



Beneficial Use of Scrap Tires for Retardation of Pesticide Movement in Golf Courses

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Abstract

Tire rubber has been found to adsorb pesticides and nitrate, and remove phosphorus by precipitation with iron released from steel wire. Golf courses are known to release pesticides and nutrients such as nitrogen and phosphorous. The feasibility of using tire rubber as an adsorbent for pesticides in golf courses was evaluated using statistical and mathematical methods. Empirical equations were proposed to predict the required tire rubber layer thickness to remove various pesticides under different conditions. It was found that a 20 cm thick tire rubber layer was capable of removing $\geq 90\%$ for 37 out of 51 pesticides. Three of the 51 pesticides required a >200 cm thick tire rubber layer, yet had high solubility and short half-life. By using scrap tires for the mitigation of pesticides and fertilizers, golf courses may be able to realize the dual benefits of waste utilization and reduced environmental contamination.

Keywords: Adsorption; Fertilizers; Golf course; Ground rubber; Pesticides; Scraps tires

Introduction

In 2007, 303 million scrap tires were generated in the United States (US) [1]. Tire-derived fuel (TDF) accounts for 54% of the recovered tires, followed by ground rubber (17%) and civil engineering applications (12%) such as subgrade fill and embankment, backfill for walls and bridge abutments, subgrade insulation for roads, landfills, septic system drain fields, etc. The total recycling rate of tires in 2011 is 44.6% [2]. Thus, more effort should be made to improve the recycling rate of tires. Tire chips are not a hazardous waste [3,4]. The concentrations of metals leaching from tire chips were all below the National Primary Drinking Water Regulation maximum contaminant levels (MCLs) [5] although the concentrations of iron and manganese exceeded MCLs of the National Secondary Drinking Water Regulation that is the guidance for nuisance chemicals especially at low pH [3,6,7]. Volatile and semi-volatile organic compounds leached from tire chips located above the water table were below detection limits but those below the water table were detectable at trace levels [3,8,9]. Studies on leachate from crumb rubber showed no deleterious effects to the environment [10,11].

Styrene-butadiene co-polymer (SBR) gaskets used as drinking water pipe joint seal were found to adsorb large quantities of organic compounds [12,13]. SBR gaskets have the similar composition to tire rubber (70% SBR, 15% steel, and 15% textile fiber for car tire [14]). Therefore, tire rubber has been proposed to use as an adsorbent in vapor phase [15], in aqueous phase [16,17], and in slurry cut-off walls [18]. Kim et al. [17] found that ground rubber had 1.1~4.4% of volatile organic compound sorption capacity of granular activated carbon. Park et al. [19] confirmed that tire chips in field cell tests significantly adsorbed arsenic, cobalt, lead, nickel, and gasoline components. Gupta et al. [20] found $\geq 95\%$ nickel removal by scrap tire.

Ground rubber mixed with compost was able to remove hydrogen sulfide effectively even at -30°C whereas a wood-chip packed biofilter failed at this temperature [21]. Wang [22] also found removal of hydrogen sulfide by tire derived rubber particles. Tire rubber was proposed to remove nitrate in fertilizer leaching from golf course putting greens [23]. Park et al. [19] concluded that although tire rubber leaches a few heavy metals and organic compounds, tire rubber is capable of adsorbing toxic organic and inorganic compounds when

the concentrations in the surrounding environment are high. Previous studies strongly indicate that tire rubber can be a good material for removing toxic contaminants while recycling scrap tires. It was also found that the constructed wetlands packed with shredded steel-belted tire had 17 to 60% increases in the phosphorus removal efficiency [24] and almost twice as much [25] compared with the wetlands packed with gravel.

