The effects of Soil amendments and Vegetation on Pb mobility in contaminated Shooting range Soils

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Abstract

The use of readily available soil amendments to immobilize Pb is a cost effective way to reduce lead mobility. This study evaluated the effects of two soil amendments (lime and phosphate rock) and vegetation on mobility of Pb in contaminated shooting range soils. St Augustine grass (Stenotaphrum secundatum) was planted in shooting range soils amended with either 5% phosphate rock (PR) or lime for ten months with un-vegetated soils serving as the control. Both lime and PR application reduced plant biomass of St Augustine grass suggesting that the application level of both soil amendments was excessive. The effectiveness of both soil amendments was reduced in a calcareous soil probably due to high calcium content of both soil amendments. Lime reduced the leaching of Pb more effectively than PR though vegetation enhanced the effectiveness of the PR treatment. Vegetation reduced leaching of Pb but increased water-soluble Pb in the soil with a few exceptions. Despite the pH limitation, PR was more effective at reducing water-soluble Pb and plant Pb uptake than lime. PR in combination with vegetation (grasses) is recommended for Pb immobilization in shooting range soils with low pH and low Ca content.

Keywords: Pb, Shooting ranges, Phosphate rock, Lime, St. Augustine grass, Immobilization.

Introduction

Soil contamination with lead is a public health concern worldwide due to its deleterious effect on human health and soil quality[1]. The U.S. Geological Survey has reported that shooting ranges are an important source of Pb contamination[2]. Conventional physical and chemical remediation methods like excavation, soil washing, electrokinetic remediation, vitrification are costly, disruptive and not sustainable[3]. A cost effective way to prevent and minimize lead migration in contaminated soils is through its in-situ immobilization. Immobilization using soil amendments reduce Pb bioavailability in the soil as opposed to soil extraction methods which increase mobility[4-9].

Lime has been used as a soil amendment in metal contaminated soils because it increases soil pH which reduces the mobility of metals[10-13]. However, it was reported that liming with calcium carbonate did not reduce the mobility of Pb in a shooting range soil while addition to an un-vegetated soil enhanced leaching of Pb[14]. A scientist conducted a study because he thought this inconsistency might be due to experimental approaches and found that the addition of lime reduced leaching of Pb in an open system while it increased leaching in a closed system[15]. Another study reported that though total soil Pb in the sand berm decreased when lime was added, it increased water-soluble Pb in some cases[16].

Lead is also effectively immobilized by addition of locally available phosphate sources like hydroxyapatite and phosphate rock[17-18]. Florida phosphate rock (PR) was able to reduce Pb mobility by 22 to 100% in aqueous solutions from 13 Pb-contaminated soils[19]. Though a lot of work has been done on liming in agricultural systems, very few have investigated the effect of liming in shooting ranges with vegetation. There has also been no greenhouse treatability study to evaluate the effect of direct application of PR in contaminated shooting range soils with vegetation. This is important because most of the shooting ranges are vegetated with grasses. This is the first study to look into direct application of PR in shooting ranges with vegetation. The objective of this study is to determine the effect of two soil amendments (lime & PR) and vegetation on Pb mobility in two shooting range soils contaminated with Pb.

Materials and method

Soil characterization: The soils used in this experiment were collected from the mid-berms of two shooting ranges in Florida (SR1 and SR3) at 100 and 200 yds from firing stand respectively. SR 1 has been in operation for 6 years and SR 3 for 30 years. The soils collected were air-dried, sieved and analyzed for particle size distribution, total Pb, organic carbon, oxalate-Fe, cation exchange capacity (CEC) and soil pH[20].

Greenhouse Study: Shooting range soil of 3.0 kg was

thoroughly mixed with either 5% lime or 5% phosphate rock (PR) in a plastic pot with a base diameter of 7.0 in and height 3.0. The soils were incubated with water one week before the grasses were planted. St Augustine grass (*Stenotaphrum secundatum*) was then planted with three plugs in each pot.

