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## Effect of fly ash on persistence, mobility and bio-efficacy of metribuzin and metsulfuron-methyl in crop fields

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### ABSTRACT

Field evaluation of two fly ashes (40 t/ha) on persistence, mobility and bioactivity of metribuzin and metsulfuron-methyl was studied in soybean and wheat crops, respectively. Metribuzin was applied as pre-emergence at 0.5 kg/ha, while metsulfuron-methyl was applied post-emergence at 8 g/ha. Results suggested that metribuzin in surface (0–15 cm) soil of fly ash unamended plots reached below detectable limit in 60 days, while herbicide persisted till 112 days in surface soil of fly ash amended plots. No metribuzin leached down to subsurface (15–30 cm) soil in fly ash amended plots, while traces of metribuzin (0.6–1.2 µg/kg) were recovered in subsurface soil of fly ash unamended plot. Metsulfuron-methyl in surface soil persisted till 15 days in control and 20 days in fly ash amended plots and no metsulfuron-methyl leached down to subsurface soil. Fly ash amendment had no adverse effect on the bioactivity of herbicides and yield of soybean and wheat. The study suggested that fly ash amendment to soil can be exploited to retain applied herbicides in surface soil.

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### 1. Introduction

Fly ash, a byproduct of lignite powered thermal power stations, has been classified as green waste by European Directive 889/ community (Anonymous, 2008). It is considered as nonhazardous waste contrary to wastes of incineration. Fly ash is recommended for soil application because, except nitrogen, it contains all macro and micronutrients required for plant growth (Kalra et al., 2003; Jala and Goyal, 2006; Pandey and Singh, 2010; Singh et al., 2010). Chassapis et al. (2010) suggested humate modified fly ash as soil conditioner for the agricultural applications. Riehl et al. (2010) suggested that silico-aluminous fly ash is better to be adopted as agricultural amendment as it improved soil cation exchange capacity, availability of nutrients and adsorption of water, a useful reserve for plants.

Fly ash amendment to soil not only improves the soil characteristics, but it significantly increased the crop productivity (Jala and Goyal, 2006; Sikka and Kansal, 1995; Ramesh et al., 2008). Lee et al. (2006) studied the effect of fly ash (40, 80 and 120 Mg/ha) on rice productivity in silt loam and loamy sand soils. Fly ash did not result in toxic accumulation of heavy metals in soil or rice grains. Maximum increase in yield (23–36% over the control) was observed

at 90 Mg/ha fly ash application. Singh and Siddiqui (2003) reported that 20% and 40% fly ash resulted in significant increase in plant growth and yield of three cultivars of rice in a greenhouse study. However, further increase in fly ash resulted in decrease in both plant growth and rice yield and was attributed to the salinity caused by fly ash application. Mishra et al. (2007) reported that fly ash up to 15 t/ha in rice significantly improved the soil quality, seed germination, growth and yield of rice, besides protein content of seeds. Aggarwal et al. (2009) reported that field application of 20 t/ha fly ash and 40 or 120 kg/ha nitrogen slightly increased the yield of sorghum and wheat, respectively. Fly ash affected the seed germination and early growth in wheat, but no effect was observed in sorghum. Recently, based on nearly 100 trials, Arivazhagan et al. (2011) reported that 50 t/ha fly ash amendment registered an increase in yield of crops: cereals (15–20%), sugarcane (20–30%), maize (40%), red gram (50%), potato (25%), plantation crops (30%), mustard (30%), and vegetable (10%). In spite of several benefits of fly ash application in agricultural soils, proper attention should be given on soil health parameters, heavy metal uptake, crop quality and continuous monitoring of soil characteristics (Singh et al., 2010). However, Ram et al. (2007) conducted long term field trials on groundnut, maize and sunhemp to study the effect of lignite fly ash (LFA) on crop growth, yield and heavy metal status of the soil. One time and repeated application of LFA (200 t/ha) was the best to improve crop yields and soil properties. Some increase in trace and heavy metal contents and in the level of  $\gamma$ -emitters in soil and crop produce was observed, but well within permissible limits.

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Soil amendments can play a significant role in managing the sorption and leaching losses of pesticides. Fly ash has shown significant pesticide retention capacity. Konstantinou and Albanis (2000) reported significant increase in sorption characteristic of atrazine, propazine, prometryne, molinate, propachlor and propanil herbicides in fly ash amended soils. Researches also indicate that fly ash application to soils increases the sorption of metribuzin, metolachlor and atrazine (Majumdar and Singh, 2007; Ghosh and Singh, 2013; Singh et al., 2012). Laboratory studies suggested that 2–5% fly ash application to sandy loam soil completely checked the metribuzin, atrazine and metolachlor leaching and herbicide was retained in the top 10 cm of column (Majumdar and Singh, 2007; Ghosh and Singh, 2012; Singh et al., 2013). Generally, it is recommended that findings of a laboratory study should be validated under real field situation. No study is available on the effect of fly ash on persistence and leaching behavior of herbicides in actual field conditions. Therefore, the present study reports the effect of two fly ashes on fate of metribuzin and metsulfuron-methyl herbicides in soybean and wheat, respectively. Effect of fly ash on weed control efficacy of herbicides was also recorded.

