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Interactions of the Aminotriazole and Imazethapyr Herbicides with Humic Acid Extracted from Moroccan Soil.

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ABSTRACT

Soil interactions of most hydrophobic organic compounds (e.g., nonpolar pesticides) are directly related to soil organic matter (SOM) content. Holmic substances are the major SOM components, containing carboxylic, phenolic, amine, quinone, and other functional groups, and specific structural configurations. In this study, Infrared spectroscopy (IR) was used to investigate the mechanism of interaction between two herbicides of different characters (Aminotriazole as basic molecular and Imazethapyr as acidic molecular) with Holmic acid (HA), extracted from surface horizon (0-20cm) of soil originating from Cahokia-Morocco. This study was affected by pH of environmental interest. The reported modifications of the infrared spectra suggest the formation of hydrogen bonds between these herbicides and humic acid. These interactions in this study may well be responsible for the transport of Imazethapyr and Aminotriazole in lower soil depths through the adsorption of these herbicides on water soluble humic substances.

Keywords: Humic Acid, Amino-1,2,4-triazole, Imazethapyr, Hydrogen Bonding, Ionic Bonding, Infrared spectra.

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INTRODUCTION

Humic substances constitute the major part of the organic carbon present in soils and sediments and surface waters (Eyheraguibel, 2004). Although the chemical structures of these compounds have not been fully established, they can be divided into three major groups, depending on their solubility in water, fulvic acids, which are soluble in water, humic acids, which are soluble only at pH >7, and humin, which is insoluble (Baglieri et al., 2014).

Humic acids (HA) have molar between 10000-100000 Da. Their chemical structure consists of aromatic rings (Sposito, 1989) interconnected by long alkyl chains and with many polar functional groups, like carboxylic, phenolic, alcoholic and amino groups. In aqueous solution HA act both as poly electrolytes and as hydrophobic compounds (McCarthy and Jimenez, 1985) and play a major role in the complexing of inorganic cations and organic micropolluants (Sense, 1992). Humic substances, especially HA, also influence the transport, bioavailability, degradation and deposition of micropolluants (Han et al., 2014; Pi et al., 2015).

The nature of the bonding or adsorption between HA and pesticides has been investigated and there are several theories. Furthermore, it has been suggested that the prevalent type of binding depends on chemical and conformational properties of humic substances because of the differences in their stereochemical nature and thus varying accessibility of specific functional groups on their surface (Senesi, 1992).

The present article investigates, by FTIR spectroscopy, the sorption behaviour of Amino-1,2,4-triazole and Imazethapyr herbicides toward a selected extracted Moroccan soil at pH 6. The two pesticides are chosen because of their different physico-chemical properties. The aim of the work is to better understand the behaviour and mobility of these pesticides in the Moroccan environment and avoid their harmful effects on target and non-target organisms.

C-amino-1, 2, 4-triazole (named Amitrole, ATA, and Amizol…) is a non-selective systemic herbicide. It is used on nonfood croplands to control annual grasses and perennial and annual broadleaf weeds, for poison ivy control and for control of aquatic weeds in marshes and drainage ditches (Hayes and Laws, 1990; Meister, 1992). This pesticide was identified as a cancerous agent in animals and has been indicated as endocrine and thyroid gland disruptors (Sellamuthu, 2014).

It is readily soluble in water (Solubility in water 28.10^4 mg/L) and does not adsorb strongly to soil particles (Howard, 1989 ; Hayes and Laws, 1990). In aquatic environment, this pesticide does not break down by hydrolysis or photolysis (Wauchope, 1992). However, concentration of Amatole which would be found in surface and groundwater will exceed the CE limit (0, 1 µg/L) and will be a potential pollutant of water (ECC., 1980; Catatonia et al., 2004).

Its pea values of 4.3 and 10.4 determined by potentiometric titration (Fontecha-Cámara et al., 2007) show the presence of different forms of Amatole ions in acidic and basic media. From the known solution chemistry of the diazoles (Either and Hauptmann, 1995), the possible routes for the formation of the Amatole ions in acidic and basic media may be depicted as shown in Figure 1.