A petri dish was placed under each pot to collect potential leachates during the experiment. The plants were grown in the greenhouse where the average temperature ranged from 14 (night) to 30°C (day), with an average photo synthetically photo active radiation of 825 μmol $m^{-2}s^{-1}$. The vegetated and un-vegetated pots were watered thrice a week with 400mL of water during the summer and twice/once a week during the cold days.

The height of the grass was measured and biomass of harvested grass was determined before a portion of it (15g) was recycled (returned to the soil). The soils were leached with water after plant samples (grass cuttings) and soil samples were taken, one month after planting (1MAP) and thereafter bimonthly. The grass was harvested ten months after planting (10MAP), separated into shoots and roots and weighed to determine their fresh and dry biomass.

Fresh plant samples were rinsed, dried in the oven for three days at 65°C and later ground in a mill. Soil samples were air-dried and analyzed for soil pH, water-soluble and total Pb; leachate collected was analyzed for Pb, pH, dissolved organic carbon (DOC) while plant samples were analyzed for total Pb.

Sample Analysis: Soil and plant samples were digested with nitric acid and hydrogen peroxide using the Hot Block Digestion System (Environmental Express, Mt. Pleasant, SC; EPA Method 3050a). Water-soluble lead was determined in a soil:solution of 1:5 after shaking for one hour, centrifuged and then filtered through 0.2μm membrane filter. Total Pb contents of soil/plant digest; filtrate and leachates were analyzed on a flame atomic absorption spectrophotometer. Dissolved organic carbon in leachates from soils was analyzed using a total organic carbon analyzer (TOC-5050 A, Shimadzu Corporation, Japan). Leachate pH was measured using a pH meter. All chemical analyses were performed using QA/QC in a NELAC-certified Laboratory at University of Florida. Standard soil reference materials from the National Institute of Science and Technology (NIST, Gaithersburg, MD) were used to assess method accuracy.

Statistical analysis: The experiment is a 2 x 3 x 2 x 3 factorial with two shooting range soils; three treatments control, lime, PR; two vegetation types (vegetated and unvegetated) each with three replications arranged in a completely randomized design. Treatment effects were determined by analysis of variance (ANOVA). Linear correlation coefficients were also computed for various parameters.

Results and Discussion

Selected soil properties: Though SR 3 has been in operation for a longer period of time (30yrs), it had a lower total soil Pb (Table-1) than SR 1 which has only been in operation for 6 years. This may be due to differences in site properties such as soil properties, shooting types and use pattern[21]. Higher organic matter and lower soil pH of SR1 soil may lead to a higher rate of weathering of bullets in the soil while lower CEC and lower oxalate Fe in SR 3 soil could indicate lower retention of Pb[22].

Table-1
Selected Soil Characteristics of shooting range soils

	SR 1	SR 3
Total Pb (mg/kg)	12,689 ± 347	10,068 ±234
Soil pH	6.11 ± 0.15	6.68 ± 0.25
CEC [Cmolc/Kg]	24.8 ± 0.23	8.34 ± 0.48
Ox-Fe (mg/kg)	959 ± 92	379 ± 34
Ox-Al (mg/kg)	278 ± 21	219 ± 23
OM (%)	1.01 ± 0.05	0.67 ± 0.03
Total Ca (mg/kg)	1829 ± 45	152 ± 13
% sand	86.6	88.0
% silt	9.46	7.07
% clay	3.93	4.96

CEC-cation exchange capacity; Ox-oxalate; OM-organic matter; SR-shooting range

Lime was more effective than PR at reducing leaching of Pb: The addition of both lime and PR reduced the leaching of Pb in both shooting range soils (Table-2). This is consistent with previous studies [23-24]. Liming in particular increased dissolved organic carbon (DOC) substantially in leachates from all soils and also increased leachate pH except in un-vegetated soils of SR1 treated with lime. This is consistent with a previous study that reported that lime increased pH and DOC but reduced the leaching of Pb[15].

