Effect of fly ash and bagasse charcoal on the mobility of atrazine in Indian sandy loam soil

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Abstract: The study was undertaken to obtain an objective and realistic overview of atrazine residue reduction in sandy loam soil using two low-cost adsorbents. Fly ash and bagasse charcoal are waste products of thermal power plant and sugar mill, respectively, and are abundant, which have a disposal problem. A laboratory-based adsorption and leaching experiments were carried out to know the percentage reduction of atrazine by mixing these two abundant materials in soil at 1% level. In adsorption and leaching studies, atrazine 50% WP was used to know the reduction of atrazine concentration in fresh soil and soil with adsorbent. It was found that adsorbent mixed soil adsorbed atrazine greater than the fresh soil and the mobility of atrazine was reduced in adsorbent mixed soil as compared to fresh soil. It was concluded that the reduction of atrazine in adsorbent mixed soil was attributed due to the adsorption properties of these adsorbents as well as reducing the porosity of soil. Hence, these adsorbents were chosen to reduce the leachability of atrazine in low organic carbon soil, which has a great potential to groundwater contamination.

Subjects: Agriculture & Environmental Sciences; Environment & Health; Soil Sciences

Keywords: low-cost adsorbent; mobility and distribution; atrazine; adsorption; soil

ABOUT THE AUTHORS
Sharma et al. have been working on pesticide residues and their different aspects under the guidance of Peter Edward Joseph for the past eight years. Since we all are well aware of the hazardous effects of pesticides in soil, especially of atrazine. In the present study, the evaluation of leaching effect of atrazine and its mobility can be reduced by using two waste products, namely bagasse and charcoal, from different sources. These products not only restrict the leaching of atrazine leading to groundwater pollution but an additional advantage is that they are cost effective, so it can be used easily as a means of prevention for pesticide mobility. As these products have issue for their disposal too, so the present research attempted a trial to use these waste products, which proved to be a successful tool for remediation of atrazine mobility issue.

PUBLIC INTEREST STATEMENT
The present research generated an interest to society/public in a way that waste materials from mills, power plants, etc. can also be utilized in an effective manner for the welfare of the society and also prevent their environmental hazards. These industrial waste products can be used as an effective remediation for reduction of groundwater contamination by leaching.
1. Introduction

Herbicides, mainly triazines are weakly sorbed in soils and have been detected in the surface and groundwater resources (Ghosh & Singh, 2013). It is the most widely detected herbicide in the surface and groundwater in the United States (Gilliom, 2007). Atrazine [2-chloro-4-(ethyl amino)-6-isopropanylamino-s-triazine] is one of the most largely applied herbicides in several crops such as sugarcane, maize, soybean, and citrus fruits (Graymore, Stagnitti, & Allinson, 2001). Although atrazine is not an extremely harmful herbicide but it interacts weakly with soil components, having a high geochemical mobility which creates groundwater contamination (Moorman, Jayachandran, & Reungsang, 2001). Atrazine was found to be degradable and had little tendency to bioaccumulate thereby limiting possible long-term adverse effects on fish and wildlife (Environmental Protection Agency, 2003; Hayes et al., 2002; Kramer, 2007). In another study it was examined that atrazine, weak base herbicides and nonionic herbicides were more sorbed than weak acidic herbicide which was closely related to the hydrophobicity of herbicide (Hiller, Krascsenits, & Čerňanský, 2008). However, according to Laabs, Amelung, Pinto, Altstaedt, and Zech (2000), atrazine shows high to medium mobility which is consistent with its high leaching potential in some types of soil lysimeter studies. In a report suggested by US Geological Survey that deethylatrazine and atrazine were the most commonly detected herbicides in 30 and 10–27% well water samples, respectively (Toccalino, Norman, & Hitt, 2010). Atrazine is dangerous for human, which causes cancer (Sathiakumar & Delzell, 1997) and damages the nervous system and mammary gland (Wiklund & Dich, 1994), and is also responsible for endocrine disruption in frogs, rats, and humans (US EPA Office of Pesticide Programs, 2002; Villanueva, Durand, Coutte, Chevrier, & Cordier, 2005). Also, in a report by USEPA Atrazine is a class C “possible human carcinogen”, has the maximum contaminant level (MCL) in drinking water 3.0 μg L⁻¹ (USEPA, 1988) and below 0.1 μg L⁻¹ for the European Union drinking water. In 2010, the Nebraska Department of Environmental Quality found that 5% of groundwater samples exceeded the reporting limit for atrazine (Nebraska Department of Environmental Quality, 2010). Another study of vernal pools in protected areas in the United States found that atrazine was the most frequently detected pesticide (53%), followed closely by deethylatrazine (47%), hydroxyatrazine (44%), and deisopropylatrazine (29%) (Battaglin, Rice, Focazio, Salmons, & Barry, 2009).

