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Effect of Organic Amendments on Degradation of Atrazine

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Abstract Pesticide contamination of soil and ground water at or near the agricultural fields is a major problem world wide. The ability of several amendments like rice straw, manure, saw dust and charcoal were used to stimulate the degradation of atrazine in soil. Field soil fortified with pesticide at two concentration levels were amended separately with rice straw, farm yard manure, saw dust and charcoal at rates of 2.5% (w/w) and maintained at field capacity moisture regime and kept at ambient temperature 25 ± 5°C. The results indicate 89.5% degradation of atrazine in farm yard manure during 60-day period followed by rice straw, saw dust charcoal and recording 87.2% and 83.8%, 67.7%, respectively, as compared to unamended treatment where 63.3% degradation was observed. The FYM was found to be most effective in soil and enhances the degradation as compared to the other amendments. Although addition of organic manures has been an integral part of sustainable agriculture practices; the present findings give a new dimension of it's utilization for removal of persistent pesticides.

Keywords Atrazine · Amendment · Biostimulation · Organic bioresource

Pesticide contamination of soils and ground water at agricultural experimental fields, dealership sites and farmsteads is a widespread problem. Bioremediation and phytoremediation processes would benefit farmers and dealers by reducing potential downward and lateral movement of chemicals, human exposure and would be a cheaper option than other methods of remediation of contaminated soils. Use of easily available agricultural field by product amendment will result in greening of the environment and reduce environmental pollution. Pesticide contamination of soils and ground water at agricultural experimental fields, dealership sites and farmsteads is a widespread problem. Bioremediation and phytoremediation processes would benefit farmers and dealers by reducing potential downward and lateral movement of chemicals, human exposure and would be a cheaper option than other methods of remediation of contaminated soils.

Atrazine is a herbicide used by farmers worldwide since 1959 (Solomon et al. 1996). Atrazine interferes with photosynthesis (photophosphorylation) in many annual broadleaf plants and grasses, while *Zea mays* (corn), *Sorghum bicolor* (sorghum), *Saccharum officinarum* (sugarcane), and a few other crops (Solomon et al. 1996) are tolerant of the chemical's effects at recommended application concentrations. After application, atrazine continues to control sprouting weeds for 5–6 weeks (Ballantine et al. 1998), allowing the desired crop to become well established without competition for moisture, nutrients and sunlight. Atrazine is much less expensive than comparable herbicides.

Atrazine residue and spills are not only toxic to plants where applied or spilled, but can runoff or leach into streams and rivers, potentially interfering with photosynthesis of aquatic plants which in turn could affect the food and shelter requirements of aquatic animals. Atrazine spills occur at agrochemical dealer sites where the chemicals are mixed and distributed, and occasionally at farms where the chemicals are delivered and loaded into dispersal equipment.

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Herbicide remediation techniques typically involve excavation of the contaminated soil for land application at half the legal rate allowed for the particular application.

Materials and Methods

Field soil from IARI experimental farms the physico-chemical characteristics listed in Table 1 was taken at plough depth (0–15 cm) taken, air dried and sieved. The amendments rice straw, farmyard manure, saw dust and charcoal were ground passed through 4 mm mesh sieve prior use. To soil sample (50 g) in glass jars were mixed with the amendments at 2.5% level. An unamended treatment was set to serve as control. All the treatments were maintained at 13% field capacity moisture regime and appropriate amount of the amendment was to the and incubated in for 48 h at room temperature 25°C. one milliliter of 1,000 μL/mL of standard solution atrazine in acetone was added to the wide mouth glass jars and allowed to evaporate. To this soil samples along with the amendments were added. Fifty gram soil samples were fortified with atrazine at 20 μg level. To the soil samples 2.5% (w/w) of the amendments of farmyard manure, rice straw, saw dust and charcoal were added. The moisture regime of all the samples was maintained at 13% field capacity levels by periodically weighing and adding appropriate amount of water. These treatments are biostimulators for degradation process in soil.

Samples were incubated at 25°C. Periodic sampling was carried out on 0, 3, 5, 10, 15, 20, 30, 40, and 60 days. Each set of experiment was carried out in triplicate. Acetone (50 mL) was added to each sample and were shaken using a horizontal shaker for 4 h. The extract was filtered, and was concentrated to 10 mL, using a rota vapour. The concentrate was transferred to a separatory funnel and 2% saline water (100 mL) was added and partitioned into dichloromethane (30 mL), passed through anhydrous sodium sulfate and stored. The aqueous portion was partitioned two more times with dichloromethane (2 × 30 mL). The combined dichloromethane phase was concentrated to dryness in a rotary evaporator and subjected to column clean up. The residue was dissolved in 10 mL hexane, and passed over a glass column (30 cm × 1.5 cm ID) packed with silica gel (5 g, 60–120 mesh), sandwiched between layers of anhydrous sodium sulfate (2 g).The column was pre-washed with 50 mL hexane, and the solvent discarded. The organic phase was further cleaned over a column of Florisil and then subjected to analysis by GLC using ECD detector.