Scrap tire chips and ground rubber have been successfully used in a number of civil engineering applications. Scrap tires have been proposed and used for lightweight fill for embankments and retaining walls [26-30], drainage layers for roads and septic tank leach fields [31], and drainage and filter layers in landfills [19]. In nearly half of Organization of Economic Cooperation and Development (OECD) countries, nutrient and pesticide concentrations in surface and groundwater in agricultural areas exceed national recommended limits for drinking water standards [32]. Golf courses use pesticides and fertilizers to provide a healthy playing condition for the game. Cohen et al. [33] claimed that widespread and/or repeated water quality impacts by golf courses did not occur at 36 golf courses studied. Snow [34] stated that nitrogen leaching amounted to 1% to 8% and pesticide leaching was up to 18%. Köck-Schulmeyer et al. [35] found considerably high concentrations of pesticides in raw wastewaters (up to 684 ng/L for diazinon) and their persistence in the treated waters after conventional secondary (and even tertiary) wastewater treatment, indicating widespread pollution and persistency of pesticides. King et al. [36] found that the turfgrass environment contributed increased nitrate/nitrite and phosphorus loads to nearby streams. Swancar [37] detected pesticides at trace levels (45% of all occurrences) and under the maximum contaminant levels (92% of all occurrences)

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in groundwater on seven of nine golf courses studied in Florida and in 52% of the samples. In six occurrences, concentrations of arsenic, bentazon, or acephate in groundwater were above the MCLs or guidance concentration. Atrazine, bromacil, diazinon, diuron, fenamiphos, metalaxyl, oxydiazon, and simazine were detected at least at one site. Kearns and Prior [38] claimed that the most regularly used pesticides leached readily in soil and were found in groundwater samples in Northern Ireland. The majority of compounds applied are listed as being toxic to wildlife with some also being very toxic to the aquatic environment and having adverse effect to human health.

Li et al. [39] found that chlorothalonil and phosfolan-methyl from golf courses influenced the surrounding water environment greatly, chemical oxygen demand (COD_{cr}) reached a maximum concentration of 122 mg/L, and total nitrogen was up to 17.8 mg/L, exceeding the surface water environment quality standards of grade V in China. Haith [40] stated that five of the 37 pesticides resulted in potential acute risk to invertebrates and fish or algae when applied at label rates on lawns, fairways, or greens. The impact to the surrounding environment was often claimed to be minimal if pesticides are applied carefully to golf courses. However, greater levels of safety and reliability could be achieved by implementing active pollutant-control measures. In this sense, tire rubber may be used in golf courses to mitigate the release of pesticides and fertilizers to the surrounding environment.

The objectives of this study were to evaluate the feasibility of using tire chips and ground tires in tees, fairways, and greens in various methods and determine the optimum tire rubber thicknesses for removals of pesticides. Statistical analysis was performed using published data to determine the relationships among various biological, physical, and chemical properties of pesticides used in golf courses. Empirical equations were developed to assess the pesticide removal efficiency by tire rubber and determine the tire rubber layer thickness. Lastly, recommendations of best practices for the use of scrap tires in golf course construction are included.

Fate and transport of pesticides applied to golf courses

In general, the following six processes affect the fate of chemicals applied to golf courses [41]:

1. Solubilization by water,
2. Sorption by soil mineral and organic matter,
3. Degradation by soil microorganisms,
4. Chemical degradation and photo-decomposition,
5. Volatilization and evaporation,
6. Plant uptake.

The relative importance of each process is controlled by the physicochemical property, temperature, water content, soil type, porosity, and advective transport. The mobility of a chemical in the environment is determined dominantly by the degree of adsorption to soil organic matter. If the soil organic carbon-water partition coefficient, K_{oc} , is high, the chemical tends to have a high affinity to the soil matrix by adsorption.

Transportation of pesticides and fertilizers typically occurs through runoff and leaching. Runoff is frequently caused by a storm event or heavy irrigation and is often the major cause of surface water pollution. Leaching occurs when water infiltrates vertically through the soil and potentially into groundwater. To minimize these chemical transportation modes, a capture layer may be installed along the runoff zone or infiltration zone to help removing pesticides and

fertilizers. Given the high adsorptive capacity of tire rubber, it can be an efficient and cost-effective material for use in these chemical control installations. Park et al. [16] derived the following equation to determine the thickness of a tire rubber layer required to remove a given amount of a chemical:

$$d = 1.00 \times 10^{-5} \times \frac{M_a}{(1-n) \rho_t} \quad (1)$$

where M_a is the required mass of tire rubber per unit area (kg/ha), n is the porosity of the tire rubber layer, and ρ_t is the density of tire rubber, g/cm³. The required mass of tire rubber can be estimated as follows:

$$M_a = \frac{f Q_r t_d \rho_t \times 10^3}{(1-f) K_d} \quad (2)$$

$$K_d = f_{oc} \cdot K_{oc} \quad (3)$$

where f is the fraction of a pesticide to be removed, Q_r is the infiltration rate (m³/ha/yr), t_d is the design life of the tire rubber layer, yrs, K_d is the soil-pesticide partition coefficient (L/kg), f_{oc} is the organic carbon fraction in tire rubber, and K_{oc} is the soil organic carbon-water partition coefficient (L/kg). Using these equations, it is possible to calculate the required thickness of tire rubber layers to prevent the transportation of pesticides and fertilizers through runoff and infiltration.

Relationships among physical/chemical properties of pesticides

Balogh and Walker [42] summarized solubilities (S), soil organic carbon-water partition coefficients (K_{oc}), octanol-water partition coefficients (K_{ow}), degradation rates in the soil root zone (K_d), and half-life ($t_{0.5}$) for various pesticides. Listed were nine insecticides and nematocides, 15 fungicides, and 27 herbicides, totaling 51 pesticides. The logarithmic relationships among S , K_{oc} , K_{ow} , K_d , and $t_{0.5}$ were determined using the values tabulated by Balogh and Walker. If the values were given as a range, the average value was used. After reviewing the properties of 51 pesticides listed, anilazine, benefin, glyphosate acid, glyphosate amine salt, and MSMA sodium salt were excluded from the regression analysis due to inconsistency in chemical and biological properties. The properties of these pesticides are summarized in Table 1.

Organic compounds must be released to solution to be degraded by microorganisms since the biodegradation rate of organic compounds is controlled by bioavailability when the organic compounds have a strong affinity for surfaces in the environment [43]. In this regard, anilazine having a high K_{oc} value of 1,070~3,000 and a short half-life of 0.5~1 is an exceptional outlier and was thus excluded. It is also generally known that the K_{oc} value tends to decrease as solubility increases for an organic compound considering the chemical properties. Thus, glyphosate acid, glyphosate amine salt, and monosodium methyl arsenate (MSMA) sodium salt having both high S and K_{oc} values were also excluded in the regression analysis. The extremely high half-life of 1,000 days for MSMA sodium salt may be due to the presence of arsenic which

Pesticides	Solubility (S), mg/L	K_{oc} , L/kg	Degradation rate (K_d), day ⁻¹	Half-life ($t_{0.5}$), days
Anilazine				
Glyphosate, acid	8.0	1,070~3,000	0.693~1.386	0.5~1
Glyphosate amine salt	12,000	2,640	0.054	44
MSMA sodium salt	900,000	24,000	0.0185	40
	985,000	200,000	0.001	1,000