Adsorption process is a surface phenomenon, which depends upon the number of sites available, porosity, and specific surface area of adsorbent as well as various types of interactions. Adsorption on soil is an important physicochemical characteristic governing the fate of pesticides in the environment. Adsorption occurs at a surface of a solid adsorbent, which forms chemical or physical bonds to remove a component, such as atrazine, from the fluid phase (Foo & Hameed, 2010). The atrazine reaches the adsorbent after undergoing three types of diffusion. First, film diffusion moves the atrazine from the bulk phase to the adsorbent surface. Second, particle diffusion moves the atrazine to the interior of the adsorbent. Third, the atrazine is adsorbed onto the surface of the adsorbent (Chingombe, Soha, & Wakeman, 2006). Compared to chemical or biological removal methods, adsorption has a low initial cost, offers flexibility and simplicity of operation, and does not form harmful intermediates (Ahmad et al., 2010).

Sorption is one of most important phenomenon which removes herbicide from the mobile phase of a soil by influencing its mobility in soil under laboratory conditions (Socias-Viciana, Fernández-Pérez, Villafranca-Sánchez, González-Prodas, & Flores-Céspedes, 1999), as well as under field conditions (Laabs et al., 2000). Using the activated carbon in the sorption study, it was found that 98% of atrazine was removed. But leading researchers examined the easily available and cheaper alternatives (Cole, 2012) to reduce the cost of activated carbon. Fly ash (FA) is a by-product from lignite–fired power stations which is an amorphous mineral residue mainly consisting of aluminosilicate; chemically, 90–99% of FA comprised Si, Al, Fe, Ca, Mg, Na, and K, and its composition varies with the change in organic components of the source coal, coal combustion conditions, ash collection, and handling methods. When applied to soils it decreases the bulk density of soils, which in turn improves soil porosity and workability and enhances water retention capacity with having uniform particle size distribution (1–10 μm). Also, the acidic or alkaline FA may be of agronomic benefit by buffering the soil pH and improving the soil nutrient status (Sikka & Kansal, 1995; Ramesh et al., 2008).
Adsorption of atrazine on soil has been attributed mainly to organic matter level, type of the clay, and pH of the soil (Bhardwaj & Gehlan, 1986). It can be noticed that clay minerals (kaolinite, illite, and montmorillonite) and oxides can adsorb cationic, anionic, and neutral species and take part in cation-anion exchange programs. Adsorption of diquat and deisopropylatrazine (intermediate compound from degradation of atrazine in water) on aqueous solutions of two montmorillonite-(Ce or Zr) phosphate crosslinked compounds (ceriummontmorillonite and zirconiummontmorillonite) showed that ceriummontmorillonite adsorbent showed higher capacity of adsorption compared with zirconiummontmorillonite (Srivastava, Jhelum, Basu, & Patanjali, 2009). The adsorption capacities of the soils increased with the increase in organic matter or clay content (Liu, Xu, Wu, Gui, & Zhu, 2010; Osborn, Edwards, Wilcox, & Haydock, 2009). The importance of organic fractions in retaining simazine and atrazine in some soils of Karnataka has been studied by Rajanna and Suseela Devi (1987). The migratory behavior was less as sorption favored high retention and vice versa. This may be also due to the higher organic matter content and less aeration (Khoury, Geahchan, Coste, Abi Antoun, & Kawar, 2001; Sharma, Sharma, Joseph, Saha, & Walia, 2013). It is not expected to strongly adsorb to sediments and may be chemically hydrolyzed forming the inactive hydroxyatrazine which in turn may be microbiologically decomposed in any soil type (Kumar, Kumar, Upadhyay, & Sharma, 2014). Adsorption-desorption study of atrazine in some selected soils of Karnataka and Hyderabad has also been reported earlier (Kumaran & Suseela Devi, 1996; Raman, Krishna, & Chandrashekhar Rao, 1988). Presently, information of adsorption/leaching using low-cost adsorbent is rarely available for Indian soils. Hence, the aim of this research work was to study the effect of two low-cost adsorbents (FA and bagasse charcoal) on alluvial soil for atrazine by leaching experiment at laboratory condition.

