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RESEARCH ARTICLE

Analysis of Nitrogen and Phosphorus Flows in a Rice-Growing Basin: The Case of the Maga Production Basin (Cameroon)

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ABSTRACT

The availability of irrigation water has favored the development of agriculture in the Maga area, located in the Far North of Cameroon, with rice growing as the dominant agricultural activity. This activity is, however, known as a source of groundwater pollution through the infiltration of substances contained in inputs used for soil fertilization. The present study is a contribution to the analysis of the sources of contamination of the waters of the Maga rice basin by nitrogen and phosphate mineral compounds as well as the spatial distribution of these compounds. The monitoring of a network of fifteen wells and boreholes covering the rice-growing area during six campaigns made it possible to carry out the physicochemical characterization of subsurface and groundwater. The results obtained reveal that nitrates (NO_3^-) are present in water in low quantities, with averages per campaign ranging from 9.01 mg/L to 20.31 mg/L. On the other hand, ammonium (NH_4^+) and phosphates (PO_4^{3-}) are in significant concentration. Their averages are of the order of 2.62 mg/L to 4.51 mg/L and then 0.65 mg/L to 5.58 mg/L for ammoniums and phosphates, respectively. Mineral fertilizers used for soil amendment and degradation of organic matter, as well as the hydrolysis of minerals contained in the soil, contribute to the mineralization of water in the study area.

Keywords: Nitrogen, Phosphorus, Pollution, Rice growing.

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1. INTRODUCTION

The contamination of water resources by polluting chemical elements constitutes a significant threat worldwide to the survival of ecosystems and human health [1], [2]. Among the sources of water pollution, agriculture occupies an important place because it modifies the quality and dynamics of water in the environment through the use of agricultural inputs and plowing techniques as well as the method of irrigation. The supply of fertilizers and pesticides associated with the mechanization of plowing in agriculture contributes to the degradation of soil and water in many production areas around the world [3]–[6]. Chemical and organic substances used in agriculture to amend the soil can infiltrate into groundwater under the influence of the nature of the substance itself, the physical properties of the receiving environment, and the possible interactions between the substances used and the solid medium or other elements present in the water [7]. Among the infiltrating polluting substances, nitrates and phosphates have properties that allow them to be found not only in the soil but also in water, either following the addition of amendments by fertilizers or by biochemical processes natural under the effect of the pedoclimatic and ecological conditions of each geographical area [8]–[10]. In addition, the cultural system including agricultural practice and the plant species cultivated, has an influence on the quantity of nitrate nitrogen and phosphates present in the different soil horizons and the mode of infiltration towards the water tables [7]. Furthermore, an excessive supply of irrigation

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water will promote the transfer of nitrates and phosphates to groundwater.

In the Maga zone in the Far North of Cameroon, the availability of water for irrigation has enabled the development of rice growing and market gardening. With dense rice farming activity and an intensification of market gardening, the area's water resources are threatened by uncontrolled use of agricultural inputs following the liberalization of the supply market for these chemicals. The modern methods applied (ploughing and chemical fertilization) promote the process of direct infiltration and migration of pollutants (NO_3^-, K_2O, SO_4^{2-}, PO_4^{3-} ...) towards groundwater [11], [12].

The objective of this study is to highlight the influence of agricultural practices on the contamination of groundwater by nitrogen and phosphate compounds as well as the evolution of the latter in time and space.

2. MATERIALS AND METHODS

2.1. Presentation of the Study Area

The Maga rice basin is located in the Mayo-Danay department, Far North Region of Cameroon (10° 21′ N, 15° 13′ E and 10° 51′ N, 14° 56′ E) with more than 7 000 ha of developed space. The climate is Sahelo-Sudanian, with a long dry season from October to the beginning of May and a short rainy season from June to September. The morphology is dominated by a floodplain [13]. The soils of the area are poorly evolved, vertisols, and tropical ferruginous soils, hydromorphic soils, and halomorphic soils [14], [15]. Agriculture in this area is dominated by the cultivation of rice, irrigation of which is provided by the waters of the artificial lake.

