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Quantification and Identification of Road Organic Matter in an Absorbing Storm Basin, RN 20 Olivet-Orléans, France.

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Abstract

The deterioration of the quality of superficial and subsurface waters by motorway organic pollution is a problem of great concern nowadays. The absorption of road runoff waters through sinkhole clay filled in a karstic area has been proposed as a way to the attenuation pollution. The groundwaters near of surface are very vulnerable at this pollution. The study of the storm basin of Belle-Croix (RN 20 Loiret) indicates a diminution of DOC levels through the first meter of infiltration in sinkhole, and then little change occurs down 5 meters. However only the > 10 KD (10 nm) organic fraction is retained. This fraction is weakly fluorescent and should correspond to black carbon (BC) matter associated to clays as it is suggested by Electron Microscopy in Transmission EMT observation. The < 10 KD fraction which are the more fluorescent account for up to 80 % of total DOC at 5 meter depth, at the contact with the limestone.

Keywords: road runoff, groundwater, karst, ultrafiltration, DOC, fluorescence, BC, EMT

1. Introduction

Knowledge about the organic chemical composition of the soil and water near highway surface is of crucial importance when studying soil behaviour such as leaching, sorption, desorption and mineralization processes. Because if we understand the behaviour of soil against organic matter we will can stopped or limited the contamination, and therefore the groundwater will be preserved and can be used to assess the security of drinking water supplies.

The leaching up of the roads by rainwater may introduce into environment a large quantity of organic matter produced by the vehicle traffic [1-2-3]. The adjacent groundwater is very vulnerable at this pollution. These latter flows without particular attenuation via karstic sinkhole [4]. One of the interests that urged us to study the rain water in the retaining basins resides in the fact that, they transport polluting elements which derive from the leaching up of the roads, and which either infiltrate in the underground which provides us with drinking waters, or is retained in the ground [5-6-7]. The complexity of road water consists in its load of heavy metal [8-9] and particulates of black carbon (BC). The BC defined as a continuum of partly charred plant material through char and charcoal to graphite and shoot particles re-condensed from the gas phase [10]. BC represents a refractory and chemically complex product of incomplete combustion of fossil fuels and biomass, including vegetation burns and forest fires [11-12-13]. The BC was found anywhere in the earth planet, thus in the atmosphere [14], ice [15], sediments [16], rivers [17], soils [18] and ocean [19]. A study [15] shows that the quantity of modern BC produced are 50 to 260 teragrams (Tg = 10^{12} g) of carbon per year (Tg C/year) from biomass burning and 12 to 24 Tg C/year from fossil fuel combustion. Recently, BC has emerged as a major contributor to global climate change second only to CO_2 as the main driver of change [20]. Also, BC is chemically inert and has a long atmospheric lifetime [21], furthermore, it is a poorly understood type of organic carbon [22], but it is present in almost all environmental systems. Due to its complexity, Preston and Schmidt [23] indicate that BC decomposes very slowly, with turnover on millennial timescales (5–7 ky). In this general context, we sought to evaluate the behaviour of the dissolved organic load of rainwater at the time of the infiltration in karst sinkhole. The study is based on the taking away of water by porous ceramics cups introduced vertically into the ground of absorbing basin. The organic load were quantified by the proportioning of dissolved organic carbon (DOC), the measurements of electric conductivity and the intensity of fluorescence in all samples and fractions obtained by tangential ultrafiltration. The identification of nanoparticules of black carbon (BC) in these samples was observed by Electron Microscopy in Transmission (EMT), a technical which is widely used for particle characterisation [24]. Our aim is to appreciate the autoepurator role of the soil vis-à-vis the organic pollution of road origin, at the time of the fast infiltration of this matter through sinkholes in the karstic area.

2. Area study of Belle-Croix basin

The site on which we fulfilled the study is the basin of the exchanger of Belle-Croix (Olivet, Loiret, Orléans, France), on the edge of the RN 20, south of Orléans. It is a retaining basin of rainwater, of the principal pavement and the slip road of the exchanger. This water arrives in the basin by only one culvert (1m of diameter) and is spread out thereafter towards the zones of loss where the porous ceramics cups were installed. This basin was arranged by the Departmental Direction of Equipment (DDE) during the eighties. It has a circular form, 50 m of diameter at the bottom and 8 m of depth. It is dug in the glacis' alluviums of Olivet to the marly summit of Beauce's limestone. Geophysics (electric surveys, seismic refraction) studies were carried out at the bottom of the basin. They show the presence of three different layers (figure 1); the first one is one meter thick, the second is four meters thick and the third starts at around five meters of depth. The surface layers are humid (low electrical resistance) and less dense (low speed of the seismic waves).
The sounding was made manually by an auger at different depth in collapses area. That shows the presence of heterogeneous sediments as described in figure 1. The top of the succession shows 1 m thick black soil sands and clay, overlying the 1.75 m thick layer which consists of a mixture of sand-clay with pebbles. Below, three thins beds 30 cm each, composed of white limestone and mud, red clay and beige mud with flint. At the bottom, there is 1.30 m thick crumbly limestone rich in water. From 5 m down, we start to dig in hard limestone.