There was a 41% to 89% reduction in Pb leached in lime treated soils and a 26% to 63% reduction in PR treated soils. Lime reduced leaching of Pb more effectively than PR except in vegetated SR1 soils treated with PR. The lower effectiveness of PR must be due to the high soil pH of both shooting ranges because soil pH above 6 is unfavorable for PR dissolution and effectiveness[2,19]. However, the effectiveness of both soil amendments to reduce leaching of Pb was higher in SR3 than SR1 except in vegetated PR treated soils probably because the high calcium content of the SR1 soil (Table 1) could have hindered dissolution of the soil amendments especially lime.

Table-2
Effect of soil amendments and vegetation on leachate Pb and DOC

	SR 1		SR3	
	Total Pb leached (mg/L)			
	Vegetated	*Unvegetated*	*Vegetated*	*Unvegetated*
Control	7.15±0.14	15.5±0.20	26.4±0.20	35.1±0.23
Lime	4.21±0.07	5.92±0.05	2.91±0.05	4.33 ±0.01
PR	2.67±0.03	11.4±0.01	17.8 ±0.18	17.4±0.06
	Total DOC (mg/L)			
Control	156±15.6	130±3.15	96.8±1.8	129±13.2
Lime	192±12.6	144±4.81	266 ±15.8	240±21.5
PR	170±17	120±12.9	131±8.93	131±29.9

DOC: Dissolved organic carbon, SR-shooting range, PR-phosphate rock

Vegetation enhanced the effectiveness of PR to reduce leaching of Pb: Vegetation reduced total Pb leached (Table-2) in both shooting range soils except in PR treated SR3 soil which had the same amount of total Pb leached in vegetated and un-vegetated soils. Lime had about the same effectiveness in vegetated and un-vegetated SR3 soil with an 89% reduction in vegetated soil and 88% reduction in un-vegetated soil. However, there was a higher reduction of Pb leached in vegetated soils treated with PR than vegetated soils treated with lime in SR1 soil.

The presence of vegetation enhanced the effectiveness of PR in SR1 probably due to acidifying effect of plants in the soil. An increase in soil acidity has been reported to enable steady and increasing dissolution rate of the phosphate rock (PR) by enhancing neutralization of the hydroxide ions released from the hydrolysis of the PR[25]. We observed an increase in leachate Pb (Figure-a and b) from control and un-vegetated SR1 soils with both soil amendments and PR treated SR3 soils at 5MAP which could be caused by a sharp decrease in leachate pH (Figure-2a and b). This decrease in pH could be caused by microbial activity in un-vegetated soils and root exudation in vegetated soils. The lowest leachate pH at 5MAP was recorded in vegetated soils treated with PR in both shooting ranges.

The leachate pH from vegetated soils was lower than un-vegetated soils showing that the presence of vegetation has an acidifying effect. We observed a drastic decrease in leachate pH (Figure-2 a and b) at 5MAP after which the leachate pH increased. It seems that the decrease in pH led to increased weathering which caused the increase in leachate pH. It has been reported that the weathering of Pb could result to an increase in soil pH of shooting range soils [22].

Generally, vegetation increased water-soluble Pb in both shooting range soils with a few exceptions. This may be due to increase in organic matter content of the soils with recycling of grass cuttings. Increasing organic matter increases weathering of the lead bullets or metallic fragments in the shooting range soil thereby increasing water-soluble Pb[22].

PR reduced water-soluble Pb and Plant Pb Uptake more effectively than lime: The addition of both soil amendments consistently reduced water-soluble Pb in both shooting range soils (Figure-3a, b, d) through the ten months of planting except in vegetated SR3 soils (Figure-3c). This is consistent with previous studies that reported that both soil amendments (lime and PR) reduced Pb mobility in the soil[26,18]. It has been reported that direct application of PR can effectively immobilize Pb in aqueous solution though its effectiveness was limited by soil pH[18-19]. In this study, despite the pH limitations, PR effectively reduced water-soluble Pb in both shooting range soils. PR was even more effective than lime in both shooting ranges with a few exceptions. This is consistent with the report of that P treatment was more effective than cement or quicklime with a faster Pb immobilization process[27].