2. Materials and methods

2.1. Samples preparations
All solvents were procured from Merck India and glass distilled before use. Before each experiment, all glassware was cleaned with chromic acid and rinsed thoroughly with distilled water followed by drying at 110°C for 5 h. The stock solution of atrazine 50% WP [Devidayal (Sales) Pvt. Ltd.] was prepared in acetone (500 μg ml⁻¹). Aliquots of stock solution containing required amount of atrazine were transferred into 1,000 ml conical flasks and left at room temperature (27 ± 3°C) for the evaporation of acetone. The residues were dissolved in 0.01 M CaCl₂ solution and used for adsorption studies. All studies were done in triplicate. The soil samples (0–15 cm depth, plowing layer) were collected from Shamshabad district of Agra (27°10’ N 78°02’ E), (UP), India. The soil was dried, crushed, and sieved through 2.0 mm sieve. The physicochemical properties of the soil were determined by standard techniques viz. pH (8.4) (Jackson, 1973), organic matter (1.70%) (Walkley & Black, 1934), cation exchange capacity (CEC) (2.1) (Gillman, 1979), and particle size (74% sand) (Day, 1965).

2.2. Experimental design for sorption and mobility
Experiment was conducted to know the residue of atrazine in control soil sample, but there was no residue detected. Hence, this soil was used for sorption/leaching studies. Bagasse charcoal (BC) was collected from Chhata Sugar Mill, Chhata, UP and FA was supplied from the NTPC plant, Kota, Rajasthan. Adsorbents were washed thoroughly with distilled water to avoid the presence of foreign impurities. The washed and dried materials were sieved to get 50 mesh sizes. Adsorption study was done in glass column (45 cm long × 2 cm ID). A cotton plug was inserted into the column and a 1 cm layer of acid washed sand was placed above the cotton plug and then the lower end of the tube was inserted into a Buchner funnel, above a conical flask. Column was filled to a height of 20 cm with soil or mixture of soil and adsorbent (1%) and then compacted. It was then pre-washed with 250 ml distilled water and then eluted with water, fortified with atrazine 50% WP at 0.5 and 1.0 ppm levels, and two liters of eluate was collected. A total of 100 ml aliquot of the supernatant was pipetted out into a separatory funnel, diluted with aqueous saturated NaCl solution, and extracted with ethyl acetate (3 × 50 ml). Pooled extract was passed through anhydrous Na₂SO₄ and evaporated using rotary evaporator under reduced pressure. Leaching studies were carried out with 50% WP formulation of atrazine in soil, soil + FA (1%), and soil + BC (1%). The six treatments (20, 40, 80, 160, 320, & 450 ml water) were carried out in triplicate along with a control. Water content in each treatment
was 0.67, 1.33, 3.67, 5.33, 10.67, 14.93 times the field capacity moisture level of soil. The leaching studies were carried out in plastic columns (50 cm long × 2 cm ID) under saturated flow conditions. Soil or adsorbent mix soil was filled up to a height of 25 cm (amount of soil used 146.15 g). Small holes were made at the lower end of the columns with the help of a pin to collect the leachate. The lower end of the columns was dipped over night into water and allowed to rise into the column by capillary action. Next day, the columns were hung vertically and the excess of water was allowed to drain out. 75 μg atrazine dissolved in acetone was spread uniformly at the top and leaching was started. Water according to treatments was added and allows leaching down under natural flow conditions (3.6 mL h⁻¹). Leachate were collected, filtered, diluted with 50 mL of saturated sodium chloride solution and extracted with ethyl acetate (3 × 50 mL). The ethyl acetate layers were combined, added anhydrous sodium sulfate and shaken well, filtered, and concentrated. At the end of the leaching experiment, soil columns were cut horizontally into five cores and dried the soil at room temperature. Atrazine residue was extracted using acetone and partitioned with ethyl acetate (3 × 75 mL). Extracts obtained from adsorption and leaching experiments were concentrated to dryness on rotary evaporator under vacuum. Residues thus obtained were dissolved in n-hexane.