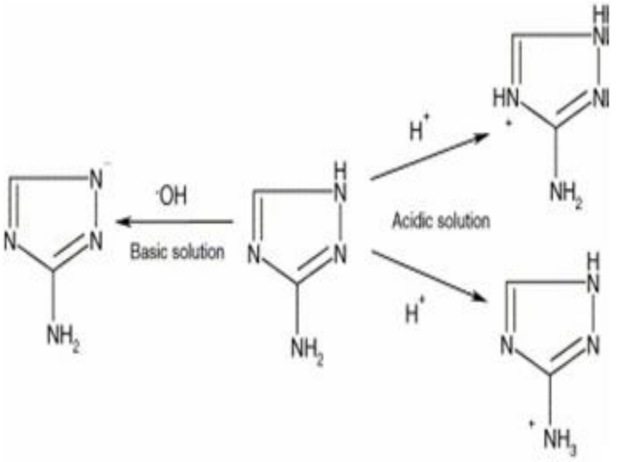

Figure 1: Proposed mechanism of Amatole ions formation in acidic and basic media.

Concerning Imazethapyr [5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid], abbreviated as IMZ, it is a selective imidazolinone herbicide used for broad-spectrum weed control in soybean and leguminous crops (Stougaard et al., 1990). In addition, Imazethapyr has both soil-residual and foliar activity (Pinto, 2009). Its water solubility is equal to 1.4 g/L (25 °C) (Outfit S et al., 2013).

The imazethapyr molecule is amphoteric of nature carrying both acidic (carboxyl) and basic (pyridine nitrogen) functional groups with pea values of pKa_1 = 2.1 and pKa_2 = 3.9 (Stougaard and Martin, 1990). Its molecular structure and acid-basic properties are presented in Figure 2.

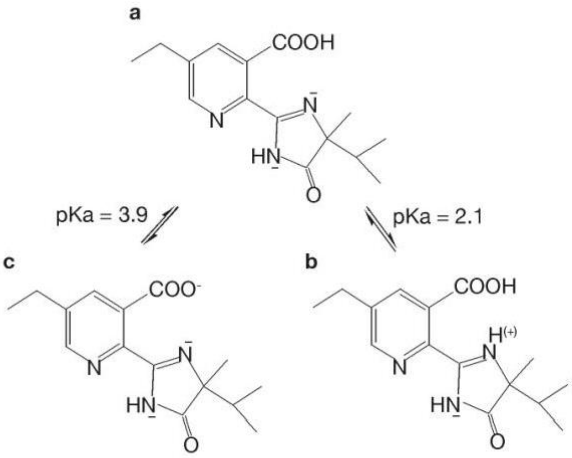

Figure 2: Chemical structure of Imazethapyr herbicide. Neutral (a), cationic (b) and anionic (c) states

Due to its nature, several factors such as soil-solution pH, sorbent-surface pH, charge, ionic strength, and soil composition may affect sorption on either soils or humid substances (Loux and Reese, 1993). Avila *et* al. (2006) show that Imazethapyr is susceptible to both direct and indirect photolysis reactions in water. The results also show that Imazethapyr photolysis in paddy water will be affected by turbidity because of its impact on the availability of sunlight to drive direct and indirect photolysis reactions. Sense *et al.* (1997) proposed that Imazethapyr may interact with humid acids through multiple-binding mechanisms, including charge transfer and ionic and hydrogen bonds, but they did not mention the extracted HA, supporting the prominent role of highly reactive SOM components in sorption.

Hydrogen bonding is an important polar interaction in aqueous media. This importance often leads to the consideration that hydrogen bonding is a special or unique bond type. The presence of oxygen and nitrogen containing functional groups, as well as hydroxyl and amino groups strongly suggests that hydrogen bonding represents an important adsorption mechanism for organic pollutants containing similar complementary groups (Xiao, 1999). A large body of evidence for hydrogen bonding was obtained from IR and DTA studies (Sparks, 1995).

The carboxyl group (-COOH) of organic acids specially Holmic Acid interacts either directly with the interlayer action or by forming a hydrogen bond with the water molecules coordinated to the exchangeable action on the soil-solid and sediment-solid clay particles (Sparks, 1995). In addition to coordination and hydrogen bonding, organic acids can be absorbed through the formation of salts with the exchangeable captions. It has been noted that anions can be absorbed by weak bonding of the carboxyl group to the positive sites of the oxide surfaces of goethite (Sparks, 1995).

