The Effect of Cations on the Extractability of Organic Chemicals Adsorbed to Soil

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Abstract

Sorption is an important factor in determining the potential impact of chemicals in the environment. There are many factors that affect the adsorption of chemicals to soil including, but not limited to; size, shape, molecular structure, polarity, solubility, configuration, polarizability and charge distribution of a chemical. Furthermore, soil has many characteristics that affect adsorption including cation exchange capacity (CEC), pH, clay content, particle size, ionic strength, as well as others. Although hydrophobic partitioning has been recognized to have a large role in sorption mechanisms, other processes such as cation exchange and surface complexation with cations also have a role in sorption to soil. Exchangeable cations commonly found in the environment (Na^+, Ca^{2+}, Mg^{2+}, K^+) influence the adsorption of organic chemicals to soil. The current study utilizes different cations found in the environment to extract organic chemicals that are adsorbed to soil for analysis. This technique uses the cation exchange capabilities of the soil to remove the organic molecule by substituting the cation on the soil for the cation that is in the extraction solvent. Different cations were tested with various oxidation states including K^+, Na^+, NH_4^+, Mg^{2+}, Fe^{2+}, and Al^{3+}. Six ^{14}C-radiolabled organic chemicals (Acetaminophen, Daidzein, TPCK, Atrazine, N-Isopropylpipecolic acid, and N,N-Diethyl-3-methylbenzamide) and four different soils with varying characteristics were used. The results showed that extractability increased for extraction solvents containing monovalent cations (K^+, NH_4^+, and Na^+) which demonstrate that cation exchange can be used as a viable technique to extract adsorbed organic chemicals from soil. The increase in extractability will allow for a more accurate evaluation of potential bioavailability and fate of organic chemicals in the environment.

Methods:

Experiment design:

- 0.01M $CaCl_2$ added to the soil (1:5 ratio of soil to solution) and shaken overnight
- [^{14}C]Test substance applied to soil/solution mixture and shaken for 24 hours
- Samples centrifuged, decanted and the aqueous layer quantified for test substance by LSC
- Extraction solvent was added to the soil, sonicated, shaken and centrifuged
- Solvent was decanted and quantified for test substance by LSC

Soil:

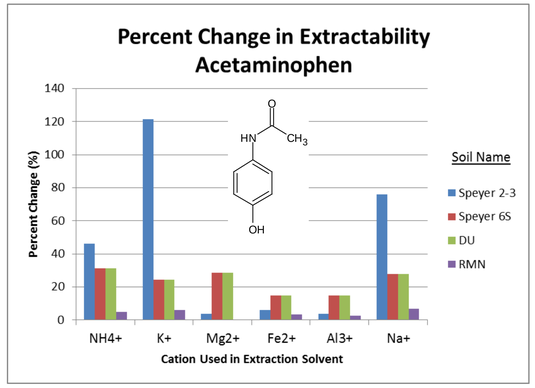
Soil Name	Location	Sand (%)	Silt (%)	Clay (%)	Organic Carbon (%)	pH in 0.01M $CaCl_2$	CEC
Speyer 2-3	EU	60	34	7	0.67	5.7	7.5
Speyer 6S	EU	25	34	41	1.77	7.2	26.5
RMN	US	84	8	8	0.81	4.8	11.0
DU	US	42	34	24	6.45	6.1	25.0

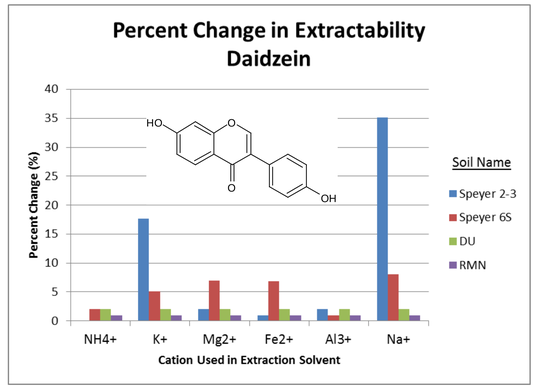
Extraction Solvents:

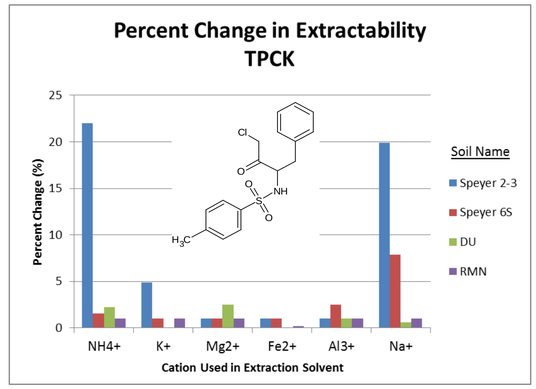
- 4:1 Acetonitrile:H_2O
- 4:1 Acetonitrile:0.1M Ammonium Carbonate in H_2O
- 4:1 Acetonitrile:0.1M Potassium Carbonate in H_2O
- 4:1 Acetonitrile:0.005M Magnesium Carbonate in H_2O
- 4:1 Acetonitrile:0.005M Ferrous (II) Carbonate in H_2O
- 4:1 Acetonitrile:0.005M Aluminum Carbonate in H_2O
- 4:1 Acetonitrile:0.1M Sodium Carbonate in H_2O