## 2. Materials and methods

### 2.1. Chemicals

Analytical sample of metribuzin (95% purity) was supplied by the Bayer India Ltd., Mumbai, India. Metsulfuron-methyl (99% purity, analytical grade) was supplied by the DuPont India Ltd., Gurgaon, India. The solvents used were of analytical grade and were purchased locally.

### 2.2. Soil and fly ash

The study was performed in the experimental farm of the Indian Agricultural Research Institute, New Delhi. Fly ash samples were collected from the thermal power plant located at Inderprastha and Badarpur, Delhi, India. The physico-chemical characteristics of the soils and fly ashes (Table 1) were determined using standard analytical procedures: pH measured at 1:1.25 soil to water ratio (Jackson, 1967) organic carbon (OC) content by the Walkley and Black method (Black et al., 1965) soil mechanical fractions employing the Bouyoucos hydrometer method (Jackson, 1967); cation exchange capacity – by the normal ammonium

**Table 1**  
Physico-chemical properties of the soils and fly ashes.

Parameter	Soil, New Delhi	Inderprastha (IP) fly ash, New Delhi	Badarpur (BP) fly ash, New Delhi
pH	7.9	6.9	6.3
Organic carbon (%)	0.39	0.48	0.41
Sand (%)	54.5	60.3	51.6
Silt (%)	23.3	38.0	44.5
Clay (%)	22.3	1.7	3.9
Cation exchange capacity (meq/100 g)	–	1.5	8.12
Heavy metals (mg/kg)			
Zn	–	68.32	69.12
Mg	–	298	221.8
Cu	–	16.94	23.6
Fe	–	18720	43340
Cr	–	17.42	19.03
Ni	–	36.98	35.62
Pb	–	–	2.14

acetate (pH – 7.0) method (Jackson, 1967). Metal content analysis of fly ash was done by digesting dry fly ash (0.5 g) in a Teflon beaker with 20 mL of a mixture of nitric acid: perchloric acid (HNO<sub>3</sub>: HClO<sub>4</sub>, 1:4) on an electric heating plate at 130–150 °C for 3 h. After cooling, 10 mL of concentrated hydrofluoric acid (HF) was added into the vessel and the samples were heated at 90–100 °C until almost dry. Then distilled water was added to the samples and allowed to cool. The digestate was filtered through a 45 µm pore filter membrane and the solution was made to 100 mL with deionized water and analyzed by Atomic Absorption Spectrometer (AAS), ElementAS AAS 4141, Electronic Corporation of India Ltd., Hyderabad, India.

### 2.3. Field experiment

Experiments on the effect of fly ash on herbicides persistence were conducted at the farm of Indian Agricultural Research Institute, New Delhi, during the rainy (*kharif* – July–November, 2011) (metribuzin in soybean) and winter (*rabi* – December, 2011 – April, 2012) (metsulfuron-methyl in wheat) season using a randomized block design. The plot size was 4 m × 2 m. The treatments included: control (no fly ash+no herbicide); no fly ash+herbicide (metribuzin/metsulfuron-methyl); Inderprastha fly ash+herbicide (metribuzin/metsulfuron-methyl); Badarpur fly ash+herbicide (metribuzin/metsulfuron-methyl) and three replicates were taken for each treatment. Fly ash was broadcasted at the rate of 40 t/ha before sowing of soybean/wheat crops. Metribuzin was applied pre-emergence at the rate of 0.5 kg/ha while metsulfuron-methyl was applied post-emergence at the rate of 8 g/ha. Soil samples were drawn randomly from 0–15 and 15–30 cm depth using tube auger from 6–7 spots in each plot at different time intervals. Samples were mixed thoroughly, air dried and 100 g representative samples were withdrawn by the quartering method. Herbicide residues were extracted from the soil and were analyzed using gas chromatography (GC) for metribuzin and high performance liquid chromatography (HPLC) for metsulfuron-methyl. Weeds [30 days after sowing (DAS) in case of pre-emergence application of metribuzin in soybean and at 60 DAS in case of post-emergence application of metsulfuron-methyl in wheat] were counted species-wise from a randomly-thrown quadrat (0.5 m × 0.5 m) in each plot/treatment across replications. Weeds were collected and sun-dried for 2 days. The sun-dried samples were dried at 70 °C till constant weight for estimating dry weight as weed dry weight is a more reliable estimate for testing herbicide bio-efficacy than weed density (Das et al., 2010) and, therefore, only weed dry weight data have been presented here. The meteorological observatory of the Indian Agricultural Research Institute, New Delhi, recorded the weather parameters (Table 2).

**Table 2**  
Weather parameters during the study period.

Month	Temperature (°C)		Rainfall (mm)
	Minimum	Maximum	
July, 2011	28.1	38.1	33.8
August, 2011	24.0	38.2	272.4
September, 2011	21.4	35.5	163.6
October, 2011	11.9	34.5	0
November, 2011	9.2	32.0	0
December, 2011	0	28.5	0
January, 2012	0.4	22	14.8
February, 2012	0.7	29.5	0
March, 2012	4.6	35.2	19.2
April, 2012	16	37.5	9.0

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