MATERIALS AND METHODS

Chemicals

Aminotriazole (C-amino-1, 2, 4-triazole) and Imazethapyr were purchased from commercial source at purity greater than 99%. Experiments were carried out at pH = 6 (pH of environmental interest). Ultra pure water was produced with a Millis system.

Humic acid (HA):

The HA used in this investigation are from surface horizon (0-20 cm) of soil originating from Cahokia-Morocco, the main agricultural and industrial area. A number of field and analytical identifications of the samples from which HA were extracted are T_{otal} = 1.56, T_{otal} = 0.06, pH $_{(H2O)}$ = 7.7.

Extraction was carried out with 0, 1 M NaOH + 0, 1 M $Na_4P_2O_7$ (v/v) mixture under nitrogen (Carmichael et al., 1993). In brief, the dried sample was suspended in 2N HCl to remove carbonate. The above mixture was added with stirring for 16 h (4-4x) with a separate alkaline solution. The solution was centrifuged to eliminate suspended clay and then acidified to below pH 2 with 6N HCl and the HA precipitate was separated by centrifugation and purified by HCl/HF (0, 5%, v/v) treatment. The dissolution into alkaline solution and precipitation by acid was repeated three times. The final alkaline solution was passed through an Ambulate IRN 77 action exchange resin column to obtain an acidic from of HA, dialyzed against distilled water and freeze dried. The characterisation of the HA was achieved by elemental analysis and determination of their acidities with the techniques described earlier (Carmichael et al., 1993). (Table 1).

Table 1: Analytical characteristics of the humid acids (HA) extracted from Cahokia-Morocco

C (%)	41.70
H (%)	2.51
N (%)	2.47
O (%) (by difference)	53.32
Total acidity (meq.g^{-1})	6.04
Phenolic acidity (meq.g^{-1})	0.77
Carboxylic acidity (meq.g^{-1})	3.93
Mineral acidity (meq.g^{-1})	1.34

The C, H, N and O contents are similar to the elemental compositions of HA reported in the literature (Warship and Aiken, 1985), whereas the total acidity and contents of carboxyl groups were higher than some of those cited in the literature (Hatcher et al., 1981). Indeed it's well known that the structure and physicochemical characteristics of HA are affected by their origins, geographic location, and climate zones (Stevenson, 1994).

Herbicide - HA complex:

After treating the HA with Aminotriazole and Imazethapyr solutions for 24 hours, the suspensions are centrifuged and the collected precipitates were washed several times with distilled water.

Fourier-transform infrared spectroscopy:

FTIR spectra were recorded with Perkin Elmer 1600 Spectrometer. The absorbance Spectra was computed from 4000 to 400 cm^{-1} at 2 cm^{-1} precision. The samples were examined in KBr pellets using 100 mg of KBr and 1 mg of samples.

RESULTS AND DISCUSSION

The infrared spectra of HA, Aminotriazole and HA-Aminotriazole-complex are reported in Figure 3; the spectra of HA, Imazethapyr and HA-IMZ-complex are given in Figure 4. Their principal band assignments, based on literature data (Bertha R and Hsu, 1976; Sathyanarayana et al., 1987; Zama et al., 2004; Singh et al., 2011), are listed in Table 2.

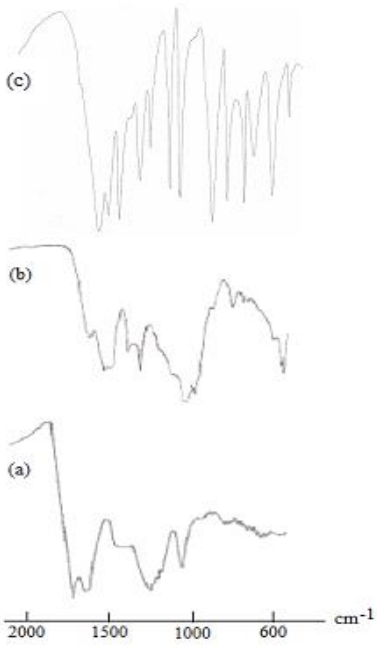

Figure 3: FTIR spectra of HA (a) Aminotriazole-AH complex (b) Aminotriazole (c)