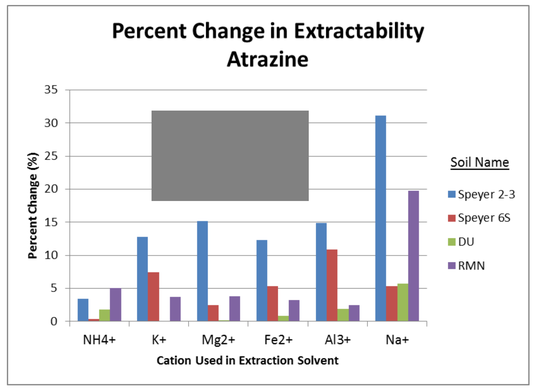
Results:

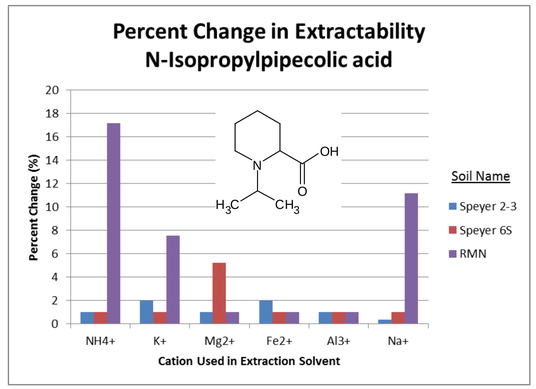
Percent Change in Extractability when compared to 4:1 Acetonitrile:H_2O

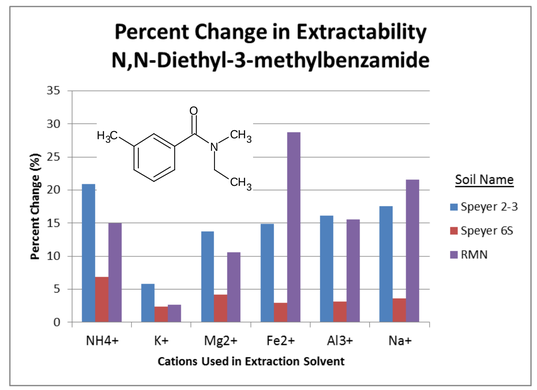












Results:

- Extraction solvents containing monovalent cations (Ammonium, Potassium, and Sodium) showed a significant increase (>10% change) in extractability for most compounds applied to the Speyer 2-3 and RMN soils
- Extraction solvents containing Magnesium, Iron and Aluminum did not demonstrate any significant trend in extractability for any compound
- Acetaminophen and Daidzein had similar results to each other and their structures also contain the same functional group; both contain a hydroxyl group (-OH) attached to a benzene ring
- TPCK, the only halogenated test material, responded best to extraction solvents containing ammonium and sodium

Conclusions:

- Cations that were unable to improve extractability were hindered by their small ionic radius relative to calcium
- Cations that were able to improve extractability have an ionic radius that is approximately the same or larger than that of calcium

Cation	Al^{3+}	Fe^{2+}	Mg^{2+}	Ca^{2+}	Na^+	K^+	NH_4^+
Radius in Picometers	54	61	72	100	102	138	175

- This relationship shows that when a calcium ion is replaced by a larger cation, the organic molecule can be extracted more efficiently
- The high cation exchange capacity of Speyer 6S and DU allowed for more calcium ions to remain in soil after the aqueous layer was decanted
- Due to the high level of calcium ions remaining in the soil, the addition of cations via extraction solvent had no observable effect
- Soils with a low CEC (Speyer 2-3 and RMN) do not have the ability to retain as many calcium ions
- Therefore, with the introduction of more cations from the extraction solvent, the ion exchange was able to occur between the calcium ion and the extraction solvent cation to increase the availability of the organic molecule
- Although the CEC of Speyer 2-3 and RMN are similar, the percentage of sand in the soil impacted the extractability
- Sand is a much larger particle compared to silt or clay and either increased or decreased extractability depending on the structure of the compound

References

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- Y. Marcus(1991). "Thermodynamics of Solvation of Ions", J. Chem. Soc. Faraday Trans.

Acknowledgments

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