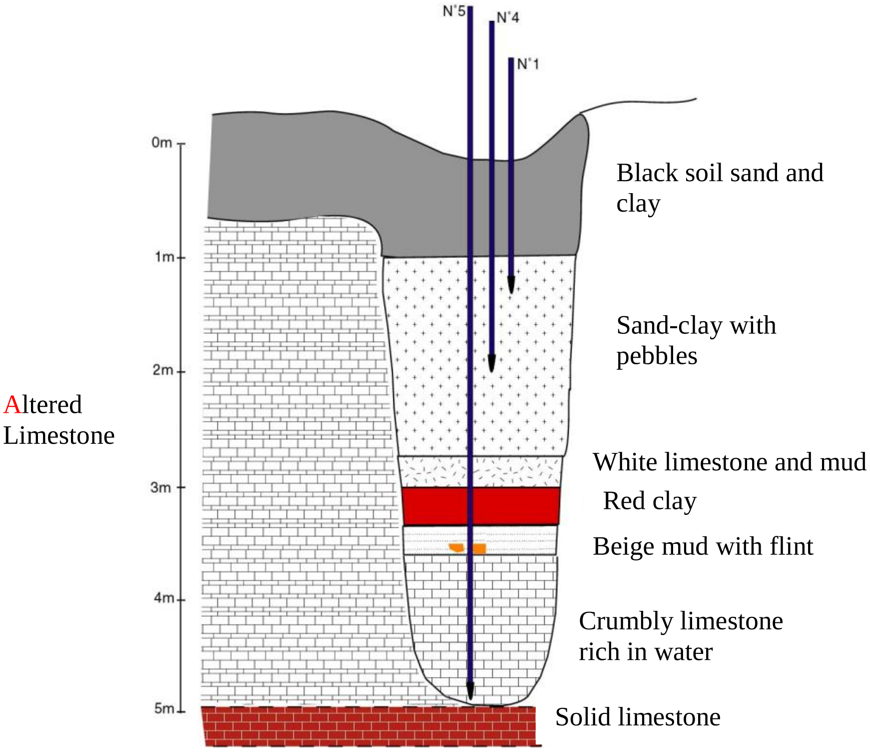


Figure1: Schematic stratigraphic log in the sinkhole and porous ceramics cups installation (N°1,4 and5)

3. Local geology and hydrogeologic context

The basin is located on the first old terrace of the Loire River (figure 2), more precisely on the one deposited at Riss, and then dug at the interglacial Riss-Würm period. This one overlies the sand of Burdigalian, which represents a lenticular stratification, with oblique laminations and traces of channels. Below we find Beauce limestone of Aquitanian age, deposited in a lacustrine environment, with a marl lenses and a crossing millstone. Limestone decarbonation allowed the formation of a green clay layer. This limestone represents an important potential of water resources in the area (Note geological map La Ferté-Saint-Aubin to 1/50 000, 1970). The groundwater exploitation belongs to three aquifers narrowly connected (figure 3):

- Modern alluviums of the Loire;
- Sand and clay of Sologne in the south of the study area;
- Limestone of Beauce.