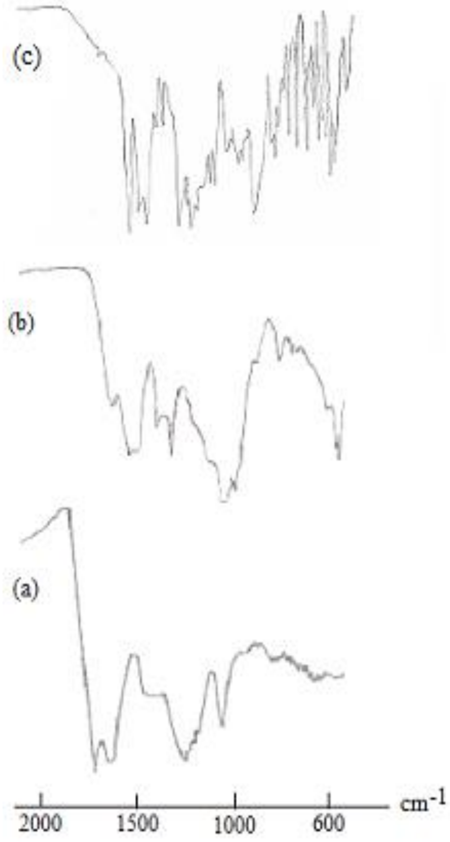

Figure 4: FTIR spectra of HA (a) Imazythapyr-AH complex (b) Imazythapyr (c)

Table 2: Infrared band assignments for Aminotriazole, Imazethapyr, HA and their complexes

Before interactions					
HA		Aminotriazole		Imazethapyr	
Wavenumbers (cm^{-1})	Vibrations	Wavenumbers (cm^{-1})	Vibrations	Wavenumbers (cm^{-1})	Vibrations
1712	$\nu_{C=O}$ (COOH)	1640	δ_{NH2}	1745	$\nu_{C=O}$ (CO_2H)
1617	$\nu_{C=C}$ (conjugated with C=O) ; δ_{NH}	1220, 1215	ν_{C-NH2}	1647	$\nu_{C=N}$
1450	δ_{CH} (aliphatic)	1212	δ_{NH}	1555	δ_{NH} (Amide)
1390	$\nu^{s}_{COO^-}$	1080	δ_{NH}	1464	δ_{NH}
1240	ν_{C-O} (CO_2H or Phenolic C-OH)	1045	δ_{CH}, r_{NH2}	1046	γ_{N-H}
1080	δ_{CH} (Alcènes)	875	γ_{CH}		
		825	γ_{NH}		
		725,705	ω_{NH2}		

After interactions	
Wavenumbers (cm^{-1})	Vibrations
1712	$\nu_{C=O}$ (CO_2H)
1617	$\nu_{C=C}$ (Aromatic conjugated with C=O) ; ν^{a}_{CO2-}
1464	δ_{NH} ; δ_{CH} (aliphatic)
1384	ν^{s}_{CO2-}
1110-1100	γ_{NH}

The spectra of HA-Amatole and HA-IMZ-complexes show some changes in the bands of HA and adsorption bands attributed to the adsorbed pesticides.

At these conditions and at pH of soil a slight decrease in the intensity of the carboxyl band at 1712 cm^{-1}, as well as a decrease in the intensity of the symmetrical C-O stretching band of the COOH groups at 1240 cm^{-1} were observed. These results could be ascribed to the partial deprotonation of carboxylic groups of the HA, corresponding to the transformation of the acid COOH to the carboxyl ate COO^-. An analogy behaviour was observed for Imazamox-HA complex (Harir, 2008).

On the spectrum of the complex of Aminotriazole we noted the persistence of the bands corresponding to the NH_2 groups; while there's appearance of a higher intensity band around 1103 cm^{-1}, due to the in-plane deformation of NH bond. This allows concluding that a transfer of proton was made between a triazolic nitrogen and hydrogen of the carboxylic group of humid acid. The site of prolongation is probably N_4 as it was the case of Aminotriazole protonated by HCl or by tartaric acid (Zama et al., 2004; Matulkova et al., 2007).

