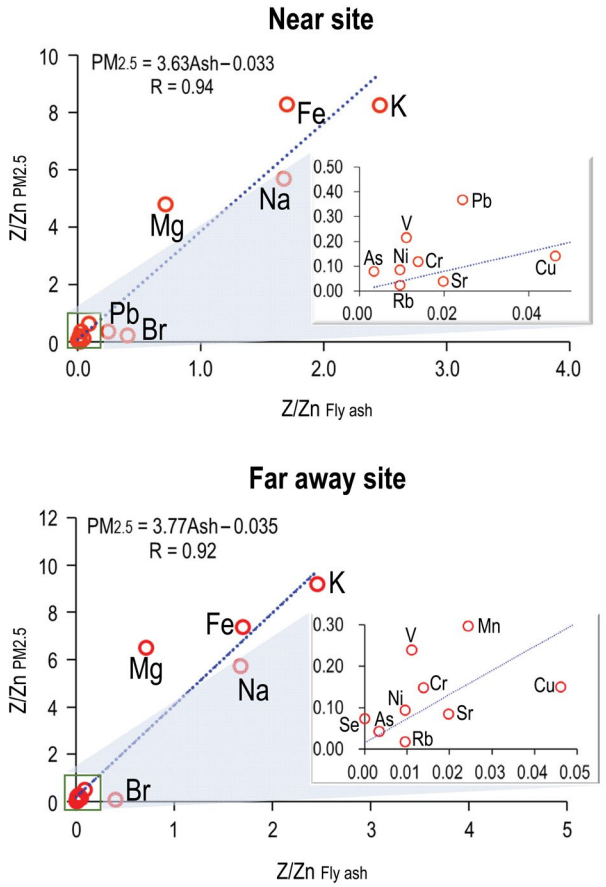


Fig. 5. Correlationships between the Z/Zn of ambient $PM_{2.5}$ collected at both near and far away sites from a incinerator and that of fly ash.

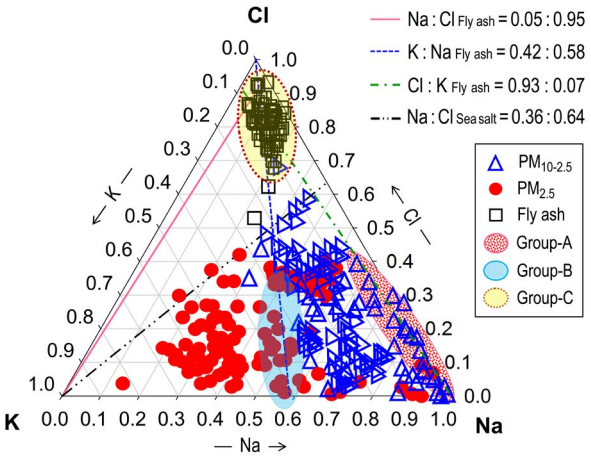


Fig. 6. Ternary plot of the relative wt% ratios of Cl, K, and Na in the ambient individual particles collected at Wonkwang Health Science Univ. (refer to Fig. 1) (total particle number of 350).

away site (0.92), the Z/Zn values of ambient $PM_{2.5}$ and those of fly ash reveal a good relationship regardless of distance. Also, according to the highlighted scattering plots in figures, several trace heavy metals including As in $PM_{2.5}$ have a positive correlation with that in fly ash at both near and far away sites. This result indicates that the trace heavy metals of ambient $PM_{2.5}$ were influenced by a municipal waste incinerator. Thus, it would be necessary to improve the combustion of fuel and raw material as well as the removing technique of pollutant for a good urban air quality. It is also very important to completely avoid the generation of harmful fly ash containing hazard metals by preventing sources from entering to waste.

A good understanding of the relative contribution from the incinerators to the airborne concentrations is crucial for the mitigation of the ambient PM in the view of health effects and air pollution reduction. The data derived by single particle analysis and individual fly ash powders can be incorporated effectively with the assessment of their source inventories. In order to categorize the individual ambient particles collected at Wonkwang Health Science Univ. (see Fig. 1) about 4 km away from an incinerator, a ternary plot was drawn. In this study, the wt% concentrations of Na, K, and, Cl in the individual ambient particles (total particle number of 350) and individual fly ash powders (total fly ash powder number of 350) determined by SEM-EDX analysis were applied to three variables (see Fig. 6). From the mass concentration ratios for three elements in sea-salt (Korona *et al.*, 2013) and incinerator (in this study), it was possible to classify 350 individual ambient particles three distinct groups. As shown in Fig. 6, the majority of individual particles with coarse fraction ($PM_{10\text{-}2.5}$) are Na-rich compared to sea-salt and some of them are classified into the Group-A with the strong influence from incinerator. Even the schemes of separate collection of food waste have been performed, a part of food wastes containing NaCl still remains in the solid waste (Notarnicola *et al.*, 2005). During combustion, the food fraction contributes to incomplete combustion because of the relatively high moisture content of this type of waste.