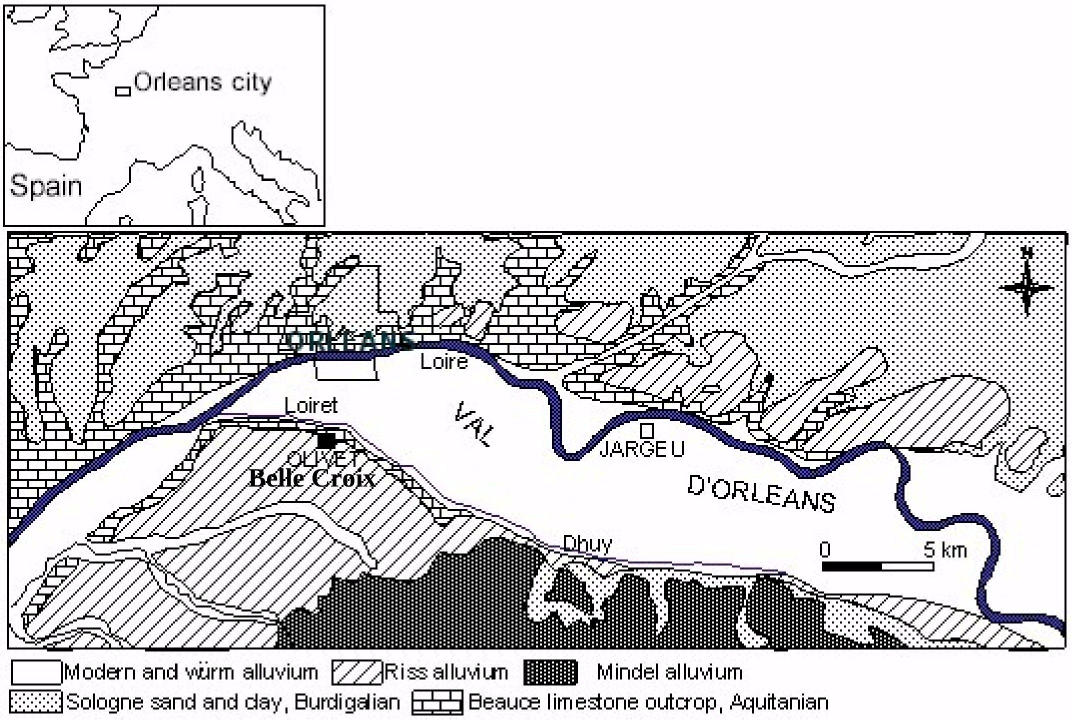


Figure 2: Simplified geological zones in the study area [25]

These waters are closely related to those of the Loire River (at least in the Val of Orléans) [25]. Those have different physiochemical qualities in relation with the circulation conditions, the reservoir lithological nature, and with the mode of feeding (weather, impacts of man...). In the following is a description of the aquifers.

- Water in the modern alluviums of Loire River:

Water circulates in the gravels and coarse sands (Jards) located at the bottom of the alluvial massive. They belong to a semi confined aquifer whose high pressure is assured by the covering of the clayey sands and the silt.

- Water in the sandy formation:

Waters are divided into superposed aquifers separated by beds of clay. An aquifer system with artesian wells was known in La Ferté-Saint-Aubin.

-Water in the Beauce limestone:

With a saturated height more than 100 m, this formation remains the principal potential reservoir. We subdivide it in three aquifers.

1. An unconfined aquifer in the north of the Loire River flows towards the Val between +100 and +95 levels following a perpendicular direction with the River.
2. In the Val, the aquifer is generally captive either under alluviums covering, or under the Orléanais marls. The reservoir is generally permeable, and crossed by karstic networks, partially plugged by sand, silts and gravels.

3. A confined aquifer in the Beauce formations under Sologne. Its equilibrium level varies between +110 and +90 resumed a flow towards the Loire River and a load loss in Cosson. It should be noted that the area is known by vaults collapses of karstic networks (Jargeau, Darvoy), which are announced each year in the low water period and of high water level. The swallow hole put in direct connection the groundwater with various pollution sources. On regional scale, the pieozometric map (figure 3) shows a very low hydraulic gradient (generally towards the west). On the other hand, the same behaviour is shown in local water table contour map (figure 4) which consist an additional obstacle for organic matter migration.

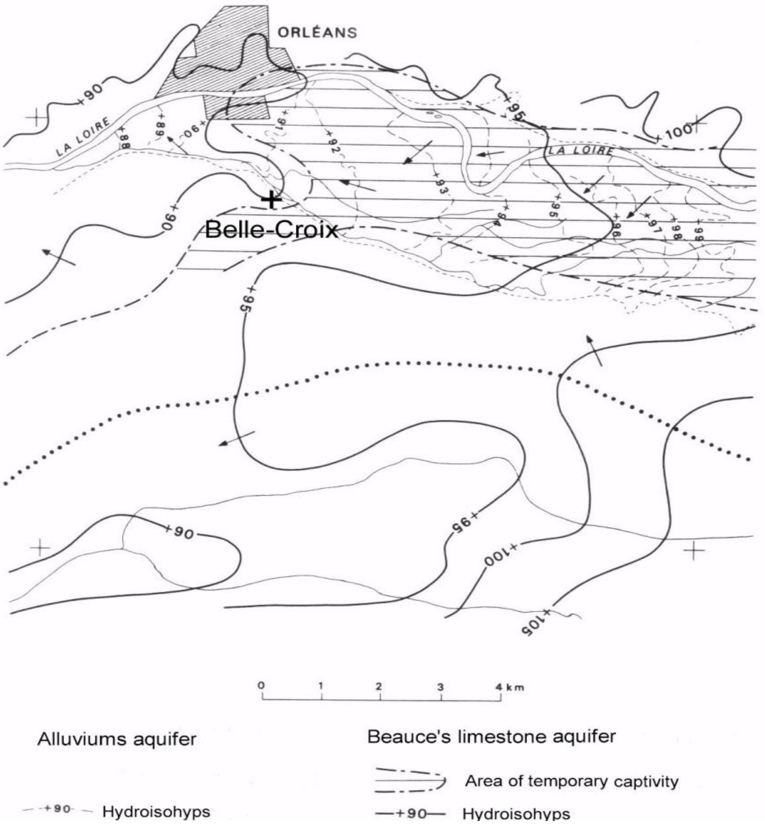


Figure 3: Piezometric map of the south Orléans city [26]

4. Detailed piezometric map

In order to improve comprehension of the groundwater circulation around the site, the realization of more detailed piezometric map (figure 4) than the one available [26] was initiated by measurements of water depth in wells and boreholes [27]. The precise topographic survey of the site was carried out with a differential system GPS, and was supplemented by levelling with the theodolite.