2.3. Analytical procedures
Analysis of atrazine was achieved using a Thermo-Finnegan Trace 2000 model GC equipped with ⁶³Ni-ECD and BP-5 capillary column (30 m × 0.25 mm, 0.25 μm). The carrier gas was high purity nitrogen (IOLAR I) with a flow rate 1 ml min⁻¹. The injector, column, and detector temperature were maintained at 250, 220, and 300°C.

The atrazine was detected at 3.3 min. The limit of detection (LOD) for atrazine was calculated 0.5 μg L⁻¹ and limit of quantitation (LOQ) were 1 μg L⁻¹ in water and 2 μg⁻¹ based on signal to noise (S/N) ratio 3 for LOD and 10 for LOQ.

3. Results and discussion
A GC with ECD detector was calibrated by standard solutions. The calibration curve was plotted between the concentration and peak area that showed a correlation coefficient (r²) of 0.9997. To determine the loss of atrazine residues, the blank (without soil) experiment was also conducted. During the blank experiment, it was found that there was no significant difference in atrazine residues. The percentage recovery of atrazine in soil and adsorbent mixed soil viz. soil + 1% FA, and soil + 1% BC were 98.40 ± 2.55%, 95.93 ± 4.21%, and 96.40 ± 3.04%, respectively. The recovery of atrazine in water solution was 98.07 ± 0.88%. Higher recovery (98.40%) was obtained in the soil and this may be due to the high content of sand (74%), which do not strongly adsorb or retain atrazine molecules. The recovery of atrazine in the adsorbent mixed soil was lower (95.93–96.40%) and this may be due to adsorbent which may cause strong adsorption of atrazine as compared to that in soil. However, the difference was not significant. The control soils, which were not treated with atrazine, did not show any atrazine residue. Physicochemical properties of soil showed that soil is sandy loam (Table 1). Texture of soil was found as sandy loam. As discussed earlier, in the introduction and reviewed from the literature that soil with large surface area and more CEC showed more adsorption capacity. The soil taken in the study has much less binding capacity with less clayey content (18%) which is generally regarded as the main factor responsible for adsorption.

| Property       | Value         |
|----------------|---------------|
| pH             | 8.4           |
| Organic matter | 1.70%         |
| CEC            | 2.1 meq/100 g |
| Sand           | 74%           |
| Silt           | 8%            |
| Clay           | 18%           |
Percentage adsorption of atrazine on soil and adsorbent mixed soil is shown in Figure 1. The standard deviation was calculated by three replicates for each experiment. The adsorption of atrazine was calculated as 38.93% with the standard deviation of 2.38 at 0.5 ppm level. In case of 1.0 ppm level, it was found 42.15% with standard deviation 3.72. For soil + 1% FA and soil + 1% BC, percentage adsorbed atrazine residues were ranged from 61.78 ± 3.12 to 65.24 ± 2.56 and 60.26 ± 3.78 to 62.68 ± 1.46%, respectively, at the same concentration level. It was observed that FA and BC enhanced the adsorption capacity of soil by adding it at 1% level. FA consists of 40–50% silica, 20–35% alumina, 12–30% carbon, and unburnt minerals having a high pH of 9–10. Both have comparatively good adsorption capacity. Adsorption of atrazine on these low-cost adsorbents was due to large surface area and higher carbon content as well as various types of interactions between adsorbent and adsorbate (Sharma, Kumar, & Joseph, 2008). Another co-worker also described high carbon content which favors adsorption but for other pesticide and in the same soil of same place (Sharma et al., 2013). Wood charcoal is the best alternative for adsorption, though it is not as efficient as activated carbon, with removal rates of 95–97%.

