Leaching Potential of Non-steroidal Anti-inflammatory Drugs (NSAIDs) in Soils

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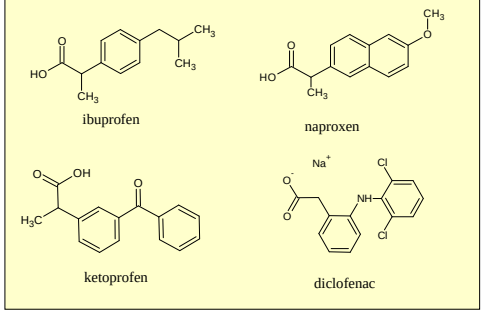
Abstract

Non-steroidal anti-inflammatory drugs (NSAIDs) in soils resulting from agricultural and landscape irrigation with municipal wastewater and land application of biosolids may migrate through or intact with soils, be transformed and reach groundwater. In this study, the leaching potential of NSAIDs in soils was evaluated, and the effect of $CaCl_2$ solution (as an index of salinity), dissolved organic matter (DOM) and polyacrylamide (PAM) amendment on leaching was investigated. Three US cropland soils, Arlington sandy loam (ASL), Palouse silt loam (PSL), and Imperial silty clay (ISC) were spiked with four NSAIDs, namely ibuprofen, naproxen, ketoprofen, and diclofenac sodium. The spiked soils were incubated for 24 h followed with 7-day storage in glass flasks, and then packed into stainless steel columns (1.5 cm i.d. × 12 cm) and leached with deionized water (DIW), 10 mM $CaCl_2$, DOM solution (DOC 34 mg L^{-1}), and PAM solution (1.0 mg L^{-1}) respectively. Initial concentrations of ibuprofen, naproxen, ketoprofen and diclofenac sodium in the three packed soils were 1.93-2.07, 1.74-2.27, 1.79-2.16, and 1.99-2.13 mg kg^{-1}, respectively. Maximum concentrations of the four NSAIDs in column effluents were 1.23, 0.92, 0.69, and 1.12 mg L^{-1}, respectively, when the soil was leached with 10 pore volumes of water. DOM and PAM did not facilitate the NSAIDs release from soils. $CaCl_2$ solution, however, reduced the amounts of NSAIDs leached from all three soils. Leaching of NSAIDs differed among the three test soils. The results suggest that the leaching potential of NSAIDs through soil to groundwater is significant, and the mobility of NSAIDs in soil is related to their chemical characteristics and soil properties. Amending soil with DOM or PAM does not significantly affect the leaching behavior of NSAIDs in soil, whereas increasing the salinity of the irrigation water can decrease the NSAIDs leaching potential.

Introduction

NSAIDs are the most commonly prescribed and used pharmaceuticals with an annual production to be several kilotons. They may be introduced into soil through irrigation with treated wastewater and land application of biosolids. Presence of NSAIDs in soil and their fate and transformation in environment have been extensively investigated around the world. However, information concerning about their leaching potential to contaminate groundwater is limited.

Application of treated wastewater and biosolids may result in an elevated dissolved organic matter (DOM) level in soil water. Besides, water-soluble polyacrylamides (PAM) are often used as soil amendments in agricultural soils for various purposes, such as minimization of surface water run-off, soil erosion and crusting, stabilization of soil structure, and enhancing infiltration. In this sense, we determined the leaching potential of NSAIDs in soils using batch and column experiments. Also, we measured the effect of salinity, DOM, and PAM amendment on the leaching process.



Experiments

Soil incubation. Aliquots (350 g) of air-dried soils were placed in 500-mL conical flasks and spiked with target chemicals in ethyl acetate solutions. The solvents were evaporated by exposing the soils for 5 h at room temperature in a darkened fume hood. Deionized water was added to keep moisture contents at 70% of soil's water holding capacity. The flasks were sealed and incubated at 20°C for 24 h. After incubation, soils were air-dried in the fume hood, and then stored at 20°C in flasks for 7 days before the experiments.

Batch extraction. Eight milliliters of solution were added to 50-mL Teflon centrifuge tubes, containing 10 g of treated soils. The tubes were capped and shaken at 20°C for 24 h, followed by centrifugation at 6708 × g for 15 min. Supernatant was decanted and extracted with dichloromethane. NSAIDs remained in soil was analyzed with ultrasonic solvent extraction.