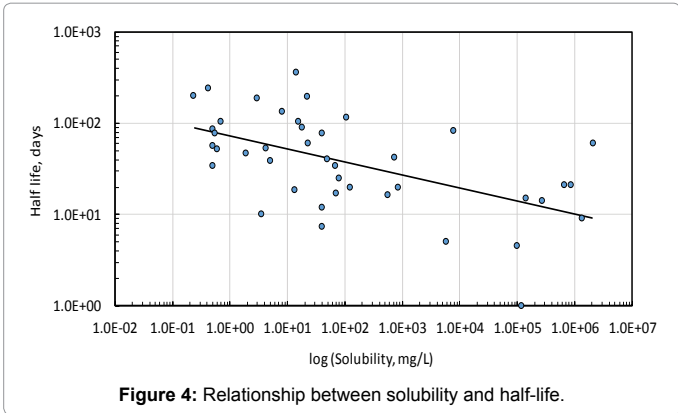
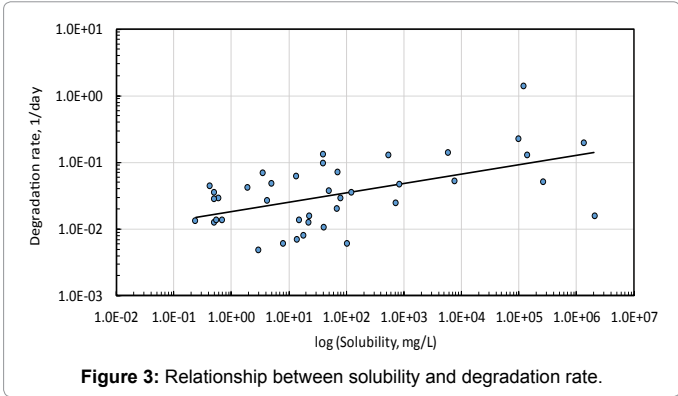
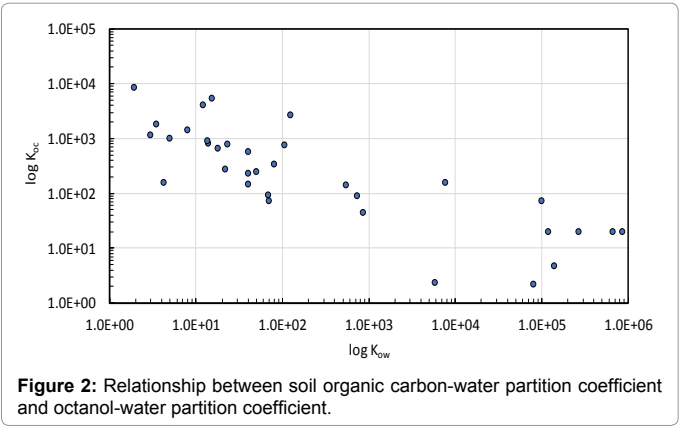
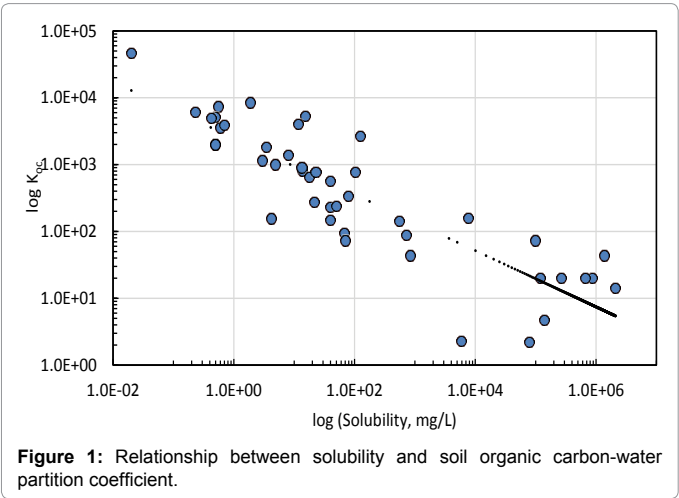
Table 1: Pesticides not included in the regression analysis.

is toxic to microorganisms. Glyphosate, a highly soluble chemical is also readily adsorbed to solids once released. Because of the limited bioavailability by strong adsorption, it also has a low degradation rate. Unlike other pesticides, the main pathway of glyphosate transport is through the movement of fine particles containing glyphosate. This may lead to a potentially high level of contamination once fine particles reach surface water and groundwater.

Figure 1 shows the relationship between K_{oc} and S . As expected, there was a strong correlation with an r^2 value of 0.757. This strong relationship justifies the exclusion of anilazine from regression analysis. Figure 2 shows the relationship between K_{oc} and K_{ow} . Although there were many missing K_{ow} values, the relationship was strong with the r^2 value of 0.878. It is suggested that missing K_{ow} values be determined for pesticides and corrected for the K_{oc} value and subsequent K_d value of specific interest of soil or adsorbent to improve the accuracy of the prediction.

Figure 3 shows the relationship between S and K_s . Figure 4 shows the relationship between S and $t_{0.5}$. The relationship between S and $t_{0.5}$ was slightly better than that between S and K_s . For chemicals that the values of K_s and $t_{0.5}$ are unknown, they can be estimated from the K_{oc} value of a chemical using the relationship shown in Figures 5 and 6, respectively. The regression equations between S and K_{oc} , K_{oc} and K_{ow} , S and K_s , S and $t_{0.5}$, K_{oc} and K_s , and K_{oc} and $t_{0.5}$ are summarized with the r^2 values in Table 2.

