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The impact of household and similar solid wastes on Kara River quality due to their potential to release nitrogen

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This study purpose to assess the real share of nitrogen the household and similar solid wastes can release in direct contact with water. The maximum amount of nitrogen could release was determined by a leaching test. The concentrations of total and organic nitrogen, ammonium and nitrates ions and the pH values were measured in the initial and incubated juices. The leaching test showed that the solid waste can release 261 mg of total nitrogen (TN) in water for 1 kg of dry waste. This amount of total nitrogen corresponds to 240.1 mg of organic nitrogen (OrgN), 17 mg of ammonium nitrogen ($NH_4^+ - N$), 3.3 mg of nitrate nitrogen ($NO_3^- - N$) and 0.4 mg of nitrite nitrogen ($NO_2^- - N$). The monitoring of the nitrogen biotransformation has shown a good disposition of the organic nitrogen to be transformed into ammonium ions and the ammonium ions into nitrate ions. By 2025, the forecast calculations of nitrogen input into the river's waters show that the zone downstream of the river and the heart of the city will be more impacted by nitrogen pollution. The expected variations in total nitrogen (TN) and nitrate ion ($NO_3^- - N$) concentrations are respectively between 6.49 and 8.85 µg/L and 0.35 and 0.87 µg/L. These concentrations are considered weak but by interacting with the release of sediments during the dry season they can participate at the eutrophication process. Leaching and incubation test can be used to forecast the negative impact of solid waste on the river.

Keywords: Solid waste, nitrogen, biotransformation, river water quality, eutrophication.

INTRODUCTION

Surface waters including lakes, lagoons and rivers in urban and peri-urban areas are generally subject to releases of anthropogenic pollutants, particularly wastewater and solid wastes (Earnhart, 2013; Vrzel et al., 2016; Li et al., 2017). These discharges have a negative impact on the quality of water resources and most often

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result in eutrophication of continental waters (Mandaric et al., 2018; Wang et al., 2019). Indeed, eutrophication is a phenomenon resulting from the natural enrichment or anthropogenic pollution of inland or coastal waters in nutritious mineral salts (phosphates, nitrates, etc.). The assessment of eutrophication is generally done by *in situ* measurement of the concentrations of the main mineral salts in the waters exposed to different discharges (Ménesguen and Lacroix, 2018).

The existence of different sources of nitrogen pollution makes it difficult to measure *in situ* the real contribution of each source (Puckett, 1995; Kroeze et al., 2016; Yang et al., 2016). To better assess the individual contribution of each source, an upstream access on the behaviors of the identified source can then facilitate the analysis and the interpretation of its impact on surface water (Bøgestrand et al., 2005; Pinto et al., 2012). The sources of pollution often identified are chemical fertilizers, sewage and sludge from industrial, domestic or urban activities (Singh et al., 2005). In the last three decades, the amount of solid waste, increasingly complex produced in all countries has steadily increased. This is particularly observed in cities in developing countries (Chen, 2018). However, management systems and practices are very different from the same country (Ferreira et al., 2017). These differences are related to the technologies used for the collection and treatment of solid waste, the availability of human and financial resources and also socio-cultural and geographical contingencies in each city. Thus, the cities are most often faced with a problem of depositing solid waste in the watercourses (Segbeaya et al., 2012). However, they have been shown to be rich in nitrogen (N) and phosphorus (P) because of changing clothes and consumption patterns (Sokka et al., 2004).

In the biodegradable solid waste matrix, the mineral elements (N and P) are found in a large extent in organic compounds in the form of organic nitrogen and phosphorus (Taherymoosavi et al., 2017). These forms of nitrogen and phosphorus are released during biodegradation processes accelerated by the initial moisture in the waste or when the waste is in contact with water (Parodi et al., 2011). Thus, the continuous discharge of biodegradable solid waste in the water can contribute to the increase in the concentrations of the different forms of nitrogen and phosphorus in these waters. The release of various forms of nitrogen and phosphorus (mineral and organic) present in solid waste is conditional by their potential for biodegradability and water solubility (Zeng et al., 2012, Baccot et al., 2017). Similarly, the subsequent transformations of the released nitrogen and phosphorus are linked to the diversity of bacteria present in the environment of waste evolution (Vargas-García et al., 2010).

According to Parodi et al. (2011), the accelerated leaching test of organic waste, potentially rich in microorganisms can provide access to water-soluble compounds that can be released by the solid waste. This test carried out with water highlights the intensity of biological activity within the waste matrix when in contact with water and also its biodegradation behavior. It then makes it possible to have access to the nitrogen and phosphorus that can be released by the waste and to make assumptions about their subsequent transformations and their interactions with the receiving environments, particularly surface water such as rivers (Baburina and Rengel, 2011). The use of this test and the monitoring of the evolution of the juice resulting from the test can make it possible to predict in the short and long term the negative impact of the discharging of these types solids wastes in surface water, in particular the impact on variations in nutrient concentrations responsible for the development of algae and thus the depletion of dissolved oxygen in the water.

In Kara, the lack of an adequate system for the collection and management of solid waste means that the streams and the Kara River draining this city receive more than 30% of the mass of household and similar waste produced in this city (Segbeaya et al., 2012). However, the studies carried out on the biodegradability and the pollutant potential of this waste have shown a strong presence of water-soluble organic compounds that are easily mobilized and that can easily revive biological activity in humid environments such as surface water, particularly lakes, lagoons and rivers (Segbeaya et al., 2012). These water-soluble organic compounds certainly contain nitrogen that can be released during the leaching process of the waste.In addition to this nitrogen bound to the water-soluble organic matter (organic nitrogen), the different forms of mineral nitrogen (NH_4^+, NO_3^-, NO_2^-) can also be released during the process of leaching waste participate in the eutrophication process of the river (Bøgestrand et al., 2005; Zhao et al., 2017).

The main objective of this study is to evaluate the impact of Kara solid waste on the water quality of the Kara River. Specifically, it is a question of quantifying the nitrogen released by the waste to analyze the transformations of the different forms of nitrogen released and to determine the variations of the nitrogen concentrations in the waters of the river from 2015 to 2025

MATERIALS AND METHODS

Study area

Kara is a medium-sized regional city located in northern Togo (9°32′55.40"N; 1°11′26.19"). In 2018, the population is estimated at more than 120,000 according to data from the 2012 General Census of Population and Housing (RPGH, 2012). The city has developed along the Kara River and is therefore drained by small streams that flow into this river (Figure 1).In the absence of town planning and sanitation schemes, streams, open gutters connected directly to streams, around streets and rivers are used as natural dumping sites for solid wastes and wastewater from the city (Segbeaya et al., 2012; Djahini et al., 2017).

