Relations between organic carbon and chemical/biological oxygen demands in French rivers

Relation entre le carbone organique et les demandes chimique et biologique en oxygène dans des rivières et fleuves français

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RÉSUMÉ

L'utilisation de substances dangereuses pour l'environnement (chrome, mercure) pour la détermination de la Demande Chimique en Oxygène (DCO) est un problème, notamment pour la gestion des déchets. Or ce paramètres est largement utilisé pour l'estimation du niveau de pollution des masses d'eau. En utilisant les bases de données des Agences de l'Eau, des relations ont été cherchées entre la teneur en carbone organique (COT) et la DCO pour plusieurs rivières et fleuves français, cela afin d'étudier la complémentarité des deux paramètres. Des relations linéaires ont été trouvées avec des coefficients de détermination satisfaisant (> 0.45) pour certains cours d'eau (Rhône, Saône, Marne) mais pas à l'échelle du bassin versant. Pour la Moselle, deux relations ont été obtenues, l'une en amont et l'autre à l'aval de sa confluence avec la Meurthe, son principal affluent dont les eaux ont des caractéristiques très différentes. En parallèle, il semble difficile d'établir une relation entre la Demande Biologique en Oxygène et le COT.

ABSTRACT

Questions are arising about the use of environmentally dangerous substances such as chromium and mercury for the determination of the Chemical Oxygen Demand (COD), which is largely used for water quality assessment. Using the databases of the Regional Water Authorities (Agences de l'Eau) relations have been sought for between the total organic carbon (TOC) content and COD for several main French rivers, order to assess the complementary of both parameters. Linear relations have been found with reasonable coefficients of determination (> 0.45) over whole watercourses such as Rhône River, Saône River and Marne River, but not on whole watershed (Rhône River watershed for example). In the case of the Moselle River, two relations were found, upstream and downstream its junction with its main tributary, whose waters modify strongly the carbon pollution pattern. In parallel, no obvious relations were found between TOC and the Biological Oxygen Demand (BOD).

KEYWORDS

Chemical oxygen demand, coefficient of determination, database,Total organic carbon.

1 INTRODUCTION

Chemical Oxygen Demand (COD) is largely used to characterize the pollution of a water body and of effluents from wastewater treatment plants. It is defined as the quantity of oxygen necessary to fully oxidize an organic substance according to the following reaction

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right) O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right) H_2O + cNH_3$$

The classical method to measure COD is based on potassium dichromate under acidic conditions, often in presence of a mercury salt used as a catalyst. One of the drawbacks of the method is the use of dangerous reagents, which may led to the prohibition of the present COD method. Total Organic Carbon (TOC) is also obtained by oxidation but it is the amount of CO_2 which is measured. The measurement can be fully automated and does not require dangerous reagents. However neither COD nor TOC enable to estimate the biodegradability of the carbonaceous pollution: this is obtained through the Biological Oxygen Demand (BOD) test, which lasts five days in general.

COD, TOC and BOD are not interchangeable. The question arises what information would be missed if COD is not used anymore as one of the parameters to estimate water pollution. As a large pool of data on COD, TOC and BOD are available in the databases on French river water quality, an evaluation of the relation between TOC and COD / BOD is proposed.

2 MATERIALS AND METHODS

Data (dissolved organic carbon, biochemical oxygen demand, chemical oxygen demand) were retrieved from the websites of the French Agences de l'Eau for several rivers. The rivers differ In terms of watershed land use and geographical and climate conditions. Only validated data were considered. The time range varies depending the river: 194 to 2012 for the Moselle, 2010 to 2013 for the Rhône River basin, 2010-2014 for the Marne River, etc. Table 1 summarizes the characteristics of some of the rivers considered in the survey as well as the websites. When the values for COD and BOD are lower than the limit of quantification (LOQ), the LOQ has been used.