There was a higher reduction in plant Pb uptake (Table-3) in PR treated soils than lime treated soils except in the shoot Pb of grasses in SR3 soil. This does not agree with a previous study that reported that P addidtion increased metal uptake in the roots of St. Augustine grass (*Stenotaphrum secundatum*)[4]. In their study, P addition also significantly reduced Pb translocation from root to shoot via formation of an insoluble Pb mineral (pyromorphite) on the root membrane[4]. Our results are quite different and this may be because an acid was added to the PR in their study which increased metal uptake in the roots. It could

also be due to differences in the source of Pb contamination because we used a shooting range soil while they used a metal contaminated site (site previously used as gasoline station, salvage yard, auto body shop, and recycling of lead batteries) for their study.

Plant biomass of grasses in treated soils were lower than control soils: The total plant biomass (Table-3) of St Augustine grass was higher in control soils than in lime and PR amended soils probably due to over-liming. The level of application of lime and PR may be excessive for both shooting range soils which were not strongly acidic before the experiment. The impact of over-liming was highest in limed SR3 which had 41% lower plant biomass than the control probably because it had the highest soil pH. Metal availability decreases with increasing soil pH while molybdenum availability increases with increasing soil pH due to an increase in surface negative charge.
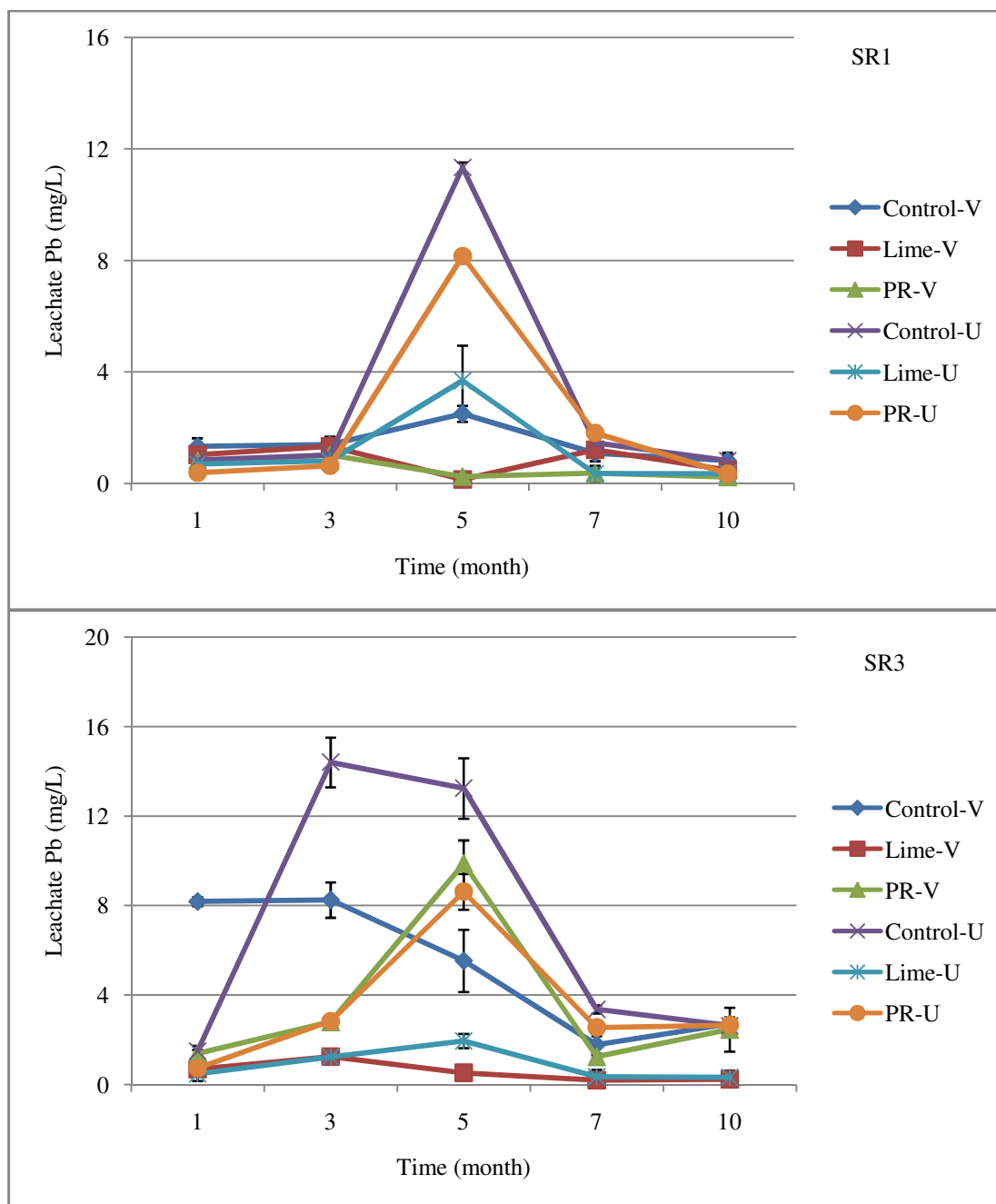

