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Study of Trace Elements (TEs) contents in a vertisol irrigated by sewage (Meknes-Morocco)

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Abstract
A profile irrigated by sewage was sampled in the vicinity of the Meknes city to analyze the concentrations of the TEs. In fact, the reuse of raw wastewater is a large practice in the urban and periurban agricultures developed around the city of Meknes favourite by a water deficiency and a small cast of wastewater. Our study is carried primarily to determine vertical evolution and second to predict the different sources of Trace Elements in studied profile. In this feel the vertical behaviours of TEs on profile are evaluated by a Chemical Assessment calculus and we are tried to determine the various relationships between the considered Trace Elements in studied profile and in sewage samples. These last are terminated by a Multivariate Analyse, a Principal Components Analysis (PCA) and a Hierarchic Ascending Classification (HAC) analyses. The results obtained show the presence of the more or less significant concentrations according to the analyzed elements. These concentrations are related to sewage application and others agricultural practices such as the fertilization, the pesticides, etc.

1. Introduction

The soil behaves as a filtering system with respect to water which crosses it. This process of filtration is a function of the soil composition and the forms of the TEs contained in this water. The retention or remobilisation of the pollutants in a horizon depended to the capacity of this horizon, i.e., the number of the free active sites to accommodate these TEs. In general, the active fractions setting concerned in the dynamics of the pollutants in the soil are clays, organic matter, calcite and the oxyhydroxides of Fe, Al and Mn (Evengelou, 1998 ; Bohn *et al.*, 2001). The pollutants reacted according to their selective affinities with respect to its fractions and according to the physicochemical properties of the soil (Hooda, 2010; Maria *et al*, 2012; Amin *et al*, 2014). Based on the literature data we can present the different factors influencing the TEs behaviours in soil in Figure 1.

Soil pollution is often caused by the uncontrolled disposal of sewage and other liquid wastes resulting from domestic uses of water, industrial wastes containing a variety of pollutants, agricultural effluents from animal husbandry and drainage of irrigation water and urban runoff (Singh *et al*, 2012; Li *et al*, 2013; Chao *et al*, 2014; Karishma and Prasad, 2014). Irrigation with sewage water causes profound changes in the irrigated soils.

Amongst various changes that are brought about in the soil as an outlet of sewage irrigation include physical changes like leaching, changes in humus content, and porosity etc., chemical changes like soil reaction, base exchange status, salinity, quantity and availability of nutrients like nitrogen, potash, phosphorus, etc. Sewage sludges pollute the soil by accumulating the metals like lead, nickel, zinc, cadmium (Singh *et al*, 2012; Raju *et al*., 2013; Ould Arby *et al*, 2013).

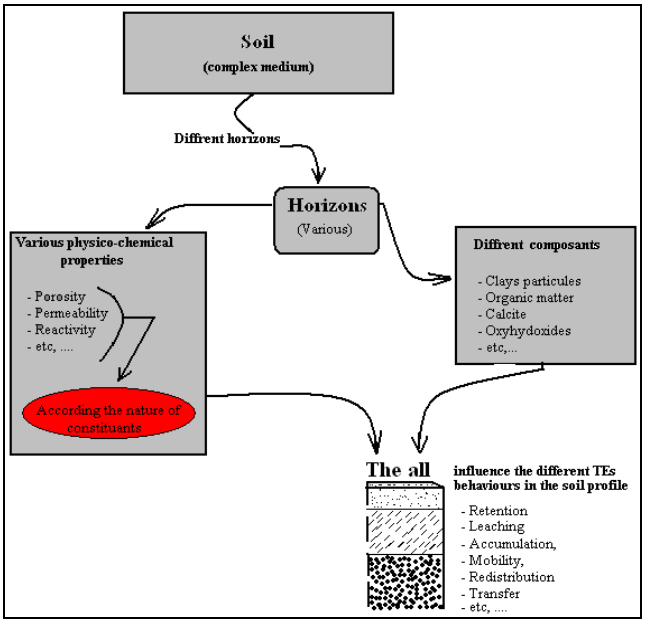

Figure 1. *The various parameters influencing the TEs behaviours in soil.*

Soil is a complex structure and contains mainly five major components i.e. mineral matter, water, air, organic matter and living organisms. The quantity of these components in the soil does not remain the same but varies with the locality.

