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Accelerated Metolachlor Degradation in Soil by Zerovalent Iron and Compost Amendments

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Abstract Soil incubation and germination tests were conducted to assess zerovalent iron (ZVI), organic compost, moisture and their combinations on metolachlor degradation in soil. The ZVI alone degraded 91% of metolachlor in soil within 40 days following bi-phasic kinetics. Organic amendment alone facilitated metolachlor degradation in soil up to 60% after 40 days depending on the amendment rate. However, the combination of ZVI with compost amendment at 30 ton ha^{-1} and 30% moisture content accelerated metolachlor degradation to 90% after 3 days and 98% after 40 days. The half life ($t_{1/2}$) of metolachlor degradation with ZVI, compost at 30 ton ha^{-1}, and 30% moisture was about 1 day, which was faster than ZVI treatment alone and 98% faster than controls. Germination and growth of lettuce (*Lactuca sativa*) and crabgrass (*Digitaria sanguinalis* L. Scop.) were severely inhibited in unamended metolachlor-contaminated soils but when these soils were amended with ZVI, germination and growth was comparable to controls (metolachlor free soil). Metolachlor degradation was greatest when ZVI, compost and moisture were used together, suggesting that these treatments will maximize in situ remediation of metolachlor-contaminated soils in the field.

Keywords Metolachlor · Degradation · Zerovalent iron · Organic amendment

Metolachlor has been defined as a possible human carcinogen by WHO (1993) and ethylmethylaniline, a metolachlor transformation product, shows genotoxic properties (Fava et al. 2000). Metolachlor and some degradates, mainly ethansulfonic acid and oxanilic acid, have been detected in surface and ground water in many countries (Senseman et al. 1997; Kolpin et al. 2000) due to their relatively high mobility in soils. Also, spills or the intensive application of metolachlor to arable land can be a point-source threat to ground and surface water. Metolachlor dissipation is mostly affected by climatic factors such as precipitation volume and rate after application (Sanchez-Martin et al. 1995), and soil physical characteristics including the type and amount of clay (Novak et al. 2001). Organic matter content, moisture levels, and temperature also affect metolachlor degradation in soil and water (Giovanni et al. 2000; Singh 2003).

The corrosion of ZVI is an electrochemical process that oxidizes Fe^0 to Fe^{2+} while releasing electrons. The reaction of Fe^{2+} with OH^- yields $Fe(OH)_2$, which can be further oxidized to green rust I and green rust II. Further oxidation results in Fe^{3+}-containing compounds such as magnetite, lepidocrocite, ferrihydrite, and goethite (Genin et al. 1998; Furukawa et al. 2002). The released electrons alter the persistent organic compounds to be less toxic. Thus, ZVI has been used to treat soil and water contaminated with organic and inorganic compounds (Comfort et al. 2001; Shea et al. 2004).

However, few studies have been conducted to investigate conditions that might increase the efficiency and longevity of ZVI for detoxifying organic compounds in soils. Satapanajaru et al. (2003a, b) showed that adding aluminum (Al) and iron salts [Fe(II) and Fe(III)] with ZVI enhanced formation of green rust, which accelerated metolachlor degradation rate because the added salts were

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readily sorbed by the corroding iron with a corresponding release of Fe(II). Soil organic matter is a key factor that controls the fate and mobility of organic substances in soil through adsorption, solubility and moisture interactions (Sanchez-Camazano et al. 1997; Graber et al. 2001; Worrell et al. 2001). The objectives of this research were to (1) assess individual and combined effects of ZVI, organic matter and moisture on the degradation of metolachlor in soil, and (2) to evaluate practical methods for field-scale remediation of metolachlor in soils.

Materials and Methods

Metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] of analytical grade (96.1% purity) was purchased from Chem Service Inc. (West Chester, PA, USA). The annealed ZVI was in the form of cast iron aggregates (Peerless Metal Powders, Detroit, MI, USA) with a specific surface area of 0.078 m^2 g^{-1} (Micromeritics, Norcross, GA, USA). The A horizon soil samples (fine, mixed, acid, mesic Typic Fluvaquents, Chuncheon Loam series) were collected from an arable field in Chuncheon, Korea, air-dried and ground to pass through a 2-mm sieve (Table 1).