Using the regression equations shown in Table 2, it is possible to predict the required tire layer thickness and thus mobility if S or K_{ow} is



Regression equation	r^2	Figures
$\log K_{oc} (L/kg) = 0.421 \log S (mg/L) + 3.396$	0.757	Figure 1
$\log K_{oc} (L/kg) = 0.660 \log K_{ow} + 0.639$	0.878	Figure 2
$\log K_s (days^{-1}) = 0.140 \log S - 1.735$	0.277	Figure 3
$\log t_{0.5} (days) = -0.143 \log S + 1.861$	0.312	Figure 4
$\log K_s (days^{-1}) = -0.276 \log K_{oc} - 0.761$	0.243	Figure 5
$\log t_{0.5} (days) = 0.324 \log K_{oc} + 0.748$	0.327	Figure 6

Table 2: Regression equations with r^2 values for various relationships.

known. If S (mg/L) or K_{ow} value is available, the following equations can be used to predict the required mass of tire rubber per unit area (kg/ha):

$$M_a = \frac{f \cdot Q_r \cdot t_d \cdot \rho_t \times 10^3}{(1-f) \cdot f_{oc} \cdot 10^{0.421 \log S (mg/L) + 3.396}} \quad (4)$$

$$M_a = \frac{f \cdot Q_r \cdot t_d \cdot \rho_t \times 10^3}{(1-f) \cdot f_{oc} \cdot 10^{0.660 \log K_{ow} + 0.639}} \quad (5)$$

Determination of tire rubber layer thickness for pesticide removal

Eqs. (1-5) can be used to determine the thickness of a tire rubber layer required for pesticide removal. The material compositions of car tire (tire chip) and tire rubber (ground rubber) are summarized in Table 3 [44]. From Table 3, it can be assumed that the f_{oc} values of car tire and tire rubber are 0.685 (rubber 47%+carbon black 21.5%) and 0.93 (rubber 62%+carbon black 31%), respectively [45].

Typical values of porosity, n , range from 0.60 to 0.70 for uncompacted tire-derived aggregate (TDA) (size range between 50 mm to 305 mm) [46] and from 0.45 to 0.55 for compacted TDA [47]. The specific gravity of tire rubber ranges between 1.02 and 1.27, with

Type	Rubber	Carbon black	Metal	Textile	Zinc oxide	Sulfur	Additives
Car tire	47%	21.5%	16.5%	5.5%	1%	1%	7.5%
Tire rubber	62%	31%	-	-	2%	1%	4%

Table 3: Material compositions of passenger car tire in the European Union and tire rubber in Canada.

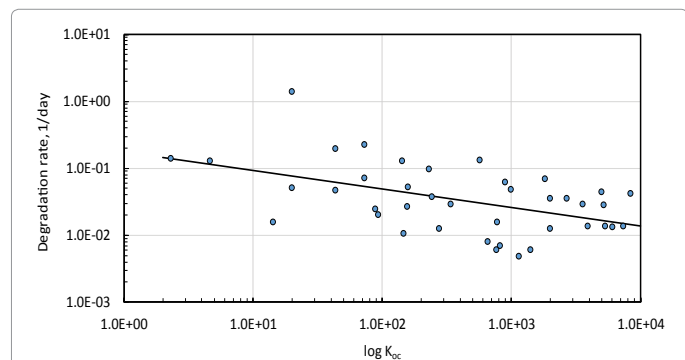


Figure 5: Relationship between soil organic carbon-water partition coefficient and degradation rate.