The city has only one intermediate dump for the collection of solid waste, and moreover does not meet the standards of safety

Figure 1. Location of Kara and Kara River in the North Region of Togo.
Courtesy: Capture maps.

and protection of the environment. The pre-collection service for household and similar waste is provided by volunteers organized in associations. These associations are limited in their services because of the lack of appropriate technical and financial means. This management method considerably reduces the pre-collection service coverage rate, which is estimated at 10% of households, based on data from the technical report of a pilot project to set up a composting platform for household waste in the city of Kara (Tchanate et al., 2017). The waters of this river, which thus receive a not less important share of the solid waste, wastewater and sludge of the city, are certainly contaminated, but unfortunately used to treat garden produce grown on the banks of this river (Djahini et al., 2017). These waters are also used by local populations for various domestic purposes. Heavy rainfall is observed from July to October; but the massive arrival of solid waste in the river (Figure 1) occurs at the beginning of the rainy season (between May and June). In the dry season (November to May) the flow of the river decreases considerably (not more than 10 m^3/s) and the decomposition of waste trapped in the sediments promotes the eutrophication of the river especially at the point of discharge massive solid waste (Segbeaya et al., 2012; Djahini et al., 2017).

Location of control points and reference parameters on the waters of the river

Six control points (Figure 2) on the river were chosen in this forecast. The select of each point is related to the presence or absence of external elements that may impact the quality of the water (Effendi, 2016). Thus, the points P_0 and P_5 are selected respectively upstream and downstream of the most densified area of the city and are less directly impacted by the waste of the city. Point P_1 located about 1.6 km from point P_0 was selected to evaluate possible nitrogen inputs from small streams between points P_0 and P_2. Points P_2, P_3 and P_4 are located in the densified area of the city and correspond to spill points in the river of major streams that receive solid waste and wastewater from the city.

The reference parameters measured at these points for predicting the evolution of eutrophication of the river are flow, temperature, pH and levels of ammonium nitrogen, nitrite and nitrate (Effendi, 2016; Wang et al., 2019). The measurements were carried out during the period April-June 2015, which corresponds to the beginning of the wet season or there is a significant inflow of solid waste into the river. The averages of the measured values are reported in Table 1. There is an overall increase in nitrogen concentrations when moving from upstream to downstream. These variations are certainly in line with the impact of the different sources of pollution on the waters of the streams that feed the river.

Data collected and used for the calculations

Data on the physicochemical characteristics of solid wastes

The deposit of waste that was the subject of this study is a waste medium (WM) constituting two deposits of fresh waste of different origins. The first deposit (G1) consists of waste coming directly from selected households in different parts of the city. The second (G2) consists of solid waste collected in the city center and transported to the city's intermediate dump. The latter is composed by waste mainly related to commerce, restaurant, office and households located in the city center. These two deposits were selected because their compositions are representative of the solid waste produced in the city of Kara. The characterization campaigns carried out between 2012 and 2017 on these two deposits made it possible to obtain the average composition, the nature, biodegradation behavior and pollutant potential of household and similar waste in the city of Kara. Table 2 presents values of the parameters of the solid waste and which were used to calculate the quantity of nitrogen that they can release (Segbeaya et al., 2012; Bonnah et al., 2018).

Data on quantities of household and similar solid wastes

To determine the amount of nitrogen that waste can bring to the

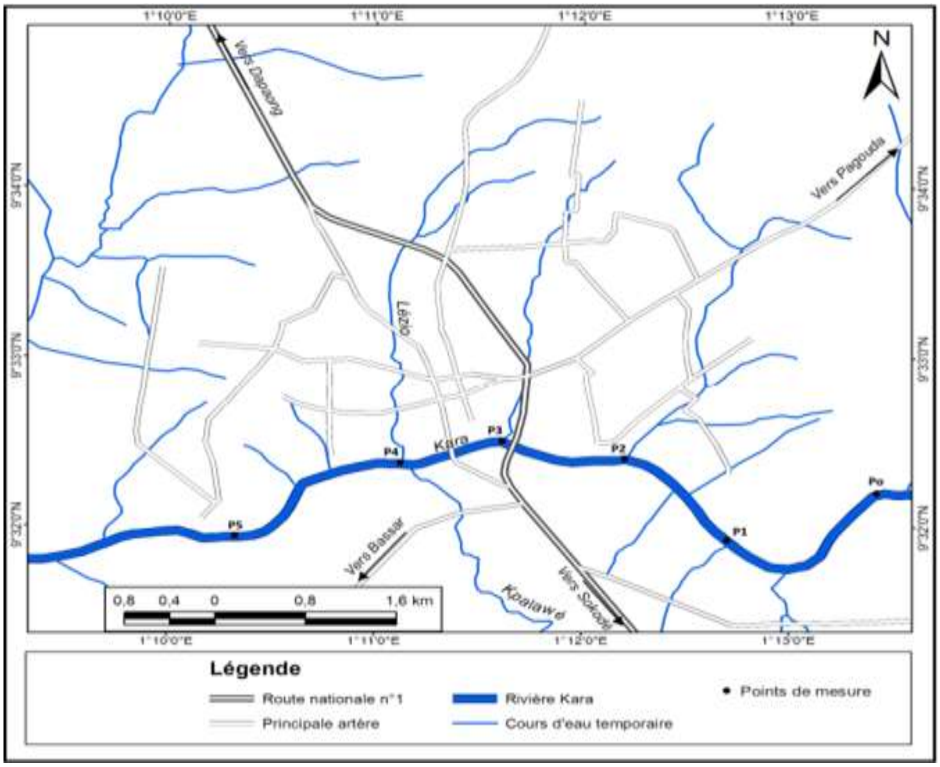

Figure 2. Location of selected control points on the river.

Table 1. Some references parameters measured at selected points for forecasts (April to June 2015).

Point	V ($m^3.s^{-1}$)	T (°C)	pH	$[NH_4^+]$ ($mgN.l^{-1}$)	$[NO_2^-]$ ($mgN.l^{-1}$)	$[NO_3^-]$ ($mgN.l^{-1}$)
P_0	8 ± 3	28 ± 1	7.7 ± 0.3	03.2 – 03.8	02.4 – 02.7	03.1 – 03.3
P_1	8 ± 3	28 ± 2	8.0 ± 0.3	03.5 – 04.2	02.3 – 03.1	03.3 – 03.8
P_2	10 ± 2	27 ± 2	7.8 ± 0.1	03.2 – 04.3	02.3 – 02.9	03.6 – 04.1
P_3	11 ± 3	29 ± 3	8.4 ± 0.6	06.3 – 08.1	02.9 – 03.3	04.4 – 05.2
P_4	12 ± 2	28 ± 2	7.8 ± 0.3	09.8 – 13.7	04.7 – 05.1	05.7 – 07.8
P_5	13 ± 2	28 ± 1	7.7 ± 0.4	10.1 – 11.3	04.4 – 04.8	05.4 – 06.0

Table 2. Some physicochemical parameters of household and similar waste in the city of Kara.