Soil samples were treated with metolachlor (Dual 8E, Syngenta, Greensboro, NC, USA) by spreading 1 kg of soil on a surface, evenly spraying metolachlor onto the soil using a hand-sprayer, and mixing thoroughly to make the final concentration of metolachlor in the soil at 200 mg kg^{-1}. Higher concentrations of metolachlor were used in our experiment to simulate worse case scenarios, e.g., intensive application, spill or leakage of metolachlor from facility. Since initial water contents in soil was 64%, moisture treatments were established by spraying appropriate volumes of water on soils based on pressure plate analysis of soil water holding capacity (26.3% with 0.33 bars of atmosphere) after completely drying the soil in oven at 105°C for 2 h.

The metolachlor-treated soil samples were thoroughly mixed then amended with three materials: 5% ZVI, commercial compost at 10 and 30 ton ha^{-1} rates (Table 2), and water at 10 and 30% (w/w) rates. All amendments were added alone and in selected combinations. Treated samples were put into pots and incubated in a growth chamber controlled at 25°C and 50% relative humidity. Pots were covered with black plastic sheeting to prevent moisture loss and to reduce photodegradation of metolachlor during the experiment. Concentrations of metolachlor were measured in soil samples collected at 0, 3, 7, 12, 19, 27, and 40 days after incubation. Metolachlor analysis was performed by extracting a 20 g soil sample with 100 mL acetone and 40 mL distilled water in a rotary shaker at

Table 1 Chemical properties of the experimental soil

pH (1:5)	EC (µS cm^{-1})	Organic matter (g kg^{-1})	Total N (mg kg^{-1})	Exchangeable K (cmolc kg^{-1})	Exchangeable Ca (cmolc kg^{-1})	Exchangeable Mg (cmolc kg^{-1})	Exchangeable Na (cmolc kg^{-1})	CEC (cmolc kg^{-1})	Fe[a] (mg kg^{-1})	Cu[a] (mg kg^{-1})	Zn[a] (mg kg^{-1})
5.75	58.6	12.6	945.7	1.76	3.18	0.66	0.84	12.16	13.75	0.68	1.15

[a] Fe, Cu and Zn: extracted by 5 mM DTPA

Table 2 Properties of the commercial organic compost used in this experiment

pH (1:5)	EC (μS cm^{-1})	Moisture content (%)	Organic matter (g kg^{-1})	NaCl	Carbon nitrogen ratio
6.94	1,381	63.53	351.9	0.5	36.3

150 rpm and 25°C for 1 h. The supernatant was filtered through a 0.45 μm filter paper. After evaporation of the acetone extract in a rotary evaporator, the residues were extracted twice with 100 mL hexane using a separatory funnel and then passed through the glass column (22 × 400 mm) filled with anhydrous sodium sulfate and silica gel for further purification. After solvent was evaporated to dryness on a rotary evaporator, the residues were dissolved in 5 mL hexane. Quantitative analysis was performed in a gas chromatograph (Hewlett Packard 6890, San Fernando, CA, USA) equipped with a flame ionization detector. A capillary column (HP-5, 30 m × 0.25 μm, I.D. Agilent, USA) was used and samples were injected with a split ratio of 20:1. The carrier gas was nitrogen at 1 mL min^{-1} and injector, detector, and column temperatures were 230, 250, and 210°C, respectively. The retention time was 7.3 min for metolachlor detection. Recovery of metolachlor from fortified samples of soil averaged 78% and detection limit was 1 ng μL^{-1}.

For each soil sample, pH (1:5, soil(w):H_2O(v)) was measured with pH meter (Orion Model 920A, Boston, MA, USA) and extractable iron concentration was measured as follows: Ten grams of each soil sample were weighed into 50 mL polystyrene centrifuge tube and extracted with 20 mL extractant consisting of 0.005 M DTPA (Diethylenetriaminepentaacetic acid), 0.1 M triethanolamine, and 0.01 M $CaCl_2$, with a pH of 7.3. The soil suspension was shaken for 2 h, filtered through 0.45 μm filter paper and the iron concentration measured on an inductively coupled plasma spectrophotometer (Perkin-Elmer, Norwalk, CT, USA). Kinetic equations were employed to describe the rate of metolachlor degradation and the half life ($t_{1/2}$), which is time elapsed to degrade half of the initial metolachlor, was calculated using the rate constant. All treatments were run in triplicate. Statistical significance was analyzed using SAS (SAS Institute Inc. Cary, NC, USA, version 9.1) by comparing r^2 values and using one-way ANOVA to compare half-life among treatments. Fisher's LSD test at $p < 0.05$ was used to compare half-life among treatments.