Column experiment. Soil columns were prepared by packing the treated soils into 1.5 cm i.d. × 12 cm length stainless steel columns. Aliquots of 22.0 g of soils were packed in each column to a bulk density of 1.55 g cm^{-3} for ASL, 1.42 g cm^{-3} for PSL, and 1.33 g cm^{-3} for ISC, respectively. The bottom end of the column was soldered with an aluminum plate, through which a stainless steel needle (1 mm i.d. × 6 cm) was centered to collect column leachates. The top end was capped with a screw cap, on which an acrylic tube was installed for water loading. DIW, 10 mM $CaCl_2$, DOM or PAM solution was applied to the column top at 0.05 mL min^{-1} with the aid of a peristaltic pump. A 1-cm constant water head was maintained on the column top by simultaneously pumping back any excess loading through a stainless steel needle installed on the side of the acrylic tube, resulting in a natural percolation of water through the columns by gravity. Leachates were collected in 15-mL headspace vials at pore-volume increments for each column, and a total of 10 pore volumes of leachates were collected. NSAIDs in the leachates were extracted with dichloromethane. After the experiment, soils from the columns were air-dried and the remaining NSAIDs were determined.

Results

Batch experiment

Compound	Initial levels	DIW			$CaCl_2$ solution			DOM solution			PAM solution		
		Extract released[a]	Soil remained[b]	Mass balance[c]	Extract released[a]	Soil remained[b]	Mass balance[c]	Extract released[a]	Soil remained[b]	Mass balance[c]	Extract released[a]	Soil remained[b]	Mass balance[c]
Arlington sandy loam													
ibuprofen	1.93(0.08)	0.51(0.04)	1.05(0.01)	0.37(0.13)	0.59(0.01)	0.91(0.02)	0.43(0.10)	0.50(0.05)	1.07(0.02)	0.36(0.15)	0.50(0.05)	1.15(0.01)	0.28(0.14)
naproxen	2.27(0.21)	0.30(0.03)	1.61(0.02)	0.37(0.26)	0.39(0.01)	1.53(0.03)	0.35(0.25)	0.31(0.02)	1.41(0.01)	0.55(0.24)	0.30(0.02)	1.63(0.02)	0.34(0.25)
ketoprofen	1.97(0.14)	0.23(0.03)	1.36(0.02)	0.39(0.19)	0.28(0.3)	1.46(0.04)	0.23(0.21)	0.23(0.03)	1.31(0.05)	0.43(0.22)	0.22(0.02)	1.32(0.02)	0.44(0.18)
diclofenac	2.01(0.06)	0.46(0.04)	0.90(0.04)	0.65(0.12)	0.45(0.03)	0.85(0.02)	0.70(0.10)	0.48(0.03)	1.08(0.03)	0.45(0.12)	0.45(0.05)	0.93(0.05)	0.63(0.15)
Imperial silty clay													
ibuprofen	2.07(0.11)	0.35(0.03)	1.29(0.02)	0.42(0.16)	0.36(0.03)	1.22(0.02)	0.49(0.16)	0.32(0.02)	1.41(0.01)	0.34(0.14)	0.33(0.02)	1.37(0.06)	0.37(0.19)
naproxen	1.74(0.07)	0.13(0.02)	1.37(0.02)	0.24(0.11)	0.13(0.02)	1.44(0.02)	0.16(0.11)	0.11(0.01)	1.52(0.03)	0.11(0.10)	0.11(0.01)	1.48(0.01)	0.15(0.08)
ketoprofen	2.16(0.01)	0.10(0.01)	1.79(0.03)	0.27(0.06)	0.10(0.02)	1.64(0.01)	0.42(0.04)	0.08(0.01)	1.75(0.04)	0.33(0.06)	0.08(0.01)	1.62(0.03)	0.46(0.05)
diclofenac	1.99(0.13)	0.22(0.01)	1.12(0.06)	0.64(0.20)	0.20(0.01)	1.10(0.01)	0.69(0.15)	0.19(0.01)	1.17(0.02)	0.63(0.15)	0.19(0.01)	1.10(0.03)	0.69(0.17)
Palouse silt loam													
ibuprofen	2.07(0.10)	0.26(0.02)	1.40(0.03)	0.40(0.15)	0.14(0.01)	1.53(0.03)	0.40(0.14)	0.25(0.01)	1.30(0.02)	0.51(0.13)	0.27(0.02)	1.47(0.04)	0.33(0.16)
naproxen	1.94(0.08)	0.09(0.01)	1.61(0.04)	0.24(0.13)	0.04(0.01)	1.75(0.05)	0.14(0.14)	0.09(0.01)	1.61(0.02)	0.24(0.10)	0.10(0.01)	1.56(0.01)	0.28(0.10)
ketoprofen	1.79(0.21)	0.21(0.01)	1.33(0.02)	0.25(0.24)	0.10(0.01)	1.49(0.01)	0.19(0.23)	0.20(0.01)	1.25(0.03)	0.34(0.25)	0.22(0.02)	1.41(0.01)	0.16(0.24)
diclofenac	2.13(0.14)	0.11(0.01)	1.37(0.04)	0.65(0.19)	0.05(0.01)	1.56(0.02)	0.52(0.16)	0.11(0.01)	1.28(0.04)	0.75(0.18)	0.11(0.01)	1.22(0.03)	0.79(0.17)