Parameter	G1	G2	WM
Putrescibles(%)	7	21	11.2
Fine fractions (%)	18	30	14.6
Small finefractions(%)	50	25	42.5
Organic matter content (% MS)	26.2	40.2	30.4
Extractable organic matter (g COD/kg MS)	8.3	16.7	10.8
Extractable Volatile Fatty Acids (g C/kg MS)	11.2	12.0	11.4
Total Nitrogen(gN/kgMS)	3.7	6.0	4.4

river, an assessment of the evolution of the quantity of waste produced in the city of Kara has been made according to the evolution of the number of inhabitants and per capita production ratio. The quantities of the various waste fractions (putrescible, fine

Table 3. Evolution of annual quantities of representative waste fractions in the MW deposit.

Year	R (kg/day)	Pn	AQSW (t)	PF (%)	SF (%)	AQPF (t)	AQSF (t)	AQPDS (t)	AQSFSD (t)
2012	0.310	94,900	10,738	13.5	55.4	1,450	5,949	507	435
2015	0.323	112,220	13,238	13.8	55.4	1,832	7,334	641	550
2016	0.328	115,490	13,815	13.9	55.4	1,921	7,654	672	576
2017	0.332	118,820	14,412	13.9	55.4	2,008	7,984	703	602
2018	0.337	112,290	15,041	14.0	54.3	2,112	8,166	739	634
2019	0.342	125,864	15,679	14.0	54.3	2,200	8,522	770	660
2020	0.346	129,543	16,382	14.2	54.0	2,322	8,849	813	697
2021	0.351	133,222	17,083	14.2	54.0	2,433	9,228	852	730
2022	0.356	137,006	17,814	14.3	53.9	2,549	9,598	892	765
2023	0.361	142,242	18,754	14.4	53.9	2,696	10,104	944	809
2024	0.366	148,643	19,873	14.4	53.7	2,871	10,676	1,005	861
2025	0.371	153,100	20,755	14.5	52.6	3,021	10,923	1,054	904

R = Per capita production ratio, **Pn** = Annual population, **AQSW** = Annual quantities of solid waste; **PF** = putrescible fractions; **SF** = Small Fractions (Fine fractions + Extra fine fractions); **AQPF** = Annual quantity of putrescible fractions; **AQSF** = Annual quantities of small fractions; **AQPDS** = Annual quantities of putrescible deposited in streams; **AQSFDS** = Annual quantities of small fractions deposited in streams.

and extra fine) that are deposited in the streams were also taken into account to determine the evolution of the quantities of the different forms of nitrogen. The MODECOM (Method of Characterization of Household Waste) developed by ADEME (Energy an Environment Control Agency) was used to quantify and sort the waste. Table 3 presents the evolution of the study parameters (population, production ratios, annual quantities of waste, and annual quantities of the different waste fractions considered in this study) from 2015 to 2025.

For each year, the estimates are made for the months of April, May and June, which correspond to the beginning of the rains and the major capsizing of the waste in the streams to the main river. This is the most significant period of impact of waste on the quality of the river's waters. Thus, to evaluate the amounts of capsized waste towards the river, some questions were asked. How much waste is deposited in the streams beds before the arrival of the first major rains? How does the most representative fraction evolve? What are the average heights of the first major rains? What is their distribution over the study period? What are the key parameters that may be decisive in capsizing stream waste to the river? What is the maximum residence time of waste in the river's waters in the study area? To these different questions, the approaches adopted are translated by the formulas of calculation of the different quantities of waste, the liberation and the evolution of the different forms of nitrogen (Kunwaret al., 2005; Ouyang et al., 2006; Pinto et al., 2012).

Calculation approach used to estimate the quantities of solid waste transferred to the river

For the transport of waste streams to the river, a scenario was defined on the basis of the phenomena observed at the arrival of the first major rains. Three large rains with a maximum height of 50 mm on the study area are considered and distributed over the three months (one rain in April, one in May and one in June) of each year. The first rain capsizes a smaller amount of waste because the mass of waste before this rain has physical characteristics (compactness, permeability, porosity) that do not promote an easy disintegration of solid waste piled up over five months. On this basis, to calculate the quantities of solid waste capsized towards the river we considered that for the first great rain, 25% of the putrescible and 30% of the fines + extrafines are transported towards the river; at the second major rain, 50% of putrescible and 70% of the remaining fines + extrafines are capsized then 75 and 95% at the third big rain.

Before the arrival of the first major rains in April, May and June, the quantity of waste deposited in the beds of the three main streams corresponds to a maximum of 30% of the annual production. Thus, from the end of the rainy season (October) to the beginning of the rainy season (April), the quantity of waste deposited each year was calculated by the formula 1 (Segbeaya et al., 2017):

$$\textbf{Formula 1}: Q_D = Q_{WP} \cdot \frac{N}{12} \cdot X$$

N= 5 months (November to March), ***X*** = Percentage of waste deposited in stream beds, Q_{WP} = Annual quantity of waste produced

After depositing in the beds of streams, the deposit of waste is subjected to several factors that cause the evolution of certain fractions including the most biodegradable fractions such as putrescible. Thus, before the arrival of the first major rain, the proportions of certain fractions in the deposited deposit will have to decrease. The factors taken into account in the calculation of the remaining quantities are: - the natural decomposition of the organic fractions, the recovery of a part of the waste by the ragpickers, -the consumption of a part of the putrescible fractions by the animals left in straying. The remaining quantities of the most representative fractions (putrescible, fines + extrafines) are calculated on the basis of the average composition of the deposit before the arrival of the first major rain. Formulas 2 and 3 allowed these quantities to be approximated (Segbeaya et al., 2017):

$$\textbf{Formula 2}: \quad Q_P = (100 - Y) \cdot \frac{Y_P \cdot Q_D}{100}$$

$$\textbf{Formula 3}: \quad Q_{SF} = (100 - Z) \cdot \frac{Z_{FE} \cdot Q_D}{100}$$

Q_P = Annual quantity of putrescible remaining in the deposit in progress, Q_{SF}= Annual quantity of fines + extra fines remaining in the deposit in evolution, ***Y*** = Percentage of putrescible extracted from deposited waste, $\boldsymbol{Y_P}$ = Percentage of putrescible in waste, ***Z*** = Percentage fines + extra fines extract deposited waste, $\boldsymbol{Z_{FE}}$= percentage of fines + extra fines in waste.