5. Material and method

It is a PVC pipe height according to the depth of the taking away samples (from 1 to 5 m in this study), with a ceramic fixed at the extremity. The pipe is vertically introduced into hole which is dug in the ground from which we want to extract the solution. Air was pumped from the cups using a small hand peristaltic pump (Master Flex) supplied with a battery of 12 V. The cups must be left under pressure before samples were collected, in order to have a solution circulation from the ground towards the interior of the ceramics. Water collected was pumped from down to the glass bottles through Teflon tube. It was checked that the passage through ceramics does not involve a loss of DOC in water filtered beforehand.

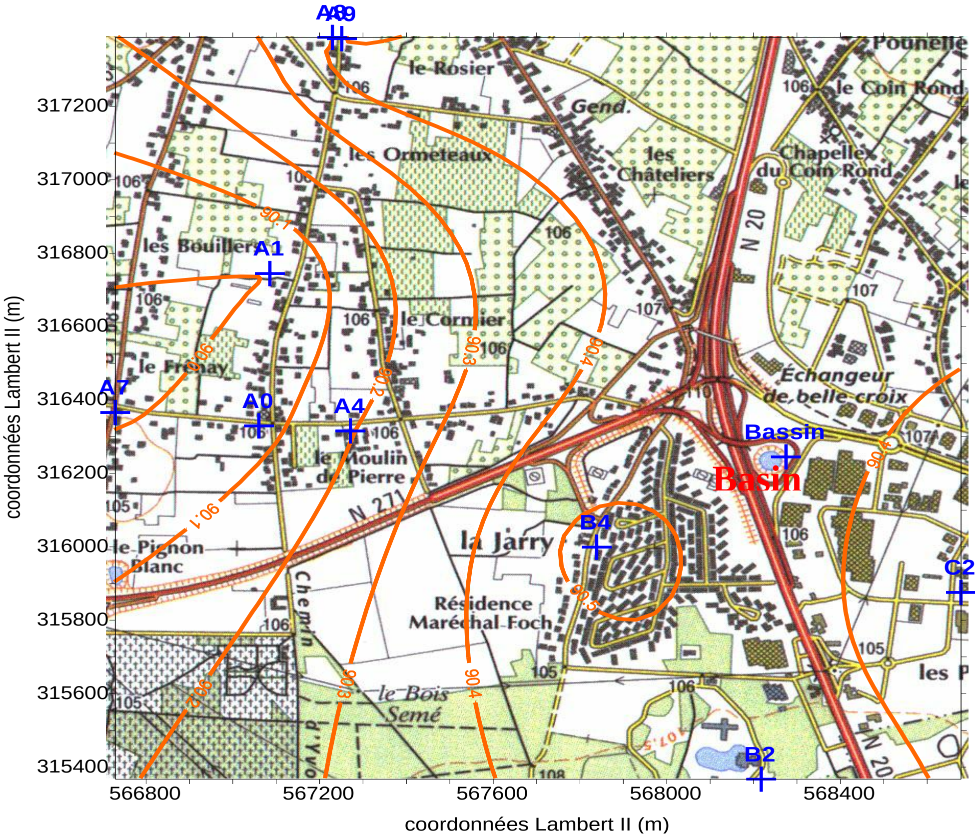


Figure 4: Piezometric and IGN map of the area close to the site

The ceramics which we used have 63 mm for external diameter, a height of 88.20 mm and 5.75 mm thick wall. That gives it a wide surface of contact with the ground. Moreover, it is airtight. Its micro porosity is of 3µm, hydraulic conductivity is K = 9.510^{-6} cm/s (average value), and its weight is 160 g. Ceramics are provided by the company Nardeux-Humisol [28], then by SDEC (Reignac/Indre, France).

The water was taken away on the:

- Culvert waterways from the road to the basin,
- Sinkhole (near surface and porous ceramics cups)

The conductivity was measured in situ with an electrical conductivity meter TetraCon®325 (WTW).