Modern, or conventional, agricultural practices use intensive tillage, monoculture, irrigation, application of inorganic fertilizers, chemical pest control, sewage irrigation and plant genome modification to maximize profit and production. These different practices cause major environment problems in soils (Ould Arby *et al.*, 2010; Dekayir *et al.*, 2010; Niu *et al*, 2013; Ould Arby *et al*, 2013, Karishma and Prasad, 2014; Amin *et al*, 2014).

2. Materials

A cultivated vertisol subjected to a spreading of sewage was selected to make this study. The profile consists of an Ap horizon, thick of 15 cm, of brown colour and with a Silty-clay-sandy texture, overcoming an A1 horizon, thick of 15cm, which differs from the Ap horizon by its clearer colour. The whole of the profile is dominated at its base by a (B)ca horizon, thick of 70cm, rich in clays and concretions limestones. 9 samples are taken to base towards the top of profile (Ould Arby *et al.*, 2010; Dekayir *et al.*, 2010).

3. Methods

The TEs contents are determined by an ICP-AES (Inductively Coupled Plasma-Atomique Emission Spectroscopy) in soil samples and in sewage samples by an ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) (data no shown here). The organic matter is determined by ignition method, and calcite by a Bernard Calcimeter.

To carry out our objectives, a Chemical Assessment is carried out in addition to one multivariate analysis which is also applied to the various physicochemical data resulting from the studied profile (Ould Arby *et al.*, 2010; Dekayir *et al.*, 2010; Ould Arby *et al*, 2013; Bao *et al*, 2014).

3.1. Chemical Assessment

To study the behaviour of the TEs along the profile we carried out a chemical assessment for each TEs by taking as immobile element Zr. The transfer functions of the various ETM considered, on the studied profiles were calculated by the following equation (Brimhall *et al.*, 1991):

$$\tau_{j,i} = \frac{\rho_w C_{j,w}}{\rho_p C_{j,p}} \times (\varepsilon_{i,w}+1)-1 \text{ with } \varepsilon_{i,w} = \frac{\rho_p C_{i,p}}{\rho_w C_{i,w}} -1$$

Where: $C_{i,p}$: Concentration of the immobile element i in the sample p (the deepest sample); $C_{j,w}$: concentration of the mobile element j in the w horizon; ε: change of intervening volume during the pedogenesis, ρ: apparent density; τ: transfer function.

3.2. Multivariate Analysis

A multivariate Analysis is carried out combining the PCA and the HAC to determine the possible sources of the pollutants on studied profile (Stanimirova *et al*, 1999; Facchinelli *et al*, 2001; Chen *et al*, 2008; Zhang *et al*, 2009; Niu *et al*, 2013). In addition to that, a calculation of the coefficients of variation was made to describe the vertical variation of the contents of TEs on the profile (Dekayir *et al.*, 2010; Maria *et al*, 2012; Chao *et al*, 2014). In PCA only the principal components have an eigenvalues highest than 1, are taken. In the HAC dendrogram the distance on axis represent the degree of association between the studied parameters.

4. Results and Discussions

The TEs in studied profile are divided into two groups according to their behaviours (Fig.2):