Technical approach for accessing the nitrogen present in the solid phase of waste

To extract maximum nitrogen from waste, leaching tests developed by Berthe et al. (2008) and Parodi et al. (2011) were used. The tests are carried out in triplicate on samples of waste ground to 20 mm with a mass ratio of the liquid on mass of the dry waste (L / S) set at 10. This ratio favors optimal release conditions according to the standard 12457 / 1- 4 and limits the saturation phenomenon (Berthe et al., 2008). A dry mass of waste of 100 ± 0.01 g is brought into contact with 1 ± 0.01 L of ultrapure water in a 2L flask sealed and stirred for five days. Three bottles are sacrificed after every 24 h for five days. The juice of the leaching test is separated from the solid phase by filtration using a mesh screen of 1 mm. For the analyzes, the juices are centrifuged at 8000G for 20 min at a temperature of 4°C. in order to limit the restart of the biological activity. The samples are stored at 4°C in polyethylene bottles and analyzed as quickly as possible to avoid any change in their characteristics (Segbeaya et al., 2017).

Analysis methods

Nitrogen content

The total nitrogen (N_{Tot}) measurement is done with a Rapid Test Kit (LCK 338, 0-20 mgN / L) according to Dr Lange® LCK 338 model (Parodi et al., 2011). Measurements of the different forms of nitrogen (NH_4^+, NO_3^- and NO_2^-) are made using the method developed by SEAL Analytical AQ2 (0.015 - 50 mgN / L) (Parodi et al., 2011; Segbeaya et al., 2012). The contents of organic nitrogen (OrgN) and Total Kjeldahl Nitrogen (TKN) are calculated respectively by relation 1 and relation 2.

Relation 1:OrgN $= \mathrm{TN} - [NH_4^+ + NO_3^- + NO_2^-]$

Relation 2:TKN **=** OrgN $+ NH_4^+$

Analysis of nitrogen transformations in juices obtained after leaching test

To understand how this nitrogen can evolve in the waters of the Kara River, a follow-up of its biotransformation has been developed. Thus, after 120 h of waste leaching, 250 ml of the non-centrifuged raw juice is collected in a 500 ml DURAN glass bottle, tightly closed and placed in an incubator set at 28°C (average temperature of the river water). The initial pH of the incubated juices is between 6.8 and 7.4. According to Vazquez-Rodriguez and Rols (1997) a pH value of 7.8 is favorable for the biological activity of nitrating bacteria. Thus, the initial pH values of the juices have not been modified but are measured during the process in order to assess the intensity of this biological activity. The tests are carried out in triplicate as in the case of the leaching test. The duration of incubation was set at 21 days, corresponding to the maximum time spent in the river water before it was transported to areas further downstream at the discharge points in the river. To monitor the biotransformation, after every 24 h, 1 mL of the evolving juice is taken from each bottle to measure pH and total nitrogen (TN), ammonium nitrogen (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-).

Figure 2 shows the process of leaching solid waste and biotransformation of the different forms of nitrogen extracted . It allows seeing the different phases of the process of biotransformation. Indeed, the decisive phases for the contribution of nitrogen in the eutrophication of surface water are the biochemical processes of nitrification of ammonium nitrogen (NH_4^+) in nitrite then in nitrate and denitrification of nitrate to gaseous nitrogen (N_2). Eutrophication occurs when the nitrification process (Equation 1 and Equation 2) is preponderant over that of denitrification (Equation 3).

$$\mathrm{NH_4^+ + 3/2O_2 \rightarrow NO_2^- + 2H^+ + H_2O}, \quad \Delta G^0 = -290.4\ kJ.mol^{-1} \text{ at pH = 7.0} \tag{1}$$

$$\mathrm{NO_2^- + 1/2O_2 \rightarrow NO_3^-}, \quad \Delta G^0 = -72.3\ kJ.mol^{-1} \text{ at pH = 7.0} \tag{2}$$

$$\mathrm{NO_3^- + 1.25\ CH_2O + H^+ \rightarrow 0.5\ N_{2(g)} + 1.75\ H_2O + 1.25\ CO_{2(g)}}, \Delta G^0 = -594.6\ kJ.mol^{-1} \text{ at pH = 7.0} \tag{3}$$

Thus, according to the evolution of the bio-physico-chemical conditions in the waters (diversity of bacteria, temperature, pH, dissolved oxygen), the quantity of NO_2^- in equilibrium with both NH_4^+ and NO_3^- may, depending on the case, and be a favorable or limiting factor for the kinetics transformation of NH_4^+ in NO_3^- (Anthonisen et al., 1976; Antoniou et al., 1990; Lee, 2003).

RESULTS AND DISCUSSION

Quantity of nitrogen released by the waste deposit

In surface waters exposed to anthropogenic discharges, the concentrations of the major nitrogen ions are decisive on the intensity of biological activity and proliferation of algae (Li et al., 2017). Thus, the concentrations of total nitrogen (TN), organic nitrogen (OrgN) and major nitrogen ions (NH_4^+, NO_3^- and NO_2^-) are measured in the solution obtained from the waste leaching test after 24 and 120 h (Table 4). In addition to these different forms of nitrogen released by the waste in the liquid phase, the nitrogen emitted in gaseous form (N_2 or N_2O) by denitrification process was evaluated in order to estimate the total capacity of the waste deposit to release nitrogen when it's contact with the water river.

The total nitrogen released after 24 and 120 h is essentially composed of organic nitrogen (respectively 87.5 and 92% N_T). This high proportion of organic nitrogen is consistent with the composition and nature of the deposit waste (Parodi et al., 2011; Segbeaya et al., 2012). In fact, the two deposits G1 and G2 used to reconstitute the deposit (MW) consisting of fresh waste such as putrescible very rich in organic matter which represents 70 to 75% of the dry matter. This organic material contains organic nitrogen compounds that enrich the waste leaching solutions with organic nitrogen and thus their proportion in the total nitrogen released (Berthe et al., 2008). In addition, it is established that Total Kjeldahl Nitrogen (N_{Org}+ $N_{Ammoniumcal}$) is the most abundant nitrogen contained in the organic matter of biotic natural waters, soils, sediments, wastewater,

Table 4. Quantities of the different forms of nitrogen released by the deposit of waste after 24h and 120h of leaching test.