Figure-1
Effect of lime and phosphate rock (PR) on Pb leached from shooting range soils (A-SR1, B-SR3). V-vegetated, U-unvegetated

Since most micronutrients are metals, an increase in soil pH decreases the availability of micronutrients. Over-liming can induce micronutrient deficiency, P deficiency, decrease Zn solubility and cause molybdenum toxicity[28]. Lime has been shown to be most effective in extremely acidic soils with very high available Pb concentrations[29]. Past research has also reported that liming resulted in K, P and Al imbalances suggesting that liming acidic soils could intensify nutrient deficiencies[30]. Incorrect use of lime fertilizer can cause changes in calcium to magnesium ratio and potassium to magnesium ratios which can affect crop yields[31].
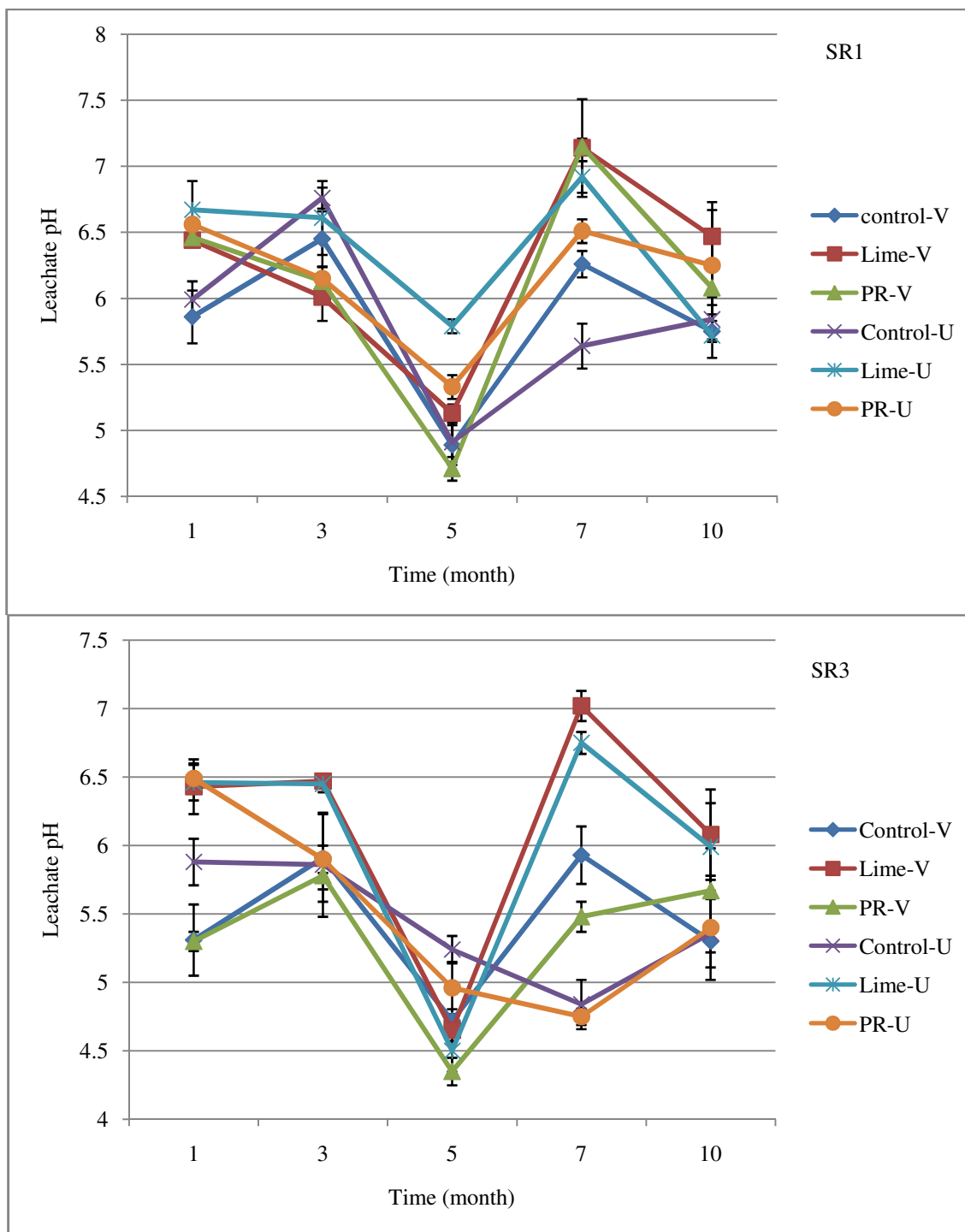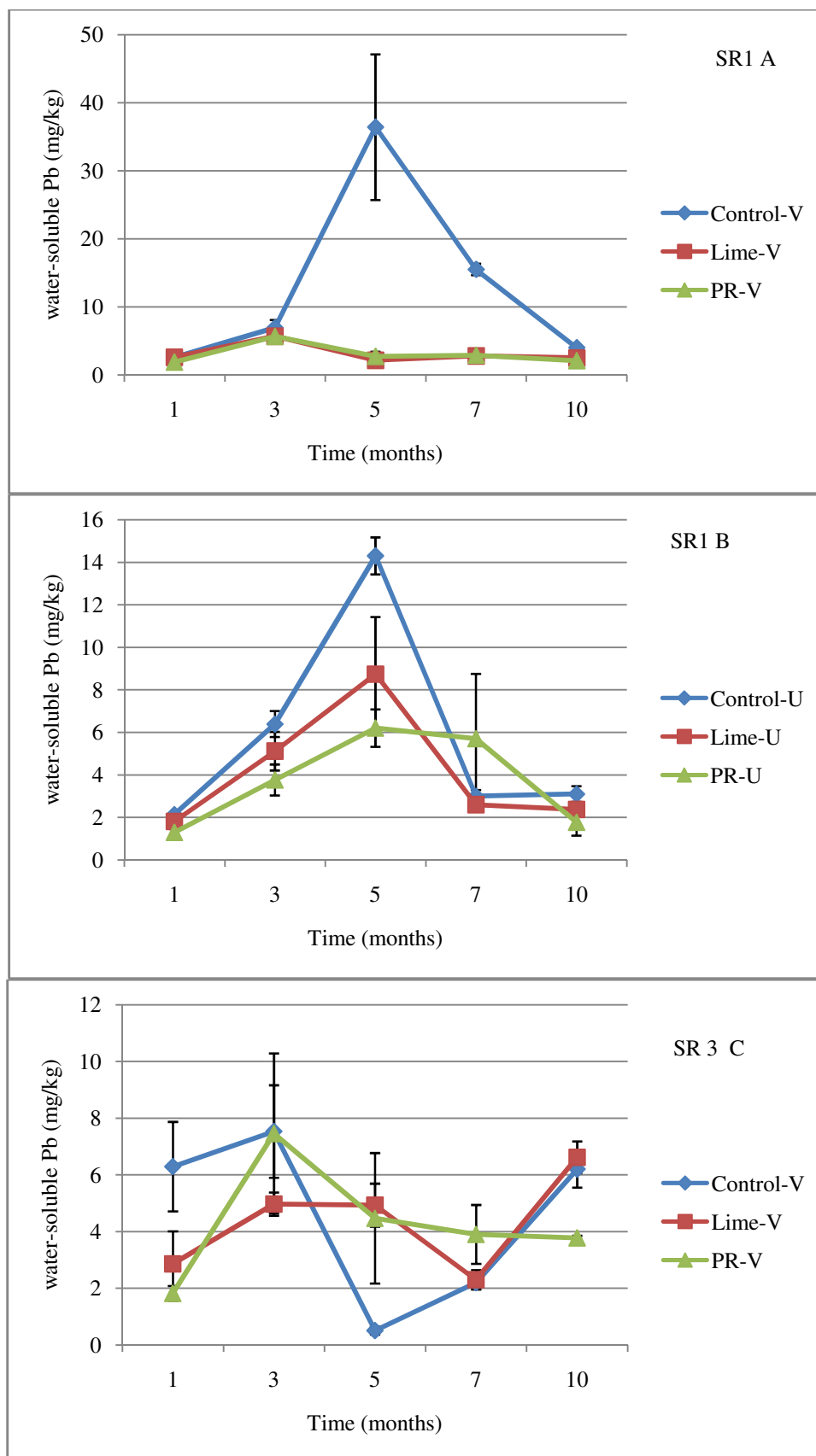