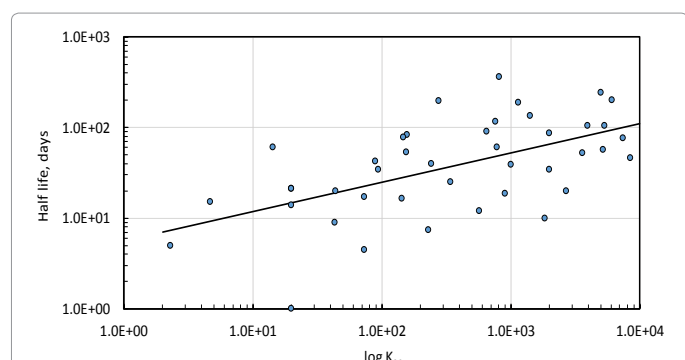


Figure 6: Relationship between soil organic carbon-water partition coefficient and half-life.

higher values corresponding to tire rubber containing steel inclusions [26,48,49]. For a tire rubber layer, assumed were the tire density of 1.2 g/cm³, the porosity of 0.55, and the f_{oc} value of 0.75. The design life was assumed to be five years, within which most pesticides adsorbed would be decomposed or desorbed. From the review of the reported property values for the pesticides, one year was thought to be sufficient for regeneration of tire rubber saturated with pesticides and fertilizers. Thus, a design life of five years provides a significant built-in factor of safety. Assuming a target removal of pesticides of 90% of the initial concentration and an infiltration rate of 2,000 m³/ha/yr, the tire rubber layer thickness was estimated using Eqs (1,2).

Based on the calculated tire rubber layer thicknesses from this study, the pesticides were classified according to the layer thickness range as shown in Table 4. Among 51 pesticides evaluated, 37 pesticides (73%) can be removed with a ≤ 20 cm thick tire rubber layer. As anticipated, the tire rubber layer thickness was linearly proportional to the infiltration rate. Thus, if the infiltration rate is 10,000 m³/ha/yr, a tire rubber layer five times the thickness computed for 2,000 m³/ha/yr is needed.

Runoff losses from Bermuda grass plots treated with 2,4-D, MCP, and dicamba after 2.52 cm rainfall at 24 hours were measured to be 7.2%, 9.6%, and 10.7%, respectively [38]. In Table 4, dicamba, the most

difficult pesticide to remove, needed the thickest tire rubber layer, followed by MCP and 2,4-D among 51 pesticides. Thus, the prediction of the tire rubber layer thickness matched well with the observation made in the field.

It may be impractical to install the tire rubber layer of >200 cm to remove pesticides that are highly mobile. Fortunately, the three pesticides requiring the tire rubber layer >200 cm tend to have relatively shorter half-lives than the pesticides that are readily adsorbed. To meet the requirements of both practicality and functionality, it is recommended that a tire rubber layer of 30~180 cm be used in applications in golf courses. In this recommended thickness range, the most mobile pesticide, dicamba can still be removed by 19~43%.

In sandy areas (soil density of 2.65 g/cm³, f_{oc} of 0.005, and porosity of 0.3), 96.4 times the tire rubber thickness would be required for 90% pesticide removal. This similar finding has been observed in the field [34]. Figure 7 shows the equivalent thickness multiplications to the base tire rubber thickness computed for Table 4. It can be seen that if the organic carbon fraction, f_{oc} is >0.1, the adsorption layer thickness can be significantly reduced. This is due to the adsorption of pesticides onto organic carbon present in tire rubber.

The correction factor was estimated for thickness at removal fractions from 0 to 0.99 and shown in Figure 8. The correction factor was set at 1 for a removal fraction of 0.9. The correction factors for thicknesses at 0.95 and 0.99 were estimated to be 2.1 and 11. It can be seen that the correction factor increases sharply when the removal fraction becomes >0.9. Thus, it would be most practical if the desired removal fraction is ≤ 0.9 .

Sorption of organic compounds onto ground tires was not significantly affected by the presence of other organic or inorganic compounds under the conditions tested [17]. Thus, the layer thickness does not need to be increased for multiple pesticides to be removed. The maximum layer thickness determined for a pesticide should be the design thickness. Since it was found that the effects of pH and temperature on the sorption were insignificant, their effects can be ignored.