Table 1. Contents of NSAIDs released into water and remaining in soil, mg kg-1 soil. Data in parentheses are standard deviations of triplicate measurements. (a) The portion of NSAIDs recovered in the extracts is on soil mass basis; (b) NSAIDs remained in soil after extraction; and (c) NSAIDs lost in the extraction process.

Column experiment

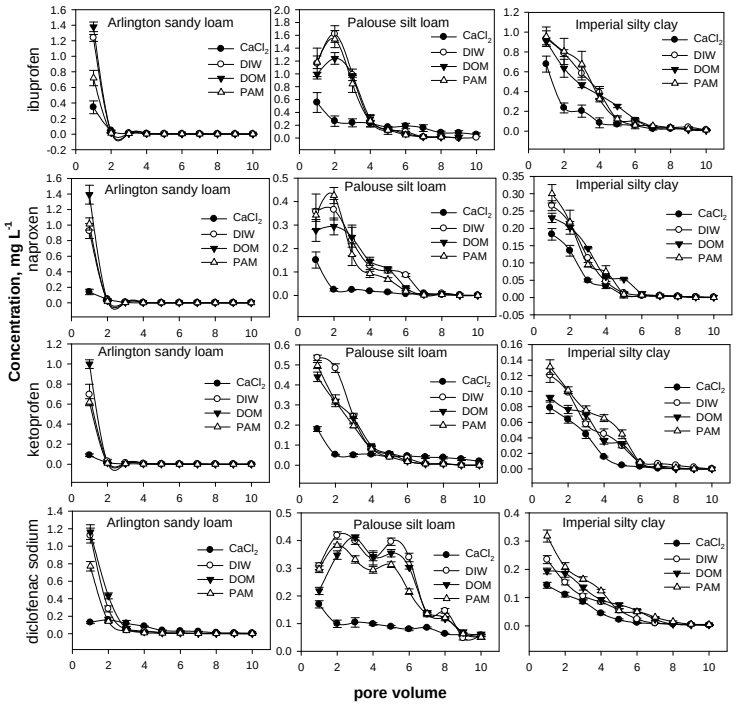


Figure 1. Concentrations of NSAIDs in effluents from soil columns leached with DIW, $CaCl_2$, DOM, and PAM solution. Error bars represent standard deviations of triplicate measurements.

NSAIDs		ASL	PSL	ISC
ibuprofen	DIW	1.07(0.13)	0.27(0.13)	0.54(0.36)
	$CaCl_2$	1.30(0.45)	0.86(0.38)	0.94(0.42)
	DOM	1.03(0.27)	0.41(0.22)	0.59(0.28)
	PAM	1.12(0.28)	0.33(0.15)	0.53(0.16)
naproxen	DIW	1.25(0.33)	0.82(0.14)	0.81(0.24)
	$CaCl_2$	1.66(0.52)	1.29(0.26)	1.04(0.31)
	DOM	1.22(0.10)	0.95(0.50)	0.85(0.16)
	PAM	1.30(0.21)	0.92(0.28)	0.82(0.14)
ketoprofen	DIW	1.17(0.22)	0.76(0.22)	1.28(0.33)
	$CaCl_2$	1.33(0.43)	0.99(0.13)	1.26(0.34)
	DOM	1.10(0.27)	0.84(0.10)	1.29(0.53)
	PAM	1.21(0.39)	0.87(0.35)	1.24(0.47)
diclofenac	DIW	0.91(0.31)	0.58(0.23)	0.94(0.22)
	$CaCl_2$	1.14(0.36)	1.03(0.37)	0.99(0.31)
	DOM	0.84(0.11)	0.62(0.33)	0.98(0.36)
	PAM	1.03(0.09)	0.66(0.26)	0.83(0.29)

Table 2. NSAIDs residues in soils after column leaching experiments, mg kg^{-1}. Data in parentheses are standard deviations of triplicate measurements.