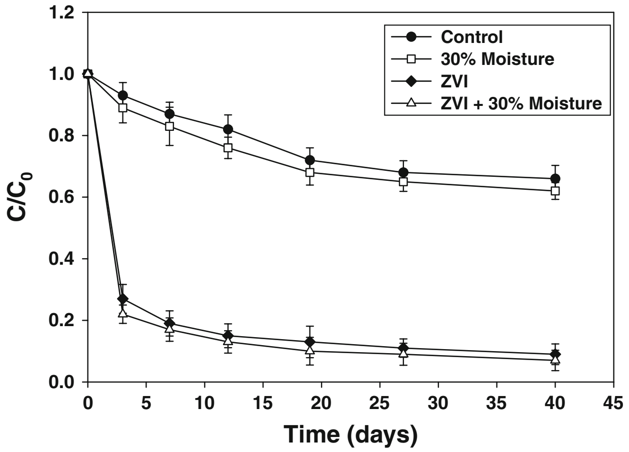


Fig. 1 Kinetics of metolachlor degradation in soil treated with zero-valent iron (ZVI) and moisture. The moisture content for control was 10%. C_0 and C are metolachlor concentration at the initial and at incubation time, respectively, and *bar* on data indicates the standard deviation

Results and Discussion

The combined effects of ZVI and moisture content on metolachlor degradation are shown in Fig. 1. When the soil was treated with water only, 34% and 38% of metolachlor in soil was degraded after 40 days at 10% and 30% moisture levels, respectively. When the metolachlor-treated soil was treated with ZVI alone, 91% of metolachlor was degraded after 40 days, while contaminated soils receiving both ZVI (5%, w/w) and 30% moisture showed only a slightly better 93% metolachlor degradation. This result suggests that the degradation of metolachlor in soil was greatly enhanced by ZVI treatment, while the effect of moisture was not significant (Table 3). The kinetics for metolachlor degradation by ZVI treatment was rapid showing 75–80% loss within 3 days, followed by slower degradation kinetics (Fig. 1). Kim et al. (2007) reported that metolachlor was completely degraded in 72 and 48 h by the unannealed and annealed ZVI in aqueous solution, respectively, yielding two metolachlor degradation by-products, which were identified as dechlorinated metolachlor ($C_{13}H_{18}NO$) and dealkylated-dechlorinated metolachlor ($C_{12}H_{17}NO$).

Dissipation of metolachlor is divided into two kinetics depending on treatments. When ZVI was treated alone or combined with other treatments, dissipation generally followed bi-phasic kinetics while first-order kinetics was observed without ZVI treatment. The pertinent kinetic parameters, including rate constants, are shown in Table 3. Half-lives ($t_{1/2}$) of metolachlor degradation in each

Table 3 Rate constants and half-lives for metolachlor degradation by treatments of moisture, organic compost, and zero-valent iron (ZVI)

Treatments	Rate constants (k or k_1 and k_2)[a]	r^2	$t_{1/2}$ (day)[†]
10% water (control)	9.6×10^{-3}	0.90***	72.2a
30% water	9.8×10^{-3}	0.90***	70.7a
ZVI	4.4×10^{-1}, 2.2×10^{-2}	0.96***, 0.89**	1.6c
ZVI + 30% water	5.0×10^{-1}, 2.5×10^{-2}	0.94***, 0.92***	1.4c
Compost-10 ton ha^{-1} + 30% water	1.1×10^{-2}	0.96***	63.0b
Compost-30 ton ha^{-1} + 30% water	1.2×10^{-2}	0.94***	61.8b
ZVI + compost-10 ton ha^{-1} + 30% water	4.4×10^{-1}, 2.5×10^{-2}	0.96***, 0.95***	1.4c
ZVI + compost-30 ton ha^{-1} + 30% water	6.1×10^{-1}, 5.6×10^{-2}	0.98***, 0.97***	1.1c

*** Significant at $p < 0.01$

** Significant at $p < 0.05$

[†] Same letters represent that half-life of each treatment is not statistically different at $p < 0.05$. In case of bi-phasic first order kinetics, half life was calculated based on first phase

[a] k for single first-order rate constant, and k_1 and k_2 for bi-phasic rate constants