2.2. Sampling and Analytical Methods

The water samples to be analyzed were taken during six campaigns for a total of 90 samples. 15 sampling points were selected to provide good spatial coverage in order to better understand the variability of water quality in space. For all water samples, pH, temperature, TDS, and EC were measured in situ using a Hanna HI 98130 multiparameter probe. For chemical analyses, the samples were transported and stored in the laboratory according to standard WHO methods [16]. The main ions were analyzed using the following methods: Volumetry for calcium (Ca^{2+}), magnesium (Mg^{2+}), hydrogen carbonate (HCO_3^-) and chloride (Cl^-) ions; spectrophotometry for sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) and phosphate (PO_4^{3-}) ions; flame photometry for the determination of sodium (Na^+) and potassium (K^+) ions. These analyses comply with the methods recommended by WHO [16] and Rodier [17]. The results of the physicochemical analyses obtained were processed using hydrochemical data interpretation methods.

3. RESULTS AND DISCUSSION

3.1. Results

3.1.1. Physical Parameters

3.1.1.1. Water Temperature and pH

Temperature values are not extreme throughout the year (Table I). They vary little from one point to another and from one campaign to another. This small variation will result in a small change in the pH of the water, as well as that of other chemical elements. Analysis results show that water has a neutral pH on average (around 7 with a standard deviation <1).

3.1.1.2. Electrical Conductivity

Electrical conductivity measurements over all the campaigns show that they range from 110 to 1260 µS/cm (Table I). Standard deviations have high values. The highest values are observed in October (campaigns 1 and 4), a month in which the water tables are strongly recharged.

3.1.2. Chemical Parameters

3.1.2.1. Calcium and Magnesium

Sample analysis values show that calcium is moderately concentrated in the water, with variations ranging from 0 to 61 mg/L (Table I). Magnesium concentrations ranged from 3 to 28 mg/L. Variations from one point to another and from one campaign to another are not great.

3.1.2.2. Sodium and Potassium

Sodium levels across all campaigns show a distribution ranging from 8.33 mg/L to 285 mg/L, with campaign averages ranging from 72.59 to 94.88 mg/L, with a high standard deviation and coefficient of variation of 70.01 mg/L and 0.89, respectively. The lowest concentrations are observed during the dry season.

According to the results obtained, potassium levels range from 0.1 mg/L to 12.2 mg/l, with averages ranging from 0.41 mg/L to 2.93 mg/L from one campaign to the next. Standard deviations ranging from 0.22 to 2.58 indicate a wide range of concentrations of this ion in water.

3.1.2.3. Chlorides

Monitoring of chloride levels in groundwater in the Maga rice-growing perimeter shows significant oscillations, although concentration values remain low. Cl^- levels range from 0 mg/L to 43 mg/L. Average concentrations range from 1.73 mg/L to 4.68 mg/L, with a standard deviation from 3.95 to 10.93 and a coefficient of variation from 2.06 to 3.24.

3.1.2.4. Sulphates

In the study area, average sulphate values range from 1.13 mg/L to 6.67 mg/L. Levels generally vary from 0 mg/L to 57 mg/L. The highest values were recorded during the high-water period in October (campaigns 1 and 4), while the lowest concentrations were obtained during the low-water period in February (campaigns 2 and 5).

3.1.2.5. Bicarbonates

The results presented in Table I show that bicarbonate ions in groundwater vary between 53 mg/L and