Unity	TN	OrgN	NH_4^+	NO_3^-	NO_2^-	$N_{Gas(Emitted)}$
				(mg /kg Dry Matter)		
24 h	279	244	26.6	7.0	1.3	-
120 h	261	240	17	3.3	0.4	173

organic waste (Pringle et al., 1999). However, the waste deposit of Kara as well as waste from cities in developing countries is very rich in organic matter (30 to 40% of dry matter) coming partly from biotic and abiotic factors; and therefore potentially rich in Kjeldahl Nitrogen (Bareither et al., 2012b). For mineral forms of released nitrogen, ammonium nitrogen compared to nitrites and nitrates appears to be the predominant form after 24 and 120 h of waste contact with water. This predominance of ammonium nitrogen during the first five days of the experiment can be explained by the large proportion of fine fractions (soils and decomposing waste) present in the waste. Indeed, the fine fractions contain organic matter in a more advanced phase of biodegradation and may release more readily ammonium nitrogen whose future transformations should give nitrites and mainly nitrates (Koledzi et al., 2016; Segbeaya et al., 2017).

The balance of total nitrogen released into the juice and emitted in gaseous form indicates the maximum potential of the waste to release nitrogen in contact with surface water. After 120 h, this potential is 434 mg / kg of dry weight of the waste. It corresponds to 9.87% of the nitrogen present in the mass of the waste deposit (WM). This percentage shows a good release of the nitrogen bound to the water-soluble organic compounds easily mobilized in the waste because according to several authors, a significant mass fraction of the organic matter potentially rich in nitrogen remains in the solid phase even after the complete process of biodegradation and stabilization of organic waste (Berthe et al., 2008; Parodi et al., 2011; El Fels et al., 2014). We can then estimate that the leaching test used to simulate the nitrogen release process responds in part to the conditions of natural environments (surface water) such as Kara River that is the subject of this study.

Transformations of nitrogen released

Nitrogen pollution in natural environments such as surface water is often evaluated by measuring total nitrogen (TN) associated with the measurement of nitrate, nitrite and ammonium contents (Juahir et al., 2011). A not less important part of this nitrogen pollution is related to the organic matter of organic waste because it usually contains nitrogenous organic compounds. To make an analysis of the process nitrogen biotransformation released by the waste deposit, a follow-up of the evolution in concentrations of total nitrogen, organic nitrogen, ammonium, nitrite and nitrate is done for identify the main biodegradation phases that occur during this biotransformation process.

The graph showing the evolution of total nitrogen concentration (Figure 3a) reveals a progressive consumption of nitrogen linked to a biological activity which converts a part of the different forms of nitrogen into volatile compounds containing nitrogen (Robertson and Groffman, 2015). This biological activity is more intense during the first 7 days of leachate incubation because there is a reduction of more than 10% of the total nitrogen concentrations between the 1st and 7th day of the experiment. It corresponds to an acidogenic phase because the pH values are between 6.2 and 7.6 (Reinhart and Al-Yousfi, 1996; Barlaz et al., 2010; Shen et al., 2017). These pH values are consistent with the increase in ammonium nitrogen concentrations, which increased from 1.7 to 2.8 mg / l between the 1st and 7th day (Figure 3c). This increase in ammonium nitrogen concentrations confirms a more or less intense biological activity and shows the installation of a leaching process that promotes the fragmentation of organic macromolecules by hydrolysis or under the effect of enzymes released by acidogenic bacteria (Shen et al., 2017). Indeed, some macromolecules are momentarily unavailable to microorganisms and must undergo multiple actions of reduction and transformation by simple or enzymatic hydrolysis before being accessible to microorganisms.

The consumption of the compounds thus obtained promotes the release of organic nitrogen whose biotransformation releases more and more ammonium nitrogen in the leachate (Segbeaya et al., 2017). The graph showing the evolution of organic nitrogen concentrations in leachates (Figure 3b) reveals a significant consumption of this form of nitrogen in the early phases of the development of biological activity because there is a significant decrease in organic nitrogen concentrations between the 3rd and 8th day. It can then be estimated that part of the organic nitrogen associated with the organic macromolecules is then released by the hydrolysis and enzymatic reduction reactions (Mlaika et al., 2019). Thus, in the leachate of waste, the evolution of the various forms of nitrogen is strongly correlated with the nature and the specificity of

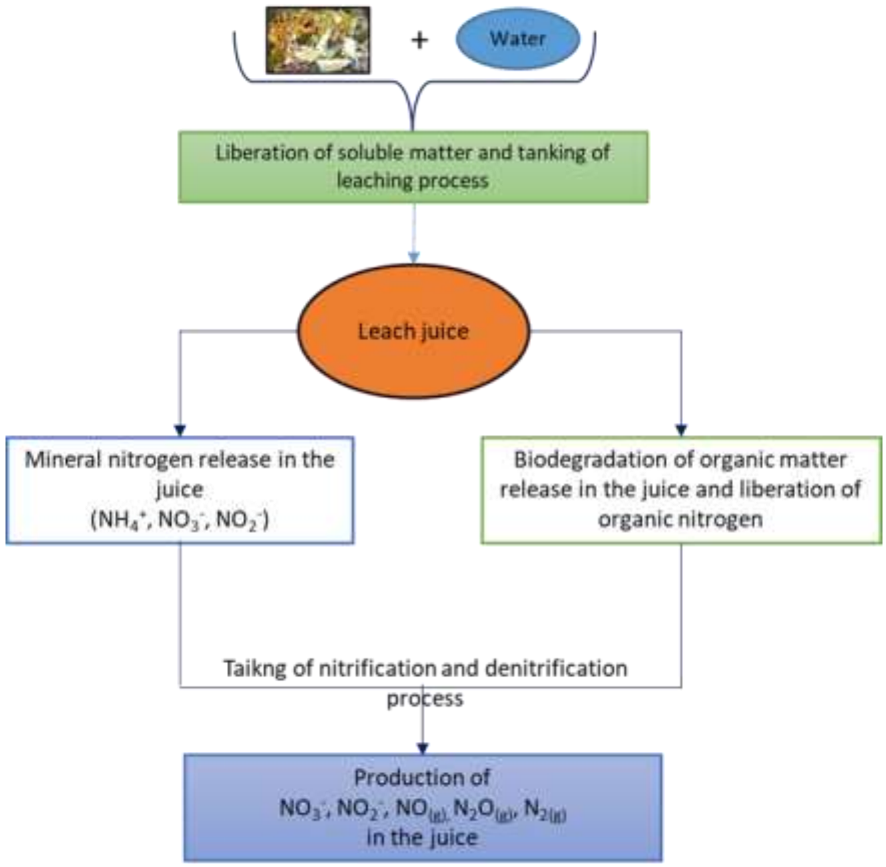

Figure 3. Process of release and biotransformation of the nitrogen present in the solid phase of the waste.

the microorganisms initially present in the waste but also the capacity of these microorganisms to produce the specific enzymes for the reactions of hydrolysis and reduction of organic macromolecules (Khalid et al. 2011; Wang N. et al., 2019).