It had been examined that adsorption of atrazine on soil and adsorbent mixed soil may be due to various types of interactions. FA has also shown significant adsorption capacity for organic pollutant like phenol, dyes, and pesticides (Alam, Dikshit, & Bandyopadhyay, 2000; Sarkar & Acharya, 2006; Sharma et al., 2008; Singh, 2009). It was also reported that the application of FA to soils at 0.2–30% levels was used for soil detoxification from 2,4-D, alachlor and metolachlor (Albanis, Danis, & Kourgia, 1998). Singh (2009) reported that coal FA has high retention capacity for metribuzin, metolachlor, and atrazine and found that atrazine showed maximum sorption. Also another research suggested that up to 25% of FA amendment to soil can immobilize atrazine, propazine, prometryne, molinate, propachlor, and propanil herbicides thus, have implications in the management of runoff and leaching losses of these herbicides (Konstantinou & Albanis, 2000). The analysis of leaching of each treatment showed that no residue of atrazine was present in any treatment except the last one. The analysis of different layers of the soil from column profile showed that in the first treatment, no residue of atrazine was found below 5 cm top layer of the soil. In the second layer (5.0–10.0 cm) of the soil, 1.099 and 3.513 μg atrazine residues were found in the second and third treatment, respectively. In the fourth treatment, 2.890 μg residue of atrazine was found in the 10–15 cm layer of the soil. In the fifth treatment, atrazine leached up to 25 cm from the top layer of the soil. In the last treatment, 0.401 μg
Atrazine residue was found in the leachate (Table 2). Conversion of volume of water used in each treatment into equivalent rainfall revealed that continuous rainfall of about 3.57 cm would be required to leach atrazine below 25 cm top layer of the soil. 320 mL water equivalent to 25.387 cm rainfall was able to distribute residue in the column profile up to 25 cm from top layer of the soil. In adsorbents

| Treatment (mL) | Atrazine residues in leachate (µg) |
|---------------|-----------------------------------|
|               | Soil     | Soil + 1% FA | Soil + 1% BC |
| 20            | ND       | ND           | ND           |
| 40            | ND       | ND           | ND           |
| 80            | ND       | ND           | ND           |
| 160           | ND       | ND           | ND           |
| 320           | ND       | ND           | ND           |
| 450           | 0.401 ± 0.08 | ND           | ND           |

Note: ND = Not Detected.

Figure 2. Percentage removal of atrazine residues by leaching experiment in soil without adsorbent.

Figure 3. Percentage removal of atrazine residues by leaching experiment in (soil + 1% FA).
mixed soil, atrazine could leach up to 10 cm from the top layer of the soil by 450 ml water, equivalent to the rainfall of 35.7 cm (Figures 2–4). Based on this study, it was observed that the mobility of atrazine was reduced in adsorbent mixed soil as compared to fresh soil.

4. Conclusion
The study suggested that reduction in mobility of atrazine in adsorbent mixed soil was attributed mainly to the adsorption property of these adsorbents as well as reducing the porosity of soil. FA and BC are waste products of thermal power plant and sugar mill, respectively, and are abundant, which have a disposal problem. Its cost is only due to transport expense which depends upon distance from the sugar mill or thermal power plant. However, FA is found to be the best among the two, as its holding capacity was more than BC. So it can bind the atrazine well with the soil matrix and its chance of moving down is low.

At laboratory level, the adsorbents (FA and BC) were found as suitable material to reduce the significant concentration of atrazine by adsorption and leaching experiment in sandy loam soil. Hence, it should apply in field condition to know the variation of atrazine distribution in different soil fractions. A study in real-field condition will provide a better scenario to understand the groundwater contamination.

Acknowledgement
Authors are thankful to the Head, Department of Chemistry and Principal, St. John’s College, Agra (UP) for providing necessary research and instruments facilities. Our thanks are also due to Late Dr. P. Dureja, Ex-Head Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi, for providing continuous research guidance.

Funding
The authors received no direct funding for this research.

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