On the spectrum of complex of Imazathapyr we noticed the decrease in the intensity of any bands assignable to HA and Imazethapyr, and the appearance of an intense band at 1106 cm^{-1}, which could be attributed to the in-plane deformation of NH bond, suggesting that complexes at these conditions may happen due to proton transfer from the carboxylic acid of the HA to the tertiary amines group of Imazethapyr.

The reported modifications of the infrared spectra suggests, in the case of the two pesticides, a proton transfer and formation of hydrogen bonds between these herbicides and humid acid (Figure 5). This mechanism of adsorption agreed with other literature studies (Xt et al., 2005). These interactions evidence in this study may well be responsible for the transport of Imazethapyr and Aminotriazole in lower soil depths through the adsorption of these herbicides on water soluble humid substances.

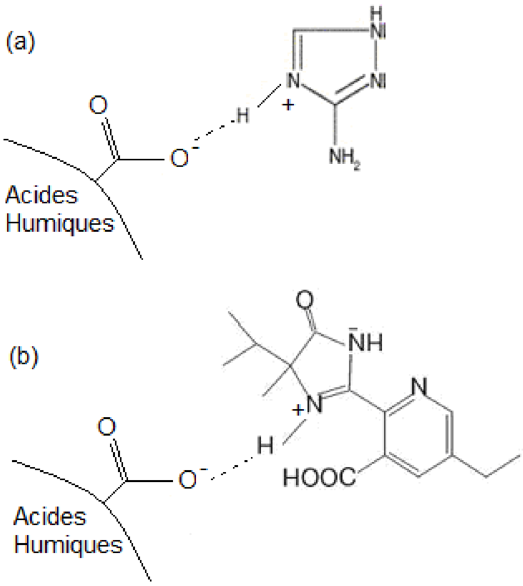

Figure 5: Possible adsorption model between Holmic Acids and Amatole (a) and Imazethapyr (b) with H-bonding and / or ionic bonding

CONCLUSION

Herbicides coming in contact with soil organic matter would be biotic ally or idiotically degraded or transported to lower soil horizons, depending on the chemical nature of the soil humid material and the way, it is linked with the mineral components. Results of this study indicated that Aminotriazole-HA and Imazethapyr-HA complexes are formed at pH of soil. The reported modifications of FTIR spectra suggest the formation of proton transfer from COOH of HA to the most basic nitrogen of the herbicide and the establishment of hydrogen bond between these nitrogen and HA. The findings imply that Aminotriazole and Imazethapyr when adsorbed on HA May easily transported in the soil environment, thereby reaching fresh water and presenting a potential health hazard.

REFERENCES

[1] Avila, L.A.; Massey, J.H.; Senseman, S.A.; Armbrust, K.L.; Lancaster S.R.; McCauley G.N. Chandler J.M. Journal of Agricultural and Food Chemistry 2006, 54(7): 2635-2639.
[2] Baglieri, A.; Vindrola , D.; Gennari, M.; Negre, M. Chemical and Biological Technologies in Agriculture 2014*, 1:9.* http://www.chembioagro.com/content/1/1/9
[3] Bertha, R.; Hsu, T.S. ACS Symp Ser. 1976, 29: 258-271.
[4] Carmichael, S.L., Murom, and L.; Hung, G.L. Handbook of Photochemistry 1993, and Marcel Dekker: Inc.: New York.
[5] Catastini, C.; Rafqah, S., Mailhot, F.; Sarakha, M. J. Photochemical. Photobiology*. A,* 2004, 162: 97-103.
[6] ECC. Directive Relating to the Quality of Water Intended for Human Consumption (80/778/ECC, Off. J. Europe. Community, 1980, 23 August, L229/1130.
[7] Either, T.; Hauptmann, S. Georg Thyme Overflag, Stuttgart. 1995, New York (Chapter 5).
[8] Eyheraguibel, B. These de Doctorate, Institute National Polytechnique de Toulouse 2004 (France).
[9] Fontecha-Cámara, M.A.; Lopez-Ramón, M.V.; Olivarez-Merino, M.A.; Moreno-Castillo C. *Langmuir*, 2007, 23 (3): 1242-1247.
[10] Han, P.; Wang, X.; Cai, L., Tong, M.; Kim, H. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014, 454: 119-127.
[11] Hariri M. These de Doctorate. University Mohammed V-Adel, 2008, Rabat-Marco
[12] Hatcher, P.G.; Mariel, G.E.; Dennis, L.W. *Org. Geochemist*. 1981, 3: 43-48.