The evolution of nitrate and nitrite concentrations in the leachate of waste is strongly linked to the processes of nitrification and denitrification of ammonium nitrogen but also the process of organic nitrogen mineralization (Li et al., 2019). Figure 3d shows a slight increase in nitrate concentrations between the 1st and the 4th day, followed by a significant increase after the 4th day. From the 5th day a constant increase more or less uniform until the 12th day and constant concentration values from the 18th day of incubation. But on the other hand, the nitrite concentrations remained practically constant.

Variations in nitrate concentrations show that the chemical and biological parameters that are favorable for nitrogen biotransformation reach their optimum value between the 5th and 12th day of leachate incubation. Indeed, the pH although it is not directly influenced by the evolution of nitrates, its production by nitrification releases hydronium ions which condition the pH of the medium. However, the pH values increased from 6.2 to 7.4 and show the gradual establishment of a less and less acidic medium that could be justified by a significant consumption of Volatile Fatty Acids (VFAs) more than a production of ammonium ions and more than the process transforming a portion of ammonium ions into nitrate by nitrification (El-Mahrouki et al., 2004; Shen et al., 2017). In addition, these pH values are favorable for the development and enzymatic activity of nitrifying bacteria because the optimum pH for nitrification is around 8.0 and it is shown that for pH values outside the range 6.0 - 8.5 the effectiveness of nitrification is affected (Jiménez et al., 2011;Huyen Le et al., 2019). As the pH of the Kara River waters is in the range 6.0 - 8.5, there is a significant probability that the massive arrival of waste in the waters of this river will be favorable to the establishment of a nitrification process if the waste should stay in the water for 15 to 20 days. The concentrations of nitrites remained very marginal compared to those of nitrates and ammonium. These low concentrations are explained by the biogeochemical cycle of nitrogen (Galloway et al., 2004). Indeed, this cycle shows that the nitrification process consumes nitrites while the denitrification process source of nitrite production continues until the production of nitrogen gas (N_2). Thus, nitration $(NO_2^- + 1/2\, O_2 \rightarrow NO_3^-)$

and denitrification are the two processes that can be advanced to explain the low levels and variations of nitrites in the evolving leachate. These low concentrations and variations are also indicators of a biotransformation of the different forms of nitrogen present in the leachate of the waste that is the subject of this study.

Evolutions of nitrogen concentrations brought by solid waste in river water from 2015-2025

Nitrogen pollution is often assessed by a measure of total nitrogen (TN) and Total Kjeldahl Nitrogen (TKN), associated with measurements of nitrate, nitrite and ammonium concentrations. A not less important part of this nitrogen pollution is linked to organic matter and corresponds to organic nitrogen (OrgN). In this study we are more interested in the evolution concentrations of total nitrogen, organic nitrogen and particularly at nitrate and ammonium in order to estimate the contribution of fresh solid waste produced in the city of Kara on the eutrophication development in the waters of Kara River. Figure 4a, b, c and d show the spatiotemporal variations that can be observed on the values calculated in concentrations of the different forms of nitrogen in the river water depending on the flow rates (min and max) and the evolution quantities of the fresh solid waste deposited in the streams beds that feed the main river. For each year considered, the estimate of the variations concentrations is made at the five points namely from the most upstream point (P_1), the most downstream (P_5) and 3 points (P_2, P_3 and P_4) located at heart of the urban area (Figures 2 and 5).

The figures show a gradual increase in concentrations over time and space for each nitrogen form considered.This gradual increase is related to the quantities of solid waste generated and also increase in the quantities of solid waste deposited in the beds streams that cross the city. In fact, assuming no action is taken over time for a more adequate solid waste management, we can only witness an increase in the quantities of solid waste in the beds streams and consequently increase in the pollution of the river's waters. This pollution will be reflected over time by more or less significant increases in the concentrations of certain pollution indicators, particularly those linked to the solid waste management method (concentrations of the different forms of nitrogen).

Case of total nitrogen (TN)

For total nitrogen (TN), the concentrations increase that could have been induced by solid waste in 2015 is estimated at 1.25 µg/L at the most upstream point (P_1) for a minimum flow rate (5 m^3/s) and 0.63 µg/L for a maximum flow rate (11 m^3/s). These values for the same flow rates at this point in 2025 are estimated at 2.92 and 1.46 µg/L. Comparing these values with those at the most downstream point (P5) which are respectively 5.70 and 4.18 µg/L in 2015 and 8.85 and 6.49 µg/L in 2025 for flow rates (11 and 15 m^3/s), we can affirm that P_5 point will be more impacted by nitrogen pollution related to the solid waste management method of Kara.These results can be extrapolated by changes in flows and positions of stream discharge points in the main river. Thus, point P_5, the most downstream, must group all the pollution coming from the urban area and point P_1, the most upstream, must be less affected by this pollution. However, the expected variations for period 2015 to 2025 are order at 57.1% for point P_1 and 35.6% for point P_5. The strong variations in time at point P_1, which receives only the lowest pollution coming from the city, can be explained by the significant variations in river flows rates from upstream to downstream (5 to 11 m^3/s for P_1 against 11 to 15 m^3/s for P_5). Indeed, a low flow rate can allow a longer retention time of the waste in the water and thus favorable to the hydration reactions and to the solid waste leaching processes. On the other hand, a medium or high flow rate can cause a faster transport of the solid waste and thus reduce to the point of discharging the impact of the hydration and leaching processes of this waste. In addition, for points or flow rates are low, the dilution phenomenon is less important and therefore can be observed at these points higher concentrations of the compounds extracted in the waste. These types variations were also observed on the Seine River between 2008 and 2009 (PIREN, 2010).

Case of organic nitrogen (OrgN)

The forecasts in terms of variations of organic nitrogen concentrations in river water are same trends as those of total nitrogen. Indeed, between 2015 and 2025, the variations at points P_1 and P_5 are respectively equal to 52.8 and 35.8% for flows rates at 5 m^3/s and 11 m^3/s then equal to 65.6 and 35.8% for flows rates at 11 m^3 /s and 15 m^3/s. There is also greater variation in pollution at the control point furthest downstream (P_1) than the most upstream control point (P_5), which can be explained in part by differences in flows rates between the two points. However, the most upstream points of the solid waste discharge points will be more impacted by organic pollution because for the 2025 horizons, the predicted values of organic nitrogen concentrations calculated for the max and min flows rates at point P_5 (5.08 at 6.73 µg/L) are significantly higher than those at point P_1 (1.45 to 2.57 µg/L) furthest downstream. If we consider the values calculated for organic nitrogen concentrations at the different points (P_2, P_3, P_4) located in heart of area urban, we note that these values are usually over than those at upstream and less than those downstream. These differences between the values calculated confirm