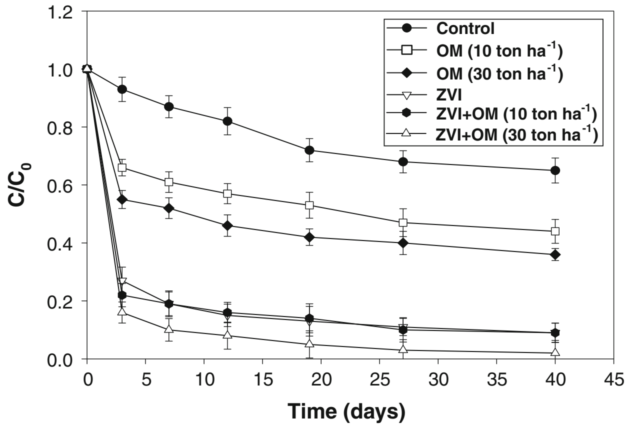


Fig. 2 Kinetics of metolachlor degradation in soil treated with zero-valent iron (ZVI) and organic matter (OM) as compost. C_0 and C are metolachlor concentration at the initial and at incubation time, respectively, and *bar* on data indicates the standard deviation

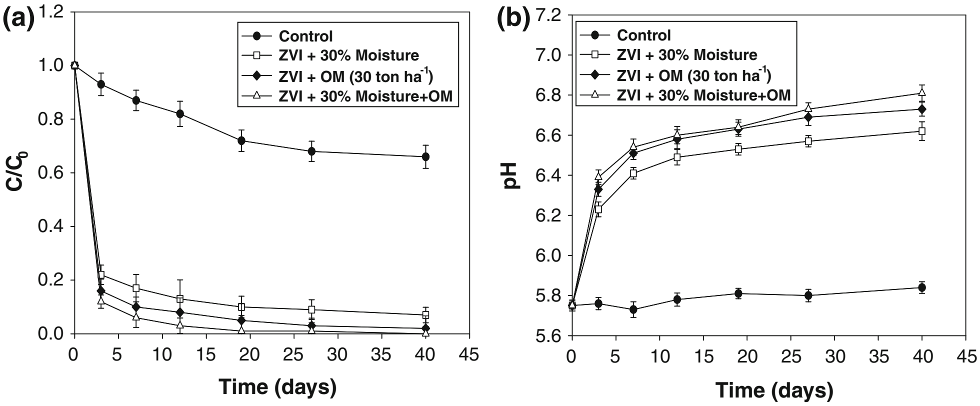
treatment were 72 and 70 days for 10% and 30% moisture levels, 1.6 and 1.4 days for ZVI and ZVI + 30% moisture treatment, respectively. Although the effect of moisture content on degradation of the chlorinated organic contaminants was not significant, moisture can act as a catalyst to increase ionization and activation of ZVI and affect biodegradation by controlling microbial activity (Aga and Thurman 2001).

Degradation of metolachlor in soil with compost amendment and ZVI is shown in Fig. 2. As the content of amended compost was increased from 10 to 30 ton ha^{-1} without ZVI treatment, metolachlor degradation, as compared to the control (10% water only), increased from 27% to 38% at 3 days, followed by an increase from 21% to 29% after 40 days. Organic amendment may increase degradation of organic pollutants because an increase in dissolved organic fraction of compost could complex with the organic pollutants (Rouchaud et al. 1994). Metolachlor degradation of ZVI combined with compost at 10 ton ha^{-1} was consistent with ZVI alone, which was 81% degradation of metolachlor at 3 days and 91% at 40 days. When 30 ton ha^{-1} of compost and ZVI were used (along with 30% moisture), metolachlor degradation was 90% at 3 days and 98% at 40 days. Delgato-Moreno and Pena (2007) showed accelerated degradation of sulfonylurea herbicide in soil amended with olive cake as an organic amendment and concluded that, depending on chemical species, organic pollutants can be degraded in soil via microbial breakdown or chemical hydrolysis or a combination of the two. During abiotic processes, soil constituents, such as mineral and organic components, play a catalytic role in degradation of organic pollutants (Delgado-Moreno and Pena 2007).

Soil is a complex structure in which organic and inorganic substances exist in association with mineral colloids and thus both aerobic and anaerobic conditions generally exist at various microcosms within the soil. Organic matter might thus enhance ZVI effects on metolachlor degradation by creating anaerobic soil conditions at microsites. Organic matter is also an electron mediator, which transports electrons from the iron as an electron donor to the bound organic contaminants as an electron acceptor and promotes fast reduction of organic contaminants in soils (Weber 1996). Therefore, adding organic amendments with ZVI can increase electron transport rates between iron and organic contaminants.