TABLE I: Results of Analysis of Physicochemical Parameters of Groundwater

	Campaign 1					Campaign 2					Campaign 3				
Parameters	Minimum	Maximum	Average	σ	CV	Minimum	Maximum	Average	σ	CV	Minimum	Maximum	Average	σ	CV
T°C	28.7	31.9	30.20	0.98	0.03	27.6	34.1	30.91	1.65	0.05	28.1	31.4	29.67	1.07	0.04
pH	6.44	8.16	7.25	0.56	0.08	6.7	8.3	7.47	0.46	0.06	6.8	8.24	7.48	0.43	0.06
CE	140	970	481.33	278.92	0.58	110	750	363.33	193.30	0.53	110	850	383.33	223.79	0.58
TDS (mg/L)	70	490	240.00	141.07	0.59	50	380	181.67	98.45	0.54	50	430	191.00	112.89	0.59
Ca^{2+} (mg/L)	0	61	12.00	19.63	1.64	0	38	4.73	9.32	1.97	1	34	7.73	10.84	1.40
Mg^{2+} (mg/L)	3	18	8.67	4.95	0.57	3	26	9.93	5.36	0.54	7	24	12.93	4.33	0.34
Na^+ (mg/L)	8.33	218.1	72.59	64.57	0.89	24.29	164.82	77.38	39.81	0.51	27.46	238.04	94.88	59.61	0.63
K^+ (mg/L)	2	12.2	2.93	2.58	0.88	1.9	5.8	2.38	0.97	0.41	2.1	2.8	2.39	0.25	0.11
NH_4^+ (mg/L)	0	40.9	3.87	10.26	2.64	1.1	7.8	2.62	1.85	0.70	2.4	13.6	4.51	3.66	0.81
Cl^- (mg/L)	0	22	1.73	5.61	3.24	0.2	16.1	1.92	3.95	2.06	0	32	3.38	7.96	2.35
NO_3^- (mg/L)	1.8	75.9	10.99	18.28	1.66	3	31.3	9.01	7.40	0.82	2	36.6	12.13	9.68	0.80
PO_4^{3-} (mg/L)	0.6	12.5	2.39	3.22	1.35	0.1	3.6	0.65	0.86	1.31	0.1	1.8	0.75	0.47	0.62
SO_4^{2-} (mg/L)	1	57	6.67	15.67	2.35	0	4	1.13	0.99	0.87	0	9	1.47	2.17	1.48
HCO_3^- (mg/L)	53.64	546.56	253.48	171.33	0.68	101.28	702.32	300.64	168.57	0.56	136.64	694.96	355.90	164.42	0.46
	Campaign 4					Campaign 5					Campaign 6				
T°C	27.6	31.9	29.57	1.19	0.04	27	31.5	29.25	1.33	0.05	28.9	31.9	30.19	0.93	0.03
pH	6.62	8.33	7.30	0.47	0.06	6.69	8.01	7.31	0.40	0.05	6.8	7.99	7.37	0.38	0.05
CE	150	1260	408.00	297.47	0.73	110	850	378.00	230.01	0.61	110	780	379.33	221.92	0.59
TDS (mg/L)	80	630	205.33	148.03	0.72	50	420	190.67	114.80	0.60	50	390	188.00	109.95	0.58
Ca^{2+} (mg/L)	0	13	2.40	3.04	1.27	1	14	2.67	3.29	1.23	1	56	9.20	15.00	1.63
Mg^{2+} (mg/L)	3	14	8.47	3.23	0.38	3	23	10.47	5.30	0.51	8	28	15.27	7.11	0.47
Na^+ (mg/L)	23	285	88.60	70.51	0.80	15	186	78.43	50.78	0.65	12.7	201	74.98	52.61	0.70
K^+ (mg/L)	0.2	1	0.41	0.22	0.52	0.1	4	0.71	1.09	1.54	1.3	3.8	2.19	0.82	0.37
NH_4^+ (mg/L)	0	11.2	3.64	2.90	0.79	0.9	21.4	4.31	5.52	1.28	0.2	15	3.06	3.56	1.16
Cl^- (mg/L)	0.3	43	4.68	10.93	2.34	0	32	2.77	8.12	2.94	0	20	1.69	5.08	3.01
NO_3^- (mg/L)	1	55.5	9.05	13.41	1.48	2.4	68.1	15.73	16.47	1.05	4.7	93.7	20.81	21.35	1.03
PO_4^{3-} (mg/L)	0.5	25.3	5.58	7.54	1.35	0.4	2.6	1.12	0.70	0.62	0.1	1.1	0.65	0.31	0.48
SO_4^{2-} (mg/L)	0	15	2.33	3.85	1.65	0	8	1.47	1.85	1.26	0	15	2.13	3.68	1.73
HCO_3^- (mg/L)	107.12	556.76	255.95	149.18	0.58	87.84	465.76	233.30	120.72	0.52	92.72	575.84	261.97	146.96	0.56

702.32 mg/L, with averages of 233.30 mg/L to 355.90 mg/L. Bicarbonate levels vary considerably, with high standard deviations ranging from 120.72 to 171.33 and coefficients of variation ranging from 0.46 to 0.68.

3.1.2.6. Nitrogenous and Phosphate Mineral Compounds

The results obtained on nitrogen and phosphate mineral compounds are presented in Table I. These results show the poor quality of these waters for nitrogen and phosphate mineral compounds, with low quantities of nitrate ions and significant quantities of ammonium and phosphate ions. Nitrates are present with concentrations that vary between 1 mg/L and 93.7 mg/L. Fig. 1 presents curves with little variation from one point to another during the same campaign, with the exception of sampling point P05. The general averages per campaign give concentration values ranging from 9.01 mg/L to 20.31 mg/L. The contribution of each sampling point to the mineralization is varied as the standard deviations vary from 7.0 to 21.35, with coefficients of variation ranging from 0.50 to 1.66 for all six campaigns.