In order to better understand the increase of conductivity, Ca^{2+}, Na^{+}, Cl^{-} and Zn^{2+} were analyzed using ICP (Induction Coupled Plasma), Ion Chromatography (761 COMPACT IC) and alkalinity (Gran method). The results are illustrated in table 2. Before analysis, all the samples were filtered on glass-fiber (Whatman GF/F) with a diameter of 47 mm and a porosity of 0.7µm. The filtered samples were kept at 2ºC until analysis. Each sample was acidified with HCl to prevent possible precipitation of metals and to eliminate the mineral carbon. To quantify dissolved organic carbon (DOC), we used the SHIMADZU TOC 5000A analyzer, equipped with automatic injection via microliter syringe useful for degasification and measuring. The results are illustrated in table 1 and 3. The fluorescence manipulation consists to excite the sample molecules, with a precise wavelength. Each molecule absorbs luminous energy and changes its configuration slightly, then reemits a light radiation with a higher wavelength. For each family of molecules, there is a wavelength of maximum excitation and a wavelength of maximum emission. The fluorescence is measured by fluorimetric detector for liquid chromatography (Shimadzu RF 530). The wavelength of excitation and emission were respectively fixed at 345 nm and 415 nm [29]. The calibration was carried out with a salicylic acid solution 0.2 mg/l, which gave an intensity of fluorescence equal to 0.022855 between 300 and 400 nm, corresponding to 1 unit of fluorescence. Two levels of tangential ultrafiltration (10000 and 1000 Daltons) were made in the laboratory on all the samples except rain of the 4/26/03. The system used is a Millipore Minitan system equipped with sheets for the 10000 Daltons (PLGC) and with the plate shape filter for the 1000 Daltons (PLAC). Both of them are regenerated with cellulose. Conservation in distilled water and a poison (NaN_3) are made after each use in order to prevent any bacterial attack.

6. Results

6.1. Filtration GF/F

During the rain, we didn't have a water sample of culvert. Figure 5 and Table 1 show that DOC concentration and decrease of the fluorescence intensity as a function of depth. The decreasing is rapidly starting from 2m. On the contrary, electric conductivity shows an increase evolution as a depth (Figure 6). Thus, we note a considerable reduction in the DOC and fluorescence intensity with a concomitant increase of electric conductivity along the first 2 meters of infiltration in the sinkhole, which underlines the growing degree of water interaction with the karstic filling.

Table1: DOC, fluorescence intensity and electric conductivity (CC ceramic cup)

	DOC mg/l	fluorescence	Conductivity µS/cm
CC 1m	8.5	0.35	250
CC 2 m	7.2	0.27	255
CC 5m	3	0.12	380

Table 2: Chemical analyses of road water

Samples	Zn ppm	Cl^- mg/l	Na^+ ppm	Ca^{2+} ppm	Alkalinity mol/l
Culvert	$2\ 10^{-3}$	29.8	26.54	26.21	$4.0\ 10^{-3}$
Sinkhole 0 m	$4\ 10^{-4}$	6.1	4.69	12.21	$0.5\ 10^{-3}$
CC 1m	$6\ 10^{-4}$	9.6	13.35	54.83	$2.7\ 10^{-3}$
CC 2m	$6\ 10^{-4}$	9.4	12.09	78.82	$1.9\ 10^{-3}$
CC 5 m	0	7.8	13.05	80.61	$4.4\ 10^{-3}$

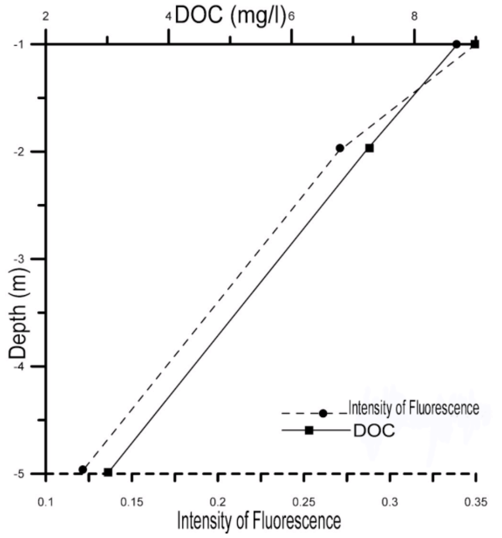


Figure 5: DOC and Fluorescence intensity as a function of depth.

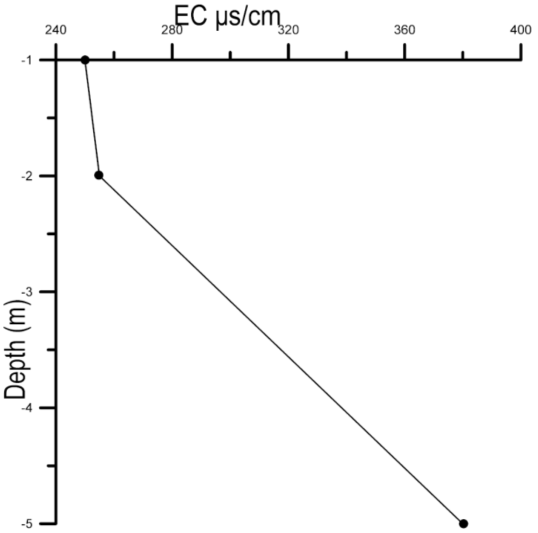


Figure 6: Electric conductivity as a function of depth.