Table 1: River characteristics and corresponding database website

River name	Length (km)	Receiving body	Website
Moselle	560 (total) 314 (France)	Rhine River	http://rhin-meuse.eaufrance.fr/
Marne	514	Seine	http://www.eau-seine-normandie.fr/
Rhône	812 522 (France)	Mediterranean Sea	http://www.rhone-mediterranee.eaufrance.fr/
Saône	480	Rhône	http://www.rhone-mediterranee.eaufrance.fr/
Durance	324	Rhône	http://www.rhone-mediterranee.eaufrance.fr/
Dordogne	483	Garonne / Atlantic Ocean	http://adour-garonne.eaufrance.fr/
Aude	224	Mediterranean Sea	http://www.rhone-mediterranee.eaufrance.fr/
Vilaine	218	Atlantic Ocean	http://osur.eau-loire-bretagne.fr/

3 RESULTS

It was not possible to find relation for each individual sampling station, as the range of variation of COD, BOD or TOC was too small. Therefore average values and standard deviations were calculated for each sampling station. Figure 1 summarizes the results obtained between the average COD and TOC for the Rhône River and its two main tributaries (Saône River and Durance River). The

coefficients of determination for linear relations varies between 0.45 (Durance River) and 0.64 (Saône River), while the slopes are in the same order of magnitude. The Durance River carries less carbon pollution than the Rhône River and the Saône River. For the Moselle River, the junction with the Meurthe River (main tributary of the Moselle River) is a key feature in the relation between COD and TOC (Figure 2), linked to a probable change in the chemical composition. For the Marne River a global linear relation was obtained for the whole watercourse, with a coefficient of determination of 0.81. The coefficient of determination is smaller for the Aude River (0.26) but there are only eight stations.

In spite of the number of available station (19), a poor correlation was found between BOD and TOC for the Dordogne River. No correlation was found for the Vilaine River (11 stations).

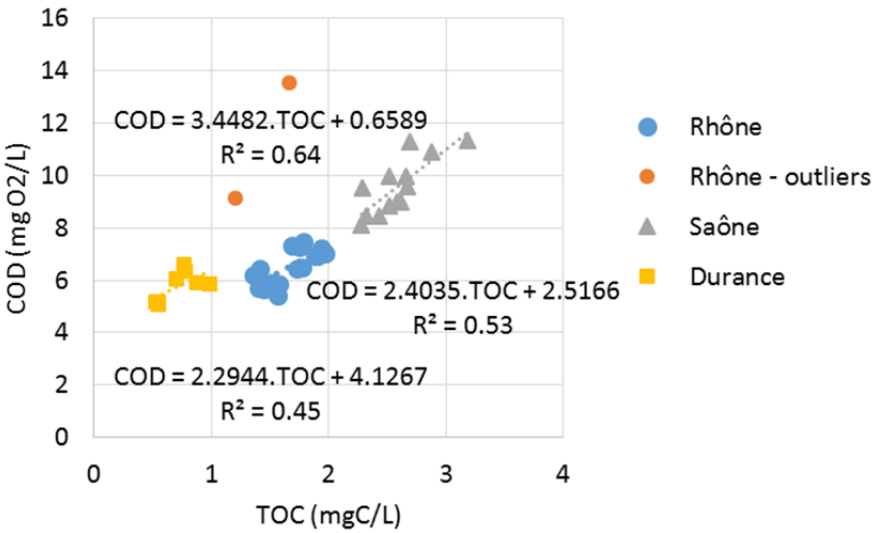

Figure 1: COD versus TOC for the Rhône River and its two main tributaries

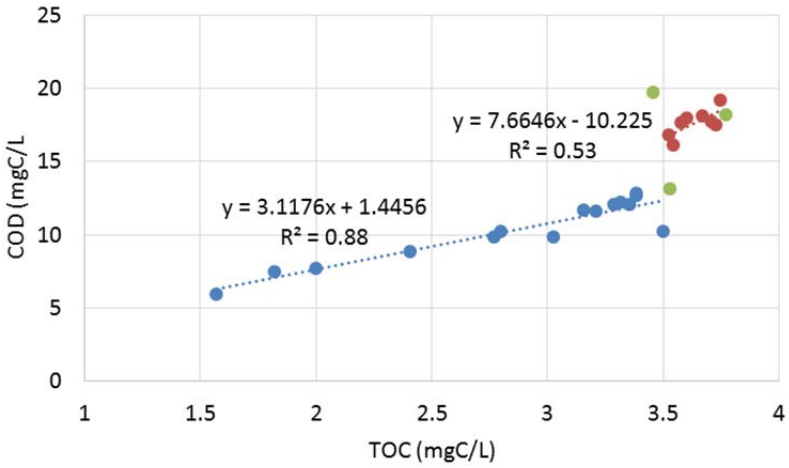

Figure 2: COD versus TOC for the Moselle River, upstream (in blue) and downstream (in red) of the junction of the Meurthe River.