Table 1 Physico-chemical properties of the IARI soil

	Values
Mechanical analysis	
Sand (%)	64.9
Silt (%)	18.0
Clay (%)	17.1
	Sandy loam
Textural class	
Bulk density (g cm^{-1})	1.45
Field capacity (%)	17.61
Chemical analysis	
pH (soil:water = 1:2.5)	7.41
Electrical conductivity (dsm^{-1}) (soil:water = 1:2.5)	0.35
Cation exchange capacity (Cmol (p^+) kg^{-1})	7.35
Organic carbon (%)	0.39

The samples were periodically taken out on day 0, 3, 5, 10, 15, 20, 30, 40, and 60 and extracted with acetone in a shaker and filtered. The extract was concentrated and saline water (2%) was added and then exchanged into dichloromethane phase. The organic phase was further cleaned over a column of Florisil and then subjected to analysis by GLC using ECD detector. The analysis was carried out with gas liquid chromatograph fitted with an electron capture detector, column used was DB-5 (30 m × 0.53 mm × 1 μ) was maintained at 180°C, injector port was 250°C and detector at 300°C. The carrier gas flow through the column was 2 mL/min and the make up gas flow was 32 mL/min. The retention time of atrazine was 3.14 min.

Results and Discussion

The results indicated initial percent degradation of atrazine by day 5 was 25.6, 22.6, 23.2, 14.5 in the soil amended with FYM, rice straw, saw dust and charcoal, respectively, as compared to unamended treatment where only 10.78% degradation of atrazine is recorded (Table 2). These treatments serve as biostimulators for the degradation process in soil. In 60-day incubation period the degradation was fastest in farm yard manure, 89.5%, followed by rice straw saw dust-, charcoal, recording 87.2%, 83.8% and 67.7%, 27%, respectively, as compared to unamended treatment where slow degradation of 63.3% was observed (Fig. 1). Dissipation data for atrazine under different amendments fitted well to first order kinetic equation, log $(C/C_0) = -K_{obs}t$, where C_0 is the initial concentration of the herbicide (μg/g), C is the concentration (μg/g) after time in days (t) (Table 3). The half life was 43 days in unamended soil as compared to 18 days in the farm yard manure (Fig. 1). The FYM was found to be most effective in soil and enhances the degradation as compared to the other amendments.

Table 2 Persistence and dissipation of atrazine using soil amendments

Days	Control	FYM	Rice straw	Saw dust	Charcoal
0	19.75	19.44 ± 0.04	19.54 ± 0.05	19.34 ± 0.03	18.67 ± 0.03
3	18.25 (7.59)	16.00 ± 0.02 (17.70)	17.32 ± 0.03 (11.46)	16.89 ± 0.02 (12.67)	16.78 ± 0.03 (10.12)
5	17.62 (10.78)	14.46 ± 0.03 (25.62)	15.12 ± 0.04 (22.62)	14.84 ± 0.05 (23.27)	15.95 ± 0.02 (14.56)
10	15.23 (22.8)	11.24 ± 0.03 (42.18)	14.08 ± 0.02 (27.94)	12.71 ± 0.05 (34.28)	13.82 ± 0.03 (25.97)
15	14.45 (26.83)	9.64 ± 0.05 (50.41)	12.42 ± 0.04 (36.44)	10.82 ± 0.07 (44.05)	12.72 ± 0.05 (31.86)
20	12.89 (34.73)	7.89 ± 0.06 (40.58)	10.24 ± 0.03 (47.59)	9.62 ± 0.05 (50.26)	11.84 ± 0.05 (36.58)
30	11.28 (42.88)	5.38 ± 0.02 (72.33)	6.91 ± 0.05 (64.69)	7.17 ± 0.06 (62.93)	9.86 ± 0.03 (47.18)
40	9.21 (53.36)	3.79 ± 0.01 (80.50)	5.26 ± 0.03 (73.08)	5.42 ± 0.05 (71.98)	7.92 ± 0.06 (57.57)
60	7.23 (63.39)	2.04 ± 0.02 (89.51)	2.50 ± 0.02 (87.21)	3.12 ± 0.03 (83.87)	6.02 ± 0.05 (67.75)