Figure-2
Effect of lime and phosphate rock (PR) on leachate pH of shooting range soils (A-SR1, B-SR3). V-vegetated, U-unvegetated
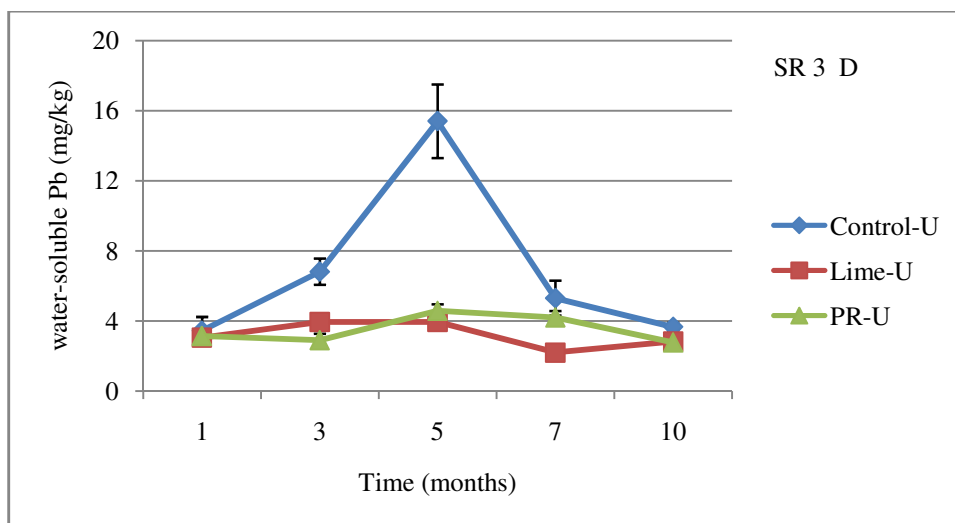
Figure-3
Effect of lime and phosphate rock (PR) on water-soluble Pb of shooting range soils (A-vegetated SR1, B-unvegetated SR1, C-vegetated SR3 soils, D-unvegetated SR3). V-vegetated, U-unvegetated
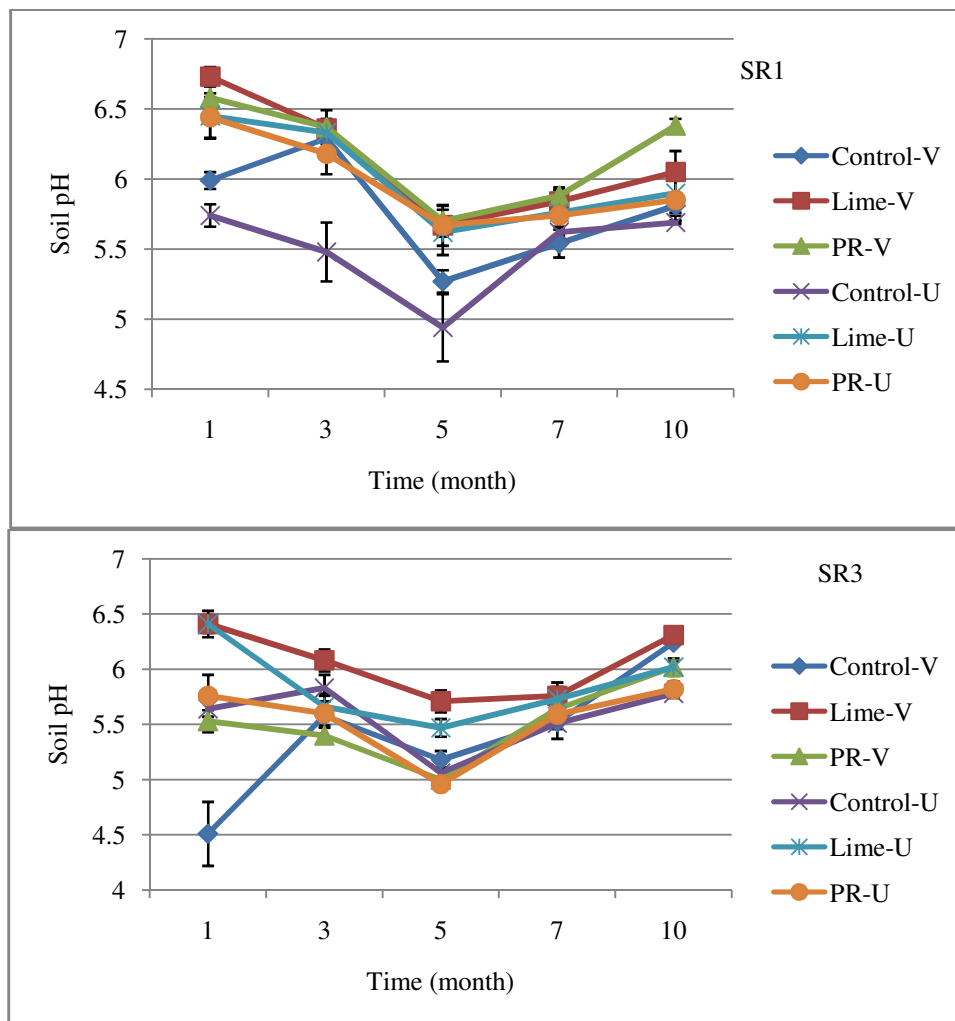