With regards to the long-term fate of chemicals in tire rubber layers, only 3.5%~7.9% of organic compounds adsorbed in tire rubber were later desorbed [16]. Thus, when high levels of pesticides enter a tire rubber layer, they are adsorbed on to the tire rubber and subsequently slowly release or degrade, implying slow regeneration of sorption capacity. Furthermore, the partition coefficient after desorption tests were found to be two to 15 times greater than those obtained from sorption tests [16], inferring increased sorption capability. Thus, the assumption that it takes five years for tire rubber to be regenerated may be overly conservative. It is anticipated that the maximum regeneration may occur within less than one year. Granular activated carbon filters in a water treatment plant in Illinois [50], USA were not regenerated or replaced for over ten years, indicating natural regeneration occurring over time.

Practical applications

The impact of pesticides applied in golf courses on the surrounding environment is minimal if the proper pesticide application procedure is employed and the best management practices are implemented. However, if there is an environmentally sensitive area or the golf course is to be constructed and managed to the highest possible standard, the use of tire rubber can substantially benefit the process while also providing a use for an otherwise waste material. Lisi et al. [23] proposed the substitution of gravels in the putting green construction method proposed by US Golf Association (USGA) [51] with ground rubber for

Layer thickness, d , cm	Pesticides ($t_{0.5}$, days)	Days
$d \leq 10$ cm	MSMA sodium salt	14 days
	2,4-D isooctyl ester	NA
	glyphosate amine salt	40 days
	trifluralin	137 days
	chlorpyrifos	46.4 days
	benefin	77 days
	PCNP	198.7 days
	bensulide	105 days
	DCPA	57 days
	bensulide	105 days
	pendimethalin	244 days
	2,4-D butoxyethylester	NA
	oxadiazon	105 days
	chlorothalonil	52 days
	etridiazole	20 day
	glyphosate acid	44 days
	anilazine	0.8 day
	mancozeb	87 days
	maneb	34 days
	trifluralin-methyl	10 days
	bendiocarb	12 days
	chloroneb	135 days
	benomyl	187.3 days
	MCPA ester	38.5 days
	iprodione	18.5 days
	fenarimol	360 days
	triclopyr	60 days
	DSMA	NA
	propiconazole	116 days
	siduron	90 days
	ethofumesate	25 days
	isofenphos	197.5 days
10 cm < $d \leq 20$ cm	Diazinon	40.1 days
	carbaryl	7.3 days
	metalaxyl	83.5 days
	simazine	53.5 days
	atrazine	78.5 days
	fenamiphos	16.5 days
20 cm < $d \leq 50$ cm	Isazofos	34 days
	ethoprop	42.3 days
	triadimefon	17 days
	endothal	4.5 days
50 cm < $d \leq 100$ cm	2,4-D acid	20 days
	2,4-D dimethylamine salt	9 days
100 cm < $d \leq 200$ cm	Fosetyl al	1 day
	MCPA salt dimethylamine	21 days
	MCPA sodium salt	14 days
	MCPA amine (Mecoprop)	21 days
	triclopyr	60 days
$d > 200$ cm	Trichlorfon	15 days
	dicamba acid	19 days
	dicamba salt	NA

NA: Not available

Table 4: Pesticides that are removed by $\geq 90\%$ by tire rubber layer at various thickness.

removal of nitrate present in fertilizers. Furthermore, since phosphorus can be removed by the reaction with iron released from steel wire in tires [24,25], algal blooms in golf course ponds may be reduced. Tire rubber can also be used as a low-cost drainage backfill material to adsorb pesticides and fertilizers applied to greens, fairway, and tee boxes as proven by Cecich et al. [52] for retaining wall structures and CalRecycle [53] for various civil engineering applications. Along water bodies, a tire rubber layer can be installed as a filter zone to remove pesticides, nitrate, and phosphorous. By using tire rubber in strategically located areas as an adsorbent and filtering layer with proper engineering considerations and design, it is possible to construct more sustainable and environmentally-friendly golf course. This approach also creates the added benefit of recycling a few hundred thousands of scrap tires for beneficial reuse.