Figure in parenthesis indicate % dissipation

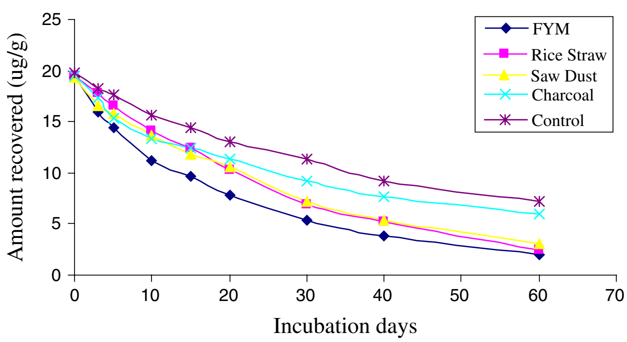

Fig. 1 Dissipation of atrazine in presence of organic amendments

Table 3 Regression equation and half life correlation coefficient

Amendment	*Y*	RL_{50}	R^2
FYM	$-0.0161x + 1.2391$	18.8	0.9924
Rice straw	$-0.0146x + 1.2876$	20.61	0.9958
Saw dust	$-0.0129x + 1.2493$	23.33	0.9942
Charcoal	$-0.0083x + 1.2375$	37.62	0.9665
Unamended treatment	$-0.0073x + 1.2739$	43	0.9873

Eriksen et al. (2008) reported that acidification of slurry with sulfuric acid is a recent agricultural practice that may serve a double purpose: reducing ammonia emission and ensuring crop sulfur sufficiency. We investigated S transformations in untreated and acidified pig slurry stored for up to 11 months at 2, 10, or 20°C. Furthermore, the fertilizer efficiency of sulfuric acid in acidified slurry was investigated in a pot experiment with spring barley. The sulfate content from acidification with sulfuric acid was relatively stable and even after 11 months of storage the majority was in the plant-available sulfate form. Microbial sulfate reduction during storage of acidified pig slurry was limited, presumably due to initial pH effects and a limitation in the availability of easily degradable organic matter. Sulfide accumulation was observed during storage but the sulfide levels in acidified slurry did not exceed those of the untreated slurry for several months after addition. The S fertilizer value of the acidified slurry was considerable as a result of the stable sulfate pool during storage. The high content of inorganic S in the acidified slurry may potentially lead to development of odorous volatile sulfur-containing compounds and investigations are needed into the relationship between odor development and the C and S composition of the slurry.

The atrazine dissipation was observed to be highest (34%) with biogas slurry. The study on synergistic effect of sodium citrate with farmyard manure showed a negative effect in initial phase, but dissipation gradually increased after first week (i.e., 32% degradation after 21 days). Although addition of organic manures has been an integral part of sustainable agriculture practices; the present findings give a new dimension of it's utilization for removal of persistent pesticides (Kadian et al. 2008). Degradation of atrazine was enhanced by 0.5% manure, 5% peat, and 5% cornstalk amendments compared to non-amended soils (Mooram et al. 2001; Pussemeir et al. 2003). A field lysimeter study with six different ground covers, bare ground, orchard grass, tall fescue, timothy, smooth bromegrass, and switch grass was conducted to assess the bioremediation capacity of five forage species to enhance atrazine dissipation in the environment via plant uptake and degradation and detoxification in the rhizosphere (Lin et al. 2008). Results suggested that the majority of the applied atrazine remained in the soil and only a relatively small fraction of herbicide leached to leachates (<15%) or was taken up by plants (<4%) (Pullicino et al. 2004). Biological degradation or chemical hydroxylation of soil atrazine was enhanced by 20%–45% in forage treatment compared with the control (Lima et al. 2009). Of the atrazine residues remaining in soil, switch grass degraded more than 80% to

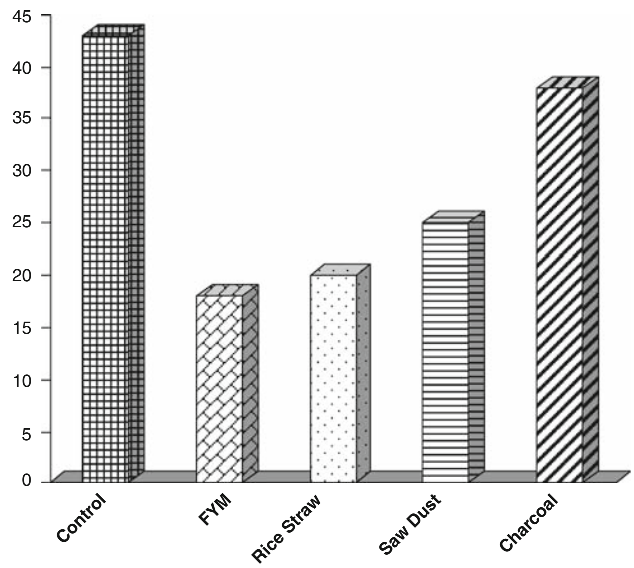

Fig. 2 Half life of atrazine in different amendments

less toxic metabolites, with 47% of these residues converted to the less mobile hydroxylated metabolites 25 days after application (Fig. 2).

Study suggests organic amendment certainly enhanced degradation of both soil applied atrazine. These results have implications in managing the persistent residues of atrazine in soil. However, to get a more realistic picture study under actual field conditions is advised.

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