Meanwhile, the individual particles in fine mode ($PM_{2.5}$) marked as the filled circles are distributed at K-rich zone. A small portion of them (Group-B) is lying on the border line (K : Na Fly ash = 0.42 : 0.58). The enriched K might be derived from biomass. Biomass combustion generates a large amount of K, Mg, and P known as plant nutrients. The K in the ashes of solid biomass

fuel are marked from 400 to 2000 mg kg^{-1} depending on wood types (Thy *et al.*, 1999).

Small portions of the fine and coarse ambient particles classified into Group A and B in Fig. 6 were directly influenced by the fly ashes emitted from a municipal solid waste incinerator.

In the case of the individual fly ash powders marked with the empty squares in figure, most of them (Group-C) show high Cl-rich, namely, the excess Cl compared to sea-salt. Cl is contained in most materials of municipal solid waste including plastics, packaging, organic materials, etc. (Zhu *et al.*, 2008).

3.3 Evaluation of Fly Ash Diffusion

Fig. 7 shows the model output for fly ash diffusion calculated at the atmospheric stability with weak unstable (class-C). In the figure, X means the horizontal distance from a plume source. The two-dimensional calculated fly ash distributions within 5 km downwind distance of an incinerator are heading for three directions, i.e., residential, agricultural, and workplace (industrial). According to the modeling result, fly ash concentration was highest at the vicinity of one kilometer from the incinerator and diminished to low levels within 5 km from a plume source. The fly ash concentration declined exponentially with increasing distance from a plume source might be due to the dilution process. Although, the fly ash concentration can vary considerably depending on meteorological conditions (especially wind direction), emission amount, plume effective height, land surface characteristic at downwind, and topography, the highest fly ash was marked 98.5 μg m^{-3} within 1.5 km from a plume source. It is therefore suggested that the air quality at the incinerator nearby areas, especially 1.5 km points, was strongly influenced by the air pollution materials emitted from an incinerator.

As mentioned earlier, the model variables of this study, especially atmospheric stability, was decided only by the weather conditions of measurement period. However, in order to realize the realistic residents' exposure to the fly ash emitted from an incinerator, atmospheric stability should be determined through the long-term weather data.

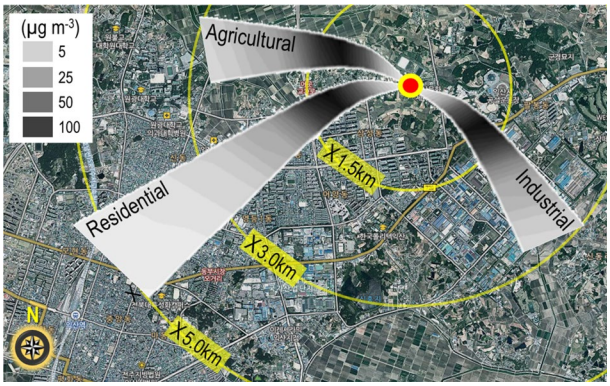


Fig. 7. Model output for fly ash under the atmospheric stability with weak unstable (class-C).

4. CONCLUSIONS

Even if the levels of some heavy elements including Zn, Br, and Pb in fly ash were significantly lower than major components (e.g., S, Cl, K, and Ca), it is the biggest concern whether there are health effects from long-term exposure to low-levels of pollutants these hazard metals. Correlationships between the Z/Zn of ambient $PM_{2.5}$ and that of fly ash suggest that the chemical property of ambient PM was likely to be influenced by an incinerator. Moreover, the modeling result pointed out that the air quality at the close area of an incinerator, especially 1.5 km points, was strongly influenced by the air pollution materials emitted from an incinerator. In respect that the bottom ash also likely to have the same chemical properties, i.e., the high content of soluble components including several toxic heavy metals, a well-established disposal technique like solidification/stabilization should therefore be required before the final landfill or recycling process. More aggressive efforts should also be undertaken to minimize pollution from municipal solid waste incineration.

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