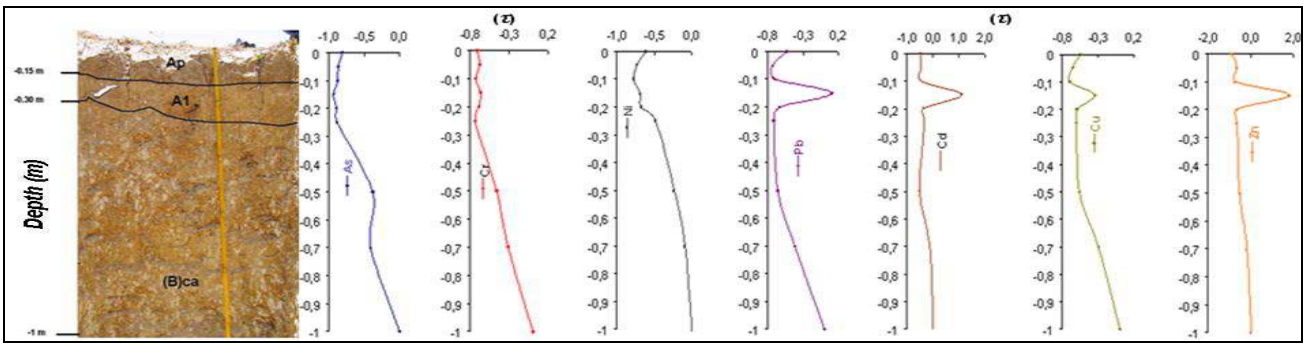

Figure 2. *Chemical Assessment of TEs contents along studied profile.*

Group 1: Pb, Cd, Cu, and Zn. These elements show similar evolutions along the profile. Indeed, the (B)ca and A1 horizons present a reduction in their contents. On the other hand, the base of the cultivated horizon Ap shows a net profit followed by a reduction towards surface (Fig. 2).

Group 2: As, Cr, and Ni. They show very close behaviours. Indeed, they show a regular reduction of their contents while going from the base of the (B)ca horizon towards the A1 horizon. In contrary, the Ap horizon shows a relative enrichment with equivalent rates (Fig. 2).

The vertical variation of the TEs contents on the profile shows that Cd, Cu, Pb, and Zn are distributed in a non-homogeneous way on the profile by their high CVs imposed by their significant accumulations on the surface. These TEs can be of exogenic origins. The As, Cr and Ni show an homogeneous distribution on profile. This can be an indication of their lithogenic origin on profile (Dekayir *et al*, 2010; Ould Arby *et al*, 2013, Niu *et al*, 2013).

The result of PCA shows three principal components which have eigenvalues higher than 1. They account for 88,95 % of the original variance (Table 1). A first component which associates Cd_V, Cu_V, Pb_V and Zn_V with a negative contribution of the As_V. This association gathers the four TEs: Cd_V, Cu_V, Pb_V and Zn_V which show a significant accumulation on the level of the surface horizon. The grouping of these four TEs is indeed shown on the dendrogram (Fig. 3). They are regarded as TEs strongly influenced by an exogenic contribution on the surface. As this association is independent of the contents of TEs in the sewage (Table 2), it is thus related to other exogenic source (Dekayir *et al*, 2010; Ould Arby *et al*, 2013). This exogenic source is probably related to others agricultural practices, such as the fertilization, the pesticides applications, etc, and/or with the diffuse pollution (Ould Arby *et al*, 2013; Karishma and Prasad, 2014; Chao *et al*, 2014).

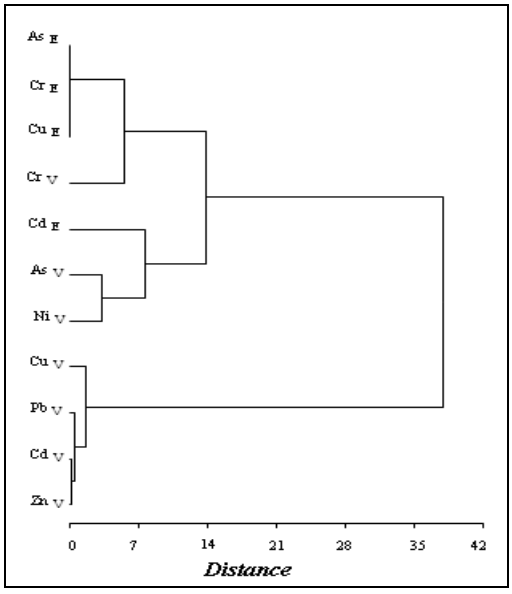

Figure 3. *Dendrogram illustrate the liaisons between the TEs contents in sewage and their contents in studied profile.*