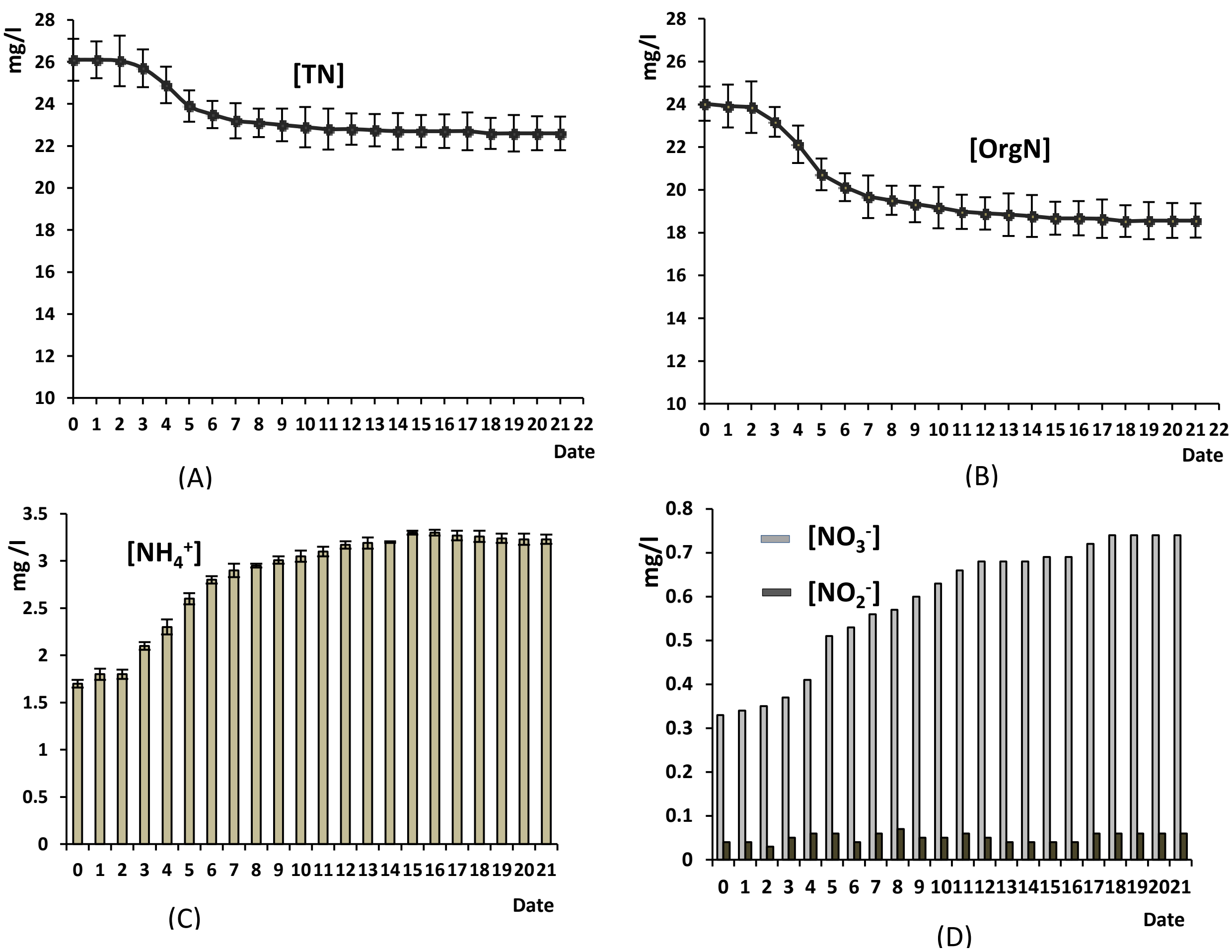

Figure 4a. Evolution of total nitrogen concentrations in incubated leachate, **b.** Evolution of organic nitrogen concentrations in incubated leachate, **c.** Evolution of ammonium nitrogen concentrations in incubated leachate, **d.** Evolution of nitrate and nitrite concentrations in incubated leachate.

that the heart of the city is most impacted by the discharged of solid waste. This difference is observed during the all period consider for our forecasting (2015-2025). Similar variations are observed in Shiyang River at the Northwest China (Ma et al., 2009). In 2015 the forecast values at points P_2, P_3 and P_4 are respectively equal at 0.65, 1.98 and 2.61 µg/L for the high flows rates and they are less than this of the downstream point (3.26 µg/L) and higher than this of the upstream point (0.50 µg/L). The same trends are observed for the year 2025 (1.94, 3.94, 5.16 µg/L for P_2, P_3, P_4, 6.73 µg/L at the downstream point and 1.45 µg/L at the upstream point).

Cases of ammonium ($NH_4^+ - N$) and nitrate ($NO_3^- - N$)

Predicted concentrations of $\mathrm{NH_4^+ - N}$ and $\mathrm{NO_3^- - N}$ are in significantly lower ranges than total nitrogen and organic nitrogen. These low values of ammonium and nitrate ion concentrations are consistent with the process of biotransformation of organic matter and organic nitrogen (Li et al., 2019). A process that transforms only a few fractions of organic nitrogen into ammonium nitrogen, ammonium nitrogen to nitrite and then nitrite to nitrate; therefore cannot cause high concentrations of ammonium and nitrates in the waters of the river (Massé et al., 2019). In addition, to observe large increases in ammonium and nitrate concentrations at the control points, a minimum retention time in water of organic matter extracted from solid waste is required for the biotransformation process and accumulation of ammonium and nitrate in these points. This retention time is strongly related to river flows at different control points (Angelika et al., 2019). Thus, the forecast values calculated at the control points show larger variations between upstream and downstream points. The calculations show at the most upstream point (P_1), the forecasts of the temporal variations in $\mathrm{NH_4^+ - N}$ and $\mathrm{NO_3^- - N}$ concentrations are order 61% between 2015 and 2025 against only 35% at the most downstream point