6.2. Ultrafiltration

DOC concentration was greatest at the start of the leaching of road (Table 3 and figure 7). The rain were very aggressive, leached up the road at the upstream of the basin, and water charged in elements, quickly took their way without any natural or artificial attenuation, towards the basin through the culvert. In the depth, the same evolution is shown here (figure7). Fractionation by ultrafiltration shows in this type of samples (table 3), that the essence of fluorescence is carried by the fraction of one KD (figure 8). That means reduction in depth of DOC especially relates to the organic fraction higher than one KD at the time of water infiltration in the first two meters (figure 7). The DOC in the fraction of one KD is practically stable along the infiltration.

As from 2 m to 5 m of depth (contacts with solid limestone), samples show that the reduction in the DOC and fluorescence continue but with a low intensity.

Table 3: DOC and fluorescence intensity of the samples

	DOC mg/L			Intensity of fluorescence		
	GF/F	10KD	1KD	GF/F	10KD	1KD
Culvert	42.9	36.8	16.6	2.38	0.94	0.34
Sinkhole 0m	6.9	4.2	2.1	0.32	0.30	0.20
CC 1m	4.9	4.0	2.0	0.29	0.27	0.19
CC 2 m	4.2	3.4	1.7	0.20	0.19	0.15
CC 5m	3.2	2.6	1.3	0.18	0.12	0.12

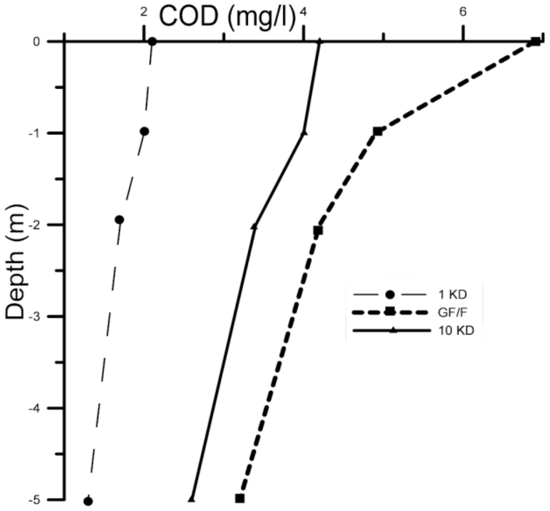


Figure 7: DOC in various fractions as a function of depth.

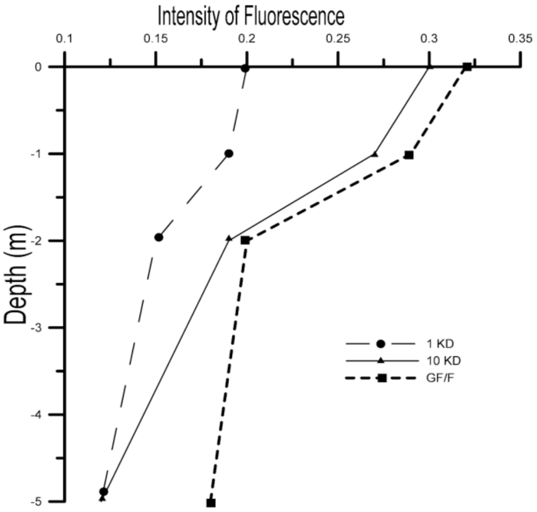
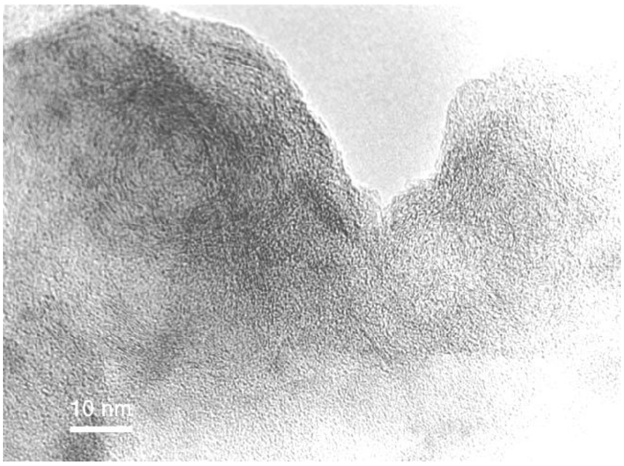