Table 1. *Contents of different studied parameters and their CVs on profile.*

Depth (m)	Samples	OM (%)	Clay (%)	CaCO3 (%)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
0	Vp2-9	26.63	19	40,64	3,4049	0,3513	29,4421	10,4149	24,8355	12,4178	41,4534
-0.05	Vp2-8	26,13	20	40,64	2,2945	0,3659	33,5827	7,7178	16,687	7,092	44,0121
-0.1	Vp2-7	25.72	19	40,64	2,1219	0,3722	27,7974	7,0024	14,4292	7,8512	36,9217
-0.15	Vp2-6	25.43	18	40,64	1,0251	1,1835	28,8649	12,3707	16,4942	24,7414	294,8345
-0.2	Vp2-5	26,10	18	40,64	1,5965	0,35	27,5402	7,5835	17,3623	8,1822	38,1172
-0.25	Vp2-4	28,77	19	51,87	1,7187	0,3768	22,5583	7,3046	27,7145	6,4452	35,8784
-0.5	Vp2-3	29,23	18	59,89	5,41	0,163	27,8564	4,9221	24,3982	4,4978	30,2113
-0.7	Vp2-2	23,96	48	48,13	4,8714	0,2783	33,5449	7,4613	27,4608	7,2352	47,9331
-1	Vp2-1	22,79	19	41,71	5,8485	0,2222	34,4884	7,5144	21,2495	8,8436	41,4534
	Mean	26,156	21,000	44,978	3,148	0,407	29,519	8,032	21,181	9,701	67,868
	SD	1,898	10,033	6,537	1,706	0,284	3,589	2,018	4,809	5,683	80,388
	CV (%)	7,4	41,9	14,5	54,3	69,7	12,2	25,1	22,7	58,6	118,4

OM: organic matter, SD: Standard deviation; CV: coefficient of variation.

Table 2. *Principal Components Matrix (after Varimax rotation) on studied profile.*

	PC1	PC2	PC3
As_E	-0,09	0,96	-0,11
Cd_E	-0,30	-0,06	0,88
Cr_E	-0,06	0,97	-0,10
Cu_E	-0,06	0,97	-0,10
As_V	-0,56	0,58	-0,11
Cd_V	0,96	-0,16	-0,14
Cr_V	-0,03	0,48	-0,82
Cu_V	0,91	-0,03	-0,08
Ni_V	-0,24	0,61	0,59
Pb_V	0,97	-0,10	-0,14
Zn_V	0,94	-0,06	-0,19
Eigenvalues	4,987	3,381	1,417
% of variance	45,334	30,737	12,880
Cumulative %	45,334	76,071	88,951

The values in fat are significant, TE_V: Trace Element in vertisol, TE_E: Trace Element in wastewater.

The second association is represented by As_E, Cr_E, Cu_E and As_V, Ni_V. And the third association, binds Cd_W with Cr_V and Ni_V. These two associations highlight the connection of the contents of these three TEs: As_V, Cr_V, Ni_V with the TEs contents in sewage. These two associations are well confirmed by the dendrogram (Fig. 3).

Therefore, the TEs contents raised on the studied profile have a various sources, lithogenic influenced by rock-mothers contents and exogenous due to various anthropical activities (Ould Arby *et al*, 2013; Wu *et al*, 2013; Chao *et al*, 2014). The lithogenous sources influence principally the TEs contents on lower horizons. The exogenous sources related to the sewage application are strongly influenced the contents of these micropollutants (explain 43,60 % of the original variance) and these related to other anthropic factors, diffuse pollution, and various agricultural practices (45,33 % of the original variance). The exogenic contributions are significant for Zn, Cd, Cu, and Pb. These TEs show also strong accumulations in the up-soil.

5. Conclusion

The chemical assessments of TEs on the studied profile show a clear accumulation of Zn, Cd, Pb and Cu in the cultivated horizon. These accumulations are related to exogenous sources. The Multivariate Analysis enabled us to distinguish various sources from the pollutants in studied soil. These sources are allotted to sewage and to others agricultural practices (fertilizers, pesticides, etc) and a diffuse pollution.

The sewage application on this cultivated soil in the Ourzirha area did not cause significant accumulations for the various analyzed pollutants, except for Zn which showed a great content of more than 294 mg/kg, in the Ap horizon.

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