The half-life ($t_{1/2}$) of metolachlor degradation at (ZVI + 30 ton ha^{-1} compost) treatment was 1.1 days, which was faster than that at ZVI treatment only and 98% faster than that of the control (Table 3). The $t_{1/2}$ value with compost at 30 ton ha^{-1} decreased about 12% as compared to that of the control. This result shows that compost

Fig. 3 Efficiency of the combined treatment of zero-valent iron (ZVI), moisture (30%) and organic matter (OM) amendments on **a** the metolachlor degradation and **b** temporal changes of pH at the respective treatments. C_0 and C are metolachlor concentration at the initial and at incubation time, respectively, and *bar* on data indicates the standard deviation



coupled with ZVI can significantly exert a synergistic effect on the degradation of metolachlor in soil.

A germination test using lettuce (*Lactuca sativa*) and crabgrass (*Digitaria sanguinalis* L. Scop.) showed that germination and growth of plants were severely inhibited in metolachlor-contaminated soils, whereas normal germination and growth occurred in ZVI-treated soils (data not shown).

Figure 3 shows the metolachlor degradation efficiencies for different treatments along with the related pH increases. Higher efficiency of metolachlor degradation followed the sequence of (ZVI + 30% moisture + OM) > (ZVI + OM) > (ZVI + 30% moisture) treatments after 40 days. The pH increases coincided with the degradation efficiencies, showing the highest final pH of 6.81 at ZVI + 30% moisture + OM treatment, followed by pH of 6.73 at ZVI + OM, and pH of 6.62 at ZVI + 30% moisture treatment. This result verifies the hypothesis that pH is increased as degradation efficiency is increased, as shown previously in studies with metolachlor and alachlor by Shea et al. (2004).

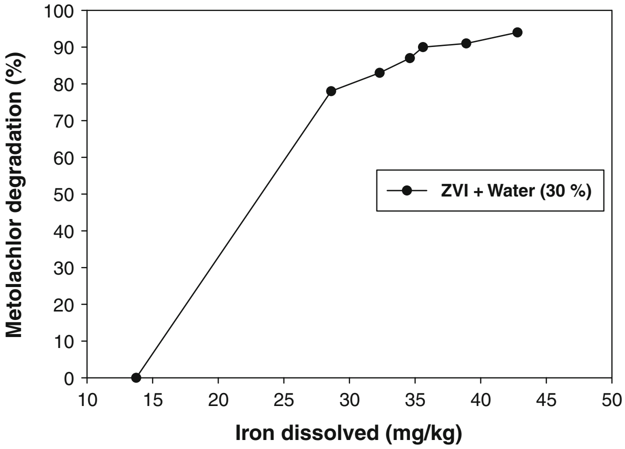


Fig. 4 Relationship between metolachlor degradation efficiency and temporal changes of dissolved iron concentration at ZVI and 30% water treatment

When ZVI (Fe^0) reacts with water or oxygen, it produces Fe^{2+} under anaerobic conditions and Fe^{3+} under aerobic conditions (Satapanajaru et al. 2003a, b). Thus, the relationship between soluble iron concentration and metolachlor concentration can provide indirect evidence for metolachlor degradation efficiency of ZVI in soil. The relationship between the extractable iron concentration and metolachlor degradation for treatment of ZVI and 30% water content is shown in Fig. 4, revealing that the soluble iron concentration increased as metolachlor dechlorination increased. When the soluble iron concentration increased to twice of its initial concentration (13.75 mg kg^{-1}) after 3 days, 75% of metolachlor was already degraded. Following this fast degradation, a gradual increase of iron concentration coincided with the slow degradation rate, as demonstrated in Fig. 1. This result can be attributed to the oxide layer formed on the ZVI surface which reduces its capacity to reduce contaminants. Satapanajaru et al. (2003a) showed that ZVI transforms metolachlor to the dechlorinated product of [*N*-(2-ethyl-6-methylphenyl)acetamide] when metolachlor accepts electrons released from the oxidation of Fe^0 to Fe^{2+} and subsequently to Fe^{3+}. Rapid reduction occurred at the beginning then slowed afterward. The increased pH and Fe concentrations in soil reveal the synergistic effect of ZVI and organic amendments for enhancement of metolachlor degradation.

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