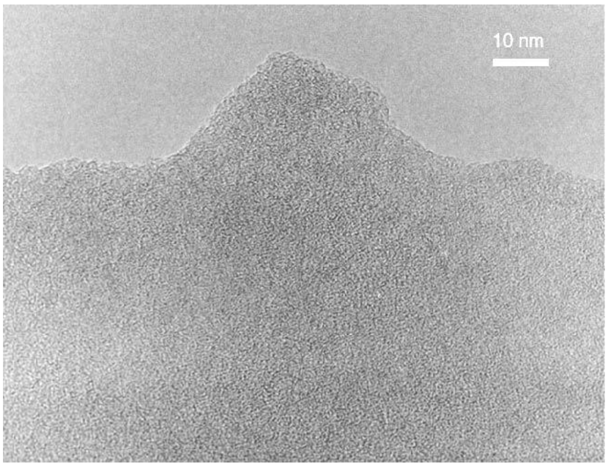
Figure 8: fluorescence intensity of various fractions as a function of depth.

6.3 Microscopic observation

The observations carried out under the Electron Microscope in Transmission (EMT) show the presence of black carbon particles (BC) (photographies 1 and 2) and the association of organic matter with clays. Our observations were made on particles sticking on the Durapore membrane (0.45) putting in alcohol and distilled water.



Photography 1: Black carbon in the fraction >45µm



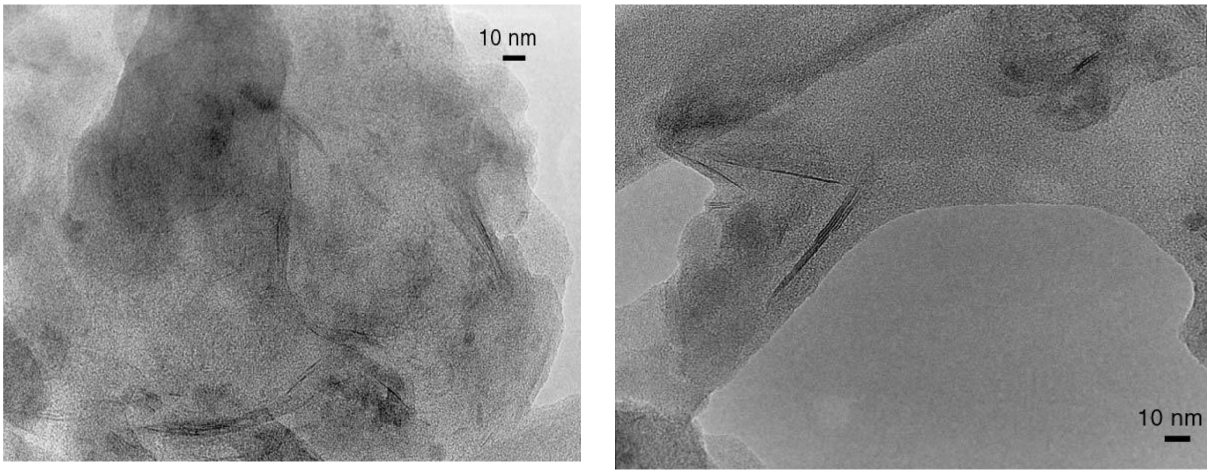
Photography 2: Amorphous carbon in fraction 0.45 µm-10 KD.

7. Discussion

As previously described, we observed a reduction of DOC up to 3.5 mg/l and fluorescence along the depth in the infiltration zones.

Conductivity measurements show an increase with depth, which testifies the interaction between infiltration water and the soil. Na^+ and Cl^- are the principal elements that causing the increasing of conductivity as suggested by previous study [27]. Therefore, this latter has been considered in comparison to the contents of

NaCl in water of the marsh that underwent a strong increase in evaporation. However, Na^+ and Cl^- are brought by the culvert during winter following the use of deicing salt. In the contrary, an increase in Ca^{2+} and alkalinity is observed at the time of the infiltration, we can conclude that the increase in conductivity is actually due to the dissolution calcareous fraction of the karstic filling. The dissolution of limestone is due to the oxidation of the organic matter after passage by material filling sinkhole [25].



Photographies 3 & 4: Association of clays and amorphous carbon in fraction 0.45µm- 10 KD

We can also explain this reduction in the DOC content by the complexation of the organic matter with cations present in the soil. Zn^{2+} decrease with depth as well as the organic matter, suggested that this heavy metal are likely to be strongly retained by BC present in roadwater. The traffic emission is also the main anthropogenic source of Zn^{2+}. The microscopic observations show the presence of amorphous carbon in ultrafiltration fractions (photography 2). However, we note few black carbon particles type with a purple structure characteristic of "slice of purple onion" (photography 1), resulting from fumes of diesel engine, and friction tires roads. On the contrary carbon matter-clays agglomerations (photographies 3 and 4) are rather abundant which explain the reduction of DOC with the depth.