Figure-4
Effect of lime and phosphate rock (PR) on soil pH of shooting range soils (A-SR1, B-SR3). V-vegetated, U-unvegetated

Table-3
Plant Pb uptake and plant biomass of St Augustine grass at 10MAP

	SR 1			SR 3		
	Shoot	**Root**	**Total**	**Shoot**	**Root**	**Total**
Plant Pb Uptake (mg/kg)						
Control	301 ± 10.4	4158 ± 1065	4459	309 ± 10.9	3269 ± 2867	3578
Lime	275 ± 2.0	1935 ± 679	2210	125 ± 2.4	1223 ± 619	1348
PR	217 ± 15.6	1398 ± 162	1615	227 ± 12.8	902 ± 351	1129
Plant Biomass(g)						
Control	209±19.3	806±94.1	1015	217±19.9	956±105	1173
Lime	221±14.6	750±68.1	971	210±14.6	562±123	772
PR	214±16.6	734±59.1	948	233±4.53	703±148	936

SR-shooting range, MAP-months after planting

Conclusion

Lime was more effective than PR at reducing leaching of Pb probably due to higher production of DOC by lime and pH limitations for PR. However, the presence of vegetation enhanced the efficiency of PR to reduce leaching of Pb. Generally, the presence of vegetation reduced the leaching of Pb though it increased water-soluble Pb with a few exceptions. Despite pH limitations, PR reduced water-soluble and plant Pb uptake more efficiently than lime in both shooting range soils. Soil amendments reduced plant biomass of St. Augustine grass probably due to excessive application. A combination of PR treatment and vegetation may be best for immobilization of Pb in shooting range soils.

Acknowledgement

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