Ammonium ions have concentrations ranging from 0 mg/L to 40.9 mg/L. These extremes are obtained during the same campaign with high standard deviations (1.85 to 10.26). The results obtained for this ion are presented graphically in Fig. 2.

Phosphate levels vary from 0.1 mg/L to 25.3 mg/L. The general averages vary from 0.65 mg/L to 5.58 mg/L over all six campaigns. The variation in concentrations is not negligible between the different points, and the different campaigns have values of the coefficient of variation greater than 1. The graphical representation (Fig. 3) of the data obtained for phosphates highlights two campaigns (1 and 4) that have concentrations going beyond the general average.

3.2. Discussion

To improve yield, farmers enrich the soil with synthetic nitrogen fertilizers. The doses of fertilizer applied depend from one farmer to another. These fertilizers contain substances that are very soluble in water, which, if not consumed by plants, easily infiltrate into the soil and gradually reach groundwater. Brought to the soil and in the presence of irrigation water, the main nitrogen fertilizers undergo the following reactions to provide nutrients:

- Ammonitrate (nitrogen content is 33.5%):

$$NH_4NO_3 \rightarrow NH_4^+ + NO_3^- \tag{1}$$

- Ammonia sulfate (nitrogen content is 21%):

$$(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^{2+} \tag{2}$$

High nitrate levels in groundwater are most often an indicator of groundwater contamination. However, in arid and semi-arid regions in Africa, naturally induced high

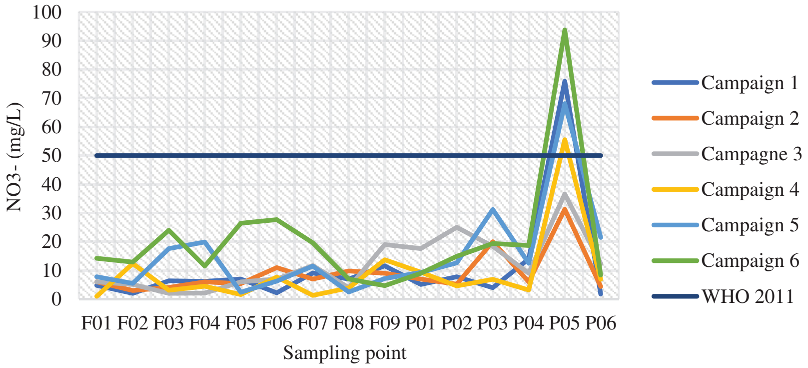

Fig. 1. Evolution of nitrates as a function of time.

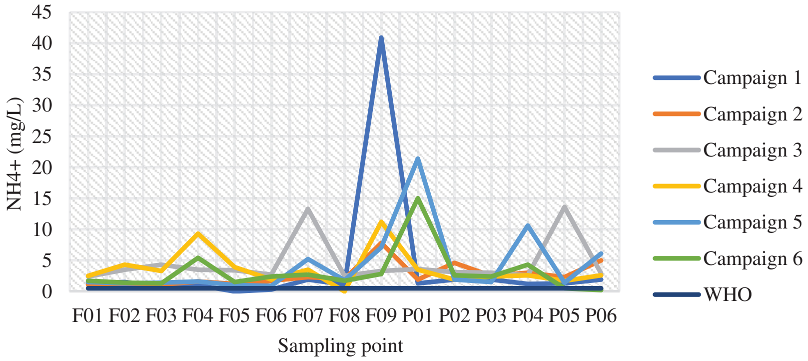

Fig. 2. Evolution of ammonium as a function of time.

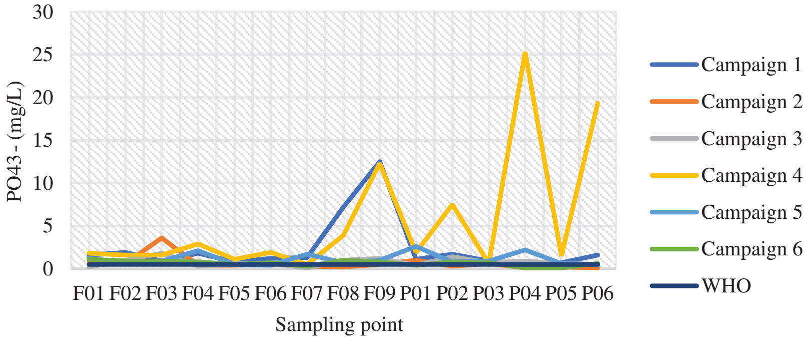

Fig. 3. Evolution of phosphates as a function of time.

nitrate concentrations due to the mineralization of soil organic matter accumulated during wet periods in the past have been reported [18].