Conclusion

The results of the present study show that the organic pollution fraction > 1KD (≈1nm) of road origin, is filtered naturally by the soil. The risk to see this fraction infiltrating to groundwater is very weak. The ultrafiltration process shows that the DOC decrease at the first meter of soil cross section is due to the hard diminution of the organic fraction between 0.45 and 10 KD (≈10nm). The no decrease of water fluorescence in the same soil section indicates that the lost organic fraction is less fluorescent. Moreover, the weak hydraulic gradient shown by the local piezometric map appears as an additional barrier in front of the fast dispersion of the organic pollution particles. This set of observations did consider the clay filled in a karstic area as a reactor particularly interesting for the transfer organic matter through a filling sinkhole. Ultrafiltration makes possible to quantify the organic proportion of carbon retained in the ground, and to specify the fluorescence size and property of the various molecular fractions.

References

1. Crabtree B., Moy F., Whitehead M., Roe A., *Water. Environ. J.* 20 (2006) 287-294.
2. Ruellan S., Cachier H., *Atmos Environ.* 35 (2001) 453-468.
3. Thrope A., Harrison R.M., *Sci. Total. Envoron.* 400 (2008) 270-280.
4. Stephenson J.B., Zhou W.F., Beck B.F., Green T.S., *Eng. Geol.* 52 (1999) 51-59.
5. Legret M., Le Marc C., Demare D., *Bull. Labor. P et Ch.* (1997) pp. 101-115.
6. Pitt R., Clark S., Field R., *Urban Water.* 1 (1999) 217-236.
7. Pagotto C., PhD Université de Poitiers. 1999 316p.

8. Pérez-Martínez P. J., Miranda R. M., Nogueira T., Guardani M. L., Fornaro A., Ynoue R., Andrade M. F. *Int. J. Environ. Sci. Technol*. 8 (2014) 2155-2168.
9. Khan A. B., Kathi S., *Int. J. Environ. Sci. Technol*. 11 (2014) 2259-227.
10. González-Pérez J.A., González-Vila F.J., Almendros G., Knicker H., *Environ. Int*. 30 (2004) 85-870.
11. Wang S.W., *Environ Mont Assess*. (2009) Doi 10.1007/s10661-009-0814-z
12. Borchard N., Ladd B., Eschemann S., Hegenberg D., Möseler B.M., Amelung W., *Geoderma*. 232-234 (2014) 236-242.
13. Wang Q., Schwarz, J.P., Cao J., Gao R., Fahey D.W., HuT., Huang R.J., Han Y., Shen Z., *Sci. Total. Environ*. 479-480 (2014) 151–158.
14. Gatari M.J. Boman J., *Atmos Environ*, 37 (2003) 1149-1154.
15. Masiello C.A., Druffel E.R.M,. *Science*. 280 (1998) 1911-1913.
16. Accardi-Dey A., Gschwend P.M., *Environ. Sci. Technol*. 36 (2000) 21-29.
17. Kuhlbusch T.A.J., *Science*, 280 (1998) 1903-1904.
18. Bucheli T.D., Blum F., Desaules A., Gustafsson O., *Chemosphere*, 56 (2004) 1061-1076.
19. Mannino A., Harvey H.R., *Limnol Oceanogr*.49 (2004) 735-740.
20. Chakrabarty R. K., Arnold I. J., Francisco D.M., Hatchett B., Hosseinpour F., Loria M., Pokharel A., Woody B.M., *J Quant Spectrosc Radiat Transf*. 122 (2013) 25-30.
21. Zhang X., Rao R., HuangY., Mao M., Berg M., Sun W., *J. Quant Spectrosc Radiat Transf*. 150 (2015) 3-11.
22. Hamilton G.A., Hartnett H.E., *Org. Geochem*. 95 (2013) 87-94.
23. Preston C.M., Schmidt M.W.I., *Biogeosciences*. 3 (2006) 397–420.
24. Gontard L.C., Knappett B.R., Wheatley A.E.H., Chang S.L.Y, Fernández A., *Carbon*. 76 (2014) 464-468.
25. Albéric P., Lepiller M., *Wat. Res*. 32 (1998) 2051-2064.
26. Desprez N. Gigout M.. Carte Géologique à 1/50 000, La Ferte –ST- Aubin (1970) XXII-20.
27. Albéric P., Noel H., Boussafir M., 20th IMOG, Nancy, September (2002).Vol. 2: 293-294.
28. Baran N., PhD Universiy of Orléans. (1996) pp 291.
29. Zumstein J., Buffle J., *Wat. Res*. 23 (1989) 229-239.

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