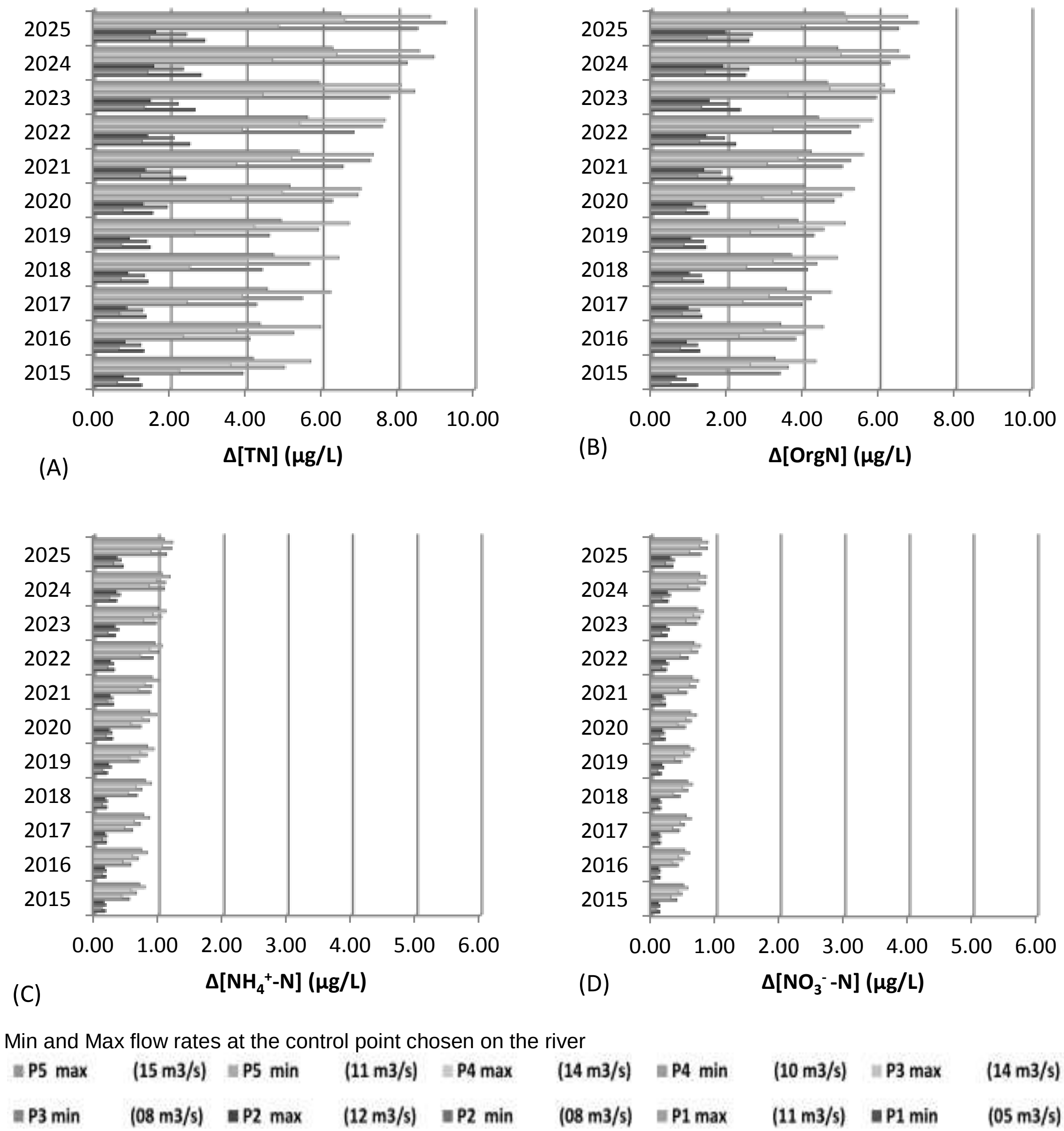

Figure 5. (a) Spatiotemporal variations of total nitrogen in Kara River related to deposition, transport by water and biodegradation of solid waste, (**b)** Spatiotemporal variations of organic nitrogen in Kara River related to deposition, transport by water and biodegradation of solid waste, (c) Spatiotemporal variations of NH_4^+-N in Kara River related to deposition, transport by water and biodegradation of solid waste, (d) Spatiotemporal variations of NO_3^--Nin Kara River related to deposition, transport by water and biodegradation of solid waste.

(P_5). However, the quantities of $NH_4^+ - N$ and $NO_3^- - N$ brought at points P_1 and P_5 are respectively estimated at 0.18 and 0.13µg/L in 2015 and then at 0.46 and 0.34 µg/L in 2025. The large difference observed on temporal variations at these two control points confirms the significant effect of flow rates on the accumulation and concentration of the compounds extracted from the solid waste. At control points P_2, P_3, P_4, which correspond to the discharge points of the solid waste drained by the three main streams that cross the city, the forecast calculations show variations in concentrations of $NH_4^+ - N$ and $NO_3^- - N$ between 45 and 56% from 2015 to 2025. The corresponding concentrations are between 0.42 and 1.21 µg/L for ammonium ions and between 0.35 and 0.87 µg/L for nitrate ions. Similar variations were observed in the Sava River Basin (China) (Huang et al., 2010) and River Seine (France) (Billen et al., 2001). Nitrogen concentrations brought by solid wastes are of the order of micrograms per liter, but the accumulation phenomenon of these small quantities in sediments can contribute to the resurgence of eutrophication which develops each year in the waters of the river during the dry period (Kotti et al., 2005; Fianko et al., 2010). In fact, a quantity of different forms of nitrogen extracted from solid waste can be trapped in sediments and during dry periods when flow rates are low, they can be released into the water and serve as nutrients for algae and cyanobacteria, responsible for eutrophication that develop during this dry period (Austin and Lee, 1973; Li X. et al., 2017; Chen et al., 2019). Thus, successive cycles of biotransformation, trapping in sediments and subsequent release of fraction nitrogen (such as ammonium, nitrate and nitrite) contained in the solid waste discharged into the streams water will gradually contribute to the eutrophication of the Kara River. However, it is important to mention that the spatiotemporal patterns and source attribution of nitrogen load in a river is too complex (Yang et al., 2016).

Conclusion

An accelerated leaching test is applied to a solid waste. Incubation at 28°C of the juice from leaching test made it possible to follow the biotransformation over 21 days (in 2015) of the different forms of nitrogen extracted from the solid waste (total nitrogen, organic nitrogen, ammonium ions and nitrates). The values obtained after 21 days of incubation are used to calculate the nitrogen concentrations brought into the river waters by solid waste. The study showed that solid waste releases 434 mgN/kg in contact with water for 120 h, including 261 mgN/kg in aqueous form. The monitoring of the biotransformation of this aqueous form has shown that organic nitrogen has a good potential to transform into ammonium ions and ammonium into nitrate ions. The predicted calculations of nitrogen concentrations brought by solid waste showed that the river zone downstream from the heart of the city is more impacted by nitrogen pollution related to poor solid waste management. Thus, by 2025 the points of the downstream zone will be able to undergo increases in total nitrogen concentrations estimated between 6.49 and 8.85 µg/L. These low values show that the management of solid waste in the city of Kara contributes to the deterioration of the water quality of the Kara River and is a source of eutrophication in this water resource.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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