[13] Hayes, W.J.; Laws, E.R. Handbook of Pesticide Toxicology, 1990, Vol. 3, Classes of Pesticides. Academic Press, Inc., New York Howard, P.H. Ed. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Lewis Publishes, Chelsea, 1989, MI, 8.
[14] Lou, M.M.; Reese, K.D. Weed Technology, 1993, 7: 452-458.
[15] Matulkova, I.; Nemec, I.; Cısarova, I.; Nemec, P.; Mi Z. J. Molecular Structure, 2007, 328-335.
[16] McCarthy, J.F.; Jimenez, B.D. Environ. Sci. Technol., 1985, 19: 1072-1076.
[17] Meister, R.T. Farm Chemicals Handbook 92. Meister Publishing Company, 1992, Willoughby, Ohio.
[18] Outfit, S.; El Madame, M.; Alou El Belghiti, M.; Zrineh, A.; El Azzouzi M. Arabian Journal of Chemistry. 2013 http://dx.doi.org/10.1016/j.arabjc.2013.11.030
[19] Pi K. ; Wang Y.; Xian X. ; Huang S.; Yu Q.; Yu M. Journal of Geochemical Exploration. 2015, 149: 8-21.
[20] Pinto, J.J.O.; Nolin, J.A.; Rosenthal, M.D.; Pinto, C.F.; Rossi, F.V. ; Machado, A. ; Pieta, L. ; Gallon, L. Plantar Danna, 2009, 27: 609-619.
[21] Sathyanarayana, D.N.; Kashmir Raja, S.V.; Shunmugam, R. *Spectrochim. Acta*, 1987, 43A(4): 501-506.
[22] Sellamuthu, R. Encyclopaedia of Toxicology. (Third edition). 2014, 203-205.
[23] Sense N. Science of the Total Environment, 1992, 123-124: 63-76.
[24] Senesi, N. ; La Cava P. ; Miano T.M. J. Environ. Qual., 1997, 26:1264-1270.
[25] Singh P.; Singh, N.P.; Yana, R.A. J. Chem. Pharm. Res. 2011, 3: 737-755.
[26] Sparks, D.L., Environmental Soil Chemistry. Academic Press, 1995, 267 p.
[27] Esposito, G. The Chemistry of Soils. Oxford University Press: New York. 1989, 277 p.
[28] Stevenson, F.J. Humus Chemistry: Genesis, Composition, Reactions (Second ed.). John Wiley & Sons, 1994
[29] Stougaard, R.N.; Shea, P.J.; Martin, A.R. Weed Sci, 1990, 38: 67-73.
[30] Udeigwe,T.K.; Ezek, P.N.; EtOH, J.M.; Satiety, M.H. Environnent International, 2011, 37(1): 258-267.
[31] Xiao, K.P.; Bühlmann, P.; Umezawa, Y. Anal. Chem. 1999, 71: 1183-1187.
[32] Xt, D.; Xt, Z.; Zhu, S.; Cao, Y.; Wang, Y.; Du, X.; Go, Q.; Li F. J. Colloid. Interface Sci. 2005, 285(1): 27-32.
[33] Wauchope, R.D.; Buttler, T.M.; Hornsby, A.G. Augustijn-Beckers P.W.M., Burt J.P. Rev. Environ. Contam. Toxicol.1992, 123: 1. 1- 157.
[34] Warship, R.L.; Aiken, G.R. Wiley, 1985
[35] Zama, S.; Guairá, F.; Haydon, S.; Said Midrise, M., Laurie, A., Romaine, F. Can. J. Anal. Sci. Spectres., 2004, 49(1): 1-10.