Conclusions and Recommendations

From the statistical analysis of the properties of 51 pesticides, the following conclusions can be drawn:

1. There was a strong relationship between solubility and soil organic carbon-water partition coefficient, K_{oc} , indicating that as the K_{oc} value decreases the solubility increases. However, there were a few exceptions among pesticides used in golf courses such as glyphosate and MSMA sodium salt. These pesticides should be applied carefully to minimize transport to the environment.
2. From the relationships between solubility or K_{oc} and degradation rate or half-life, it was found that the degradation rate increases or half-life decreases as the solubility increases or K_{oc} decreases. This implies that highly mobile pesticides due to high solubility and K_{oc} may not move long distance due to high degradation rate or low half-life.

From the estimation of the tire rubber layer thickness computation, the following conclusions can be drawn:

1. Out of 51 pesticides, 37 pesticides were estimated to be removed with the tire rubber layer thickness of ≤ 20 cm under a typical scenario.
2. There were three pesticides that require more than a 200 cm thick tire rubber layer. However, due to relatively low half-lives of 1~60 days, it is anticipated that these pesticides are readily decomposed and thus the impact to the environment may be minimal.
3. If the organic carbon fraction, f_{oc} , is >0.1 (10%), the reaction layer thickness can be significantly reduced.

With respect to the application of tire rubber for the mitigation of pesticides and fertilizers from golf courses, the following recommendations can be made:

1. The use of tire rubber in golf courses will significantly lower the release of pesticides to the surrounding environment.
2. The potential applications of tire rubber include greens, fairways, tee boxes, bunkers, and wetlands in golf courses.
3. Various forms of tire rubber can be employed as filter layers, backfill materials, drainage packing materials, wetlands growth support layer fill materials, and lightweight fill materials for island greens and soft foundation areas.
4. If properly designed and installed, many scrap tires can be beneficially recycled in a golf course to make the golf course more sustainable and environmentally benign.

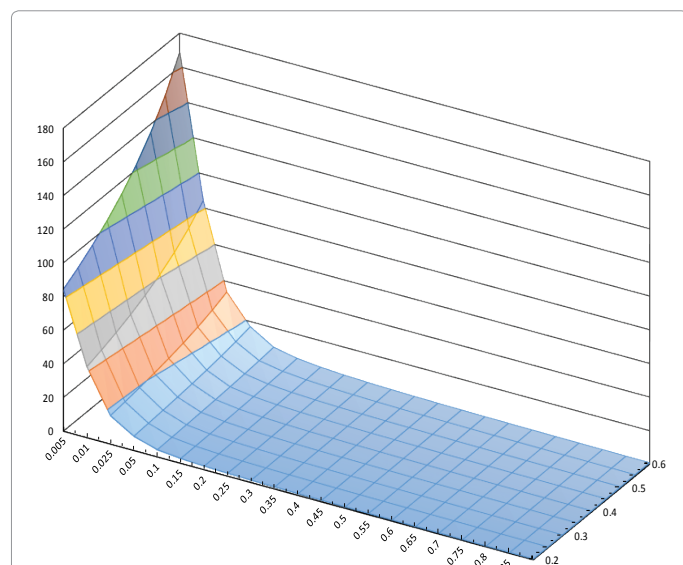


Figure 7: Equivalent distance multiplication for 90% pesticide removal by tire rubber at different organic carbon fraction and porosity.

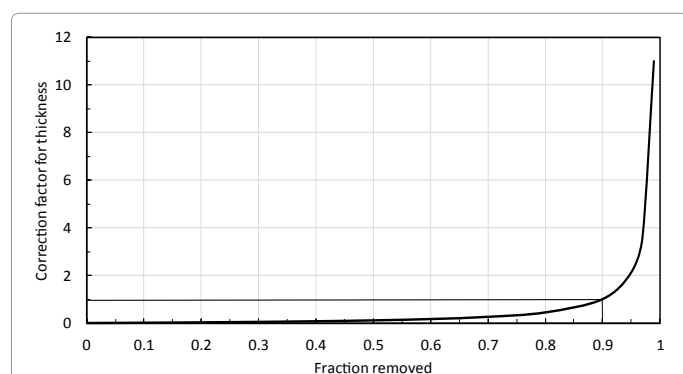


Figure 8: Correction factors for tire rubber layer thickness estimation at different removal fractions.

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