However, in the study area, the distribution of nitrate levels is linked to anthropogenic polluting factors, as reported by several authors who have carried out studies in the area [19]–[21], and in particular agricultural activity. The clay roof of the groundwater has the ability to bind nitrate ions and protect the groundwater from high levels of pollution. With the exception of data from a single well located in the town of Maga (Fig. 1), all other points have nitrate contents below WHO standards [16]. The high concentrations (above the WHO guideline value) obtained in this well probably have an origin other than agricultural activities. Located on the outskirts of rice fields and with a surrounding town, the hypothesis of a double supply of nitrate ions by fertilizers and septic tanks in this well is possible.

An observation in Fig. 1 shows that nitrate ions evolve almost in the same way throughout the study period, with slight variations from one campaign to another. Fertilizers used for soil fertilization would, therefore, release little nitrate into the water. The clayey nature of the soil, as well as the alternating cultivation of rice plots, which reduces the quantity of fertilizer applied per rice growing season, play an important role in limiting the quantities that infiltrate into groundwater. Subsurface waters represented here by wells show the highest concentrations, followed by deep waters represented by drilling.

Fig. 2 shows that ammonium ions evolve almost in the same way throughout the study period, with variations noted from one campaign to another. The curve of campaign 3 presents a stable and high appearance compared to the others. Peaks are observed at several points during the different campaigns, which reflect various contributions to the concentration of this ion.

The measured content of ammonium ions in most cases is high compared to WHO [16] standards for water for human consumption (Fig. 2). In addition to the contributions obtained in the reactions of equations (1) and (2),

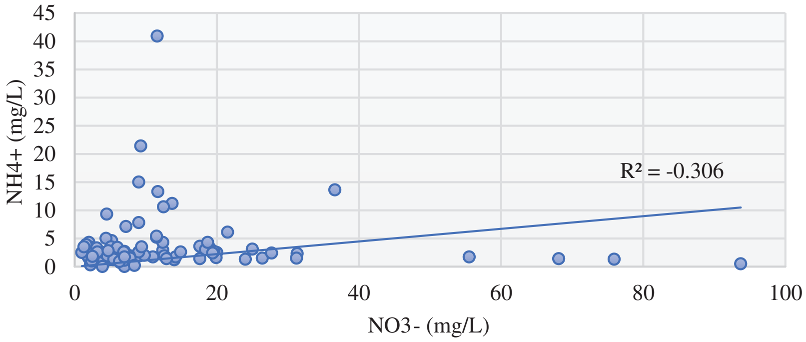

Fig. 4. Evolution of nitrates as a function of ammonium.

the ammonium ion can also find its source through the reduction of nitrates following the equation:

$$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \quad (3)$$

This is due to the fact that in the upper layers of the soil, microorganisms are involved in the degradation of organic matter which will produce nitrogen compounds [22]. Another direct contribution of these nitrogen compounds is the use of nitrogen fertilizers for the fertilization of fields, the area being a vast rice growing area where fertilizers such as ammonitrates and ammonia sulfates are in high demand. Considering these two sources of ammonium ion intake, the evolution in the water of this ion must be the opposite of nitrate ions because the two are, respectively, the reduced and oxidized forms of nitrogen. However, the evolution of ammonium in the present study does not present a correlation with nitrate ions (Fig. 4). We must, therefore, admit sources other than the first two cited.

Fixed ammonium constitutes, in structured clay soils, a significant component of the nitrogen cycle [23], [24]. This form of ammonium has always been neglected in the reasoning of nitrogen fertilization of crops. Indeed, 2:1 type clays can contain, in their inter-layer space, appreciable quantities of ammonium [25]. These ions, selectively fixed in the interfoliar positions of clay minerals, can be released, in part, during the growing season and contribute to crop nutrition [26]. NH_4^+ inputs (fertilization, ammonification) induce ammonium fixation [27], [28]. On the other hand, the release of NH_4^+ (nitrification, microbial assimilation, uptake by the plant) generates a release of fixed ammonium [27]–[29]. This second situation can better explain the high levels of NH_4^+ ions in water, which are not linked to the concentrations of NO_3^- ions.

In water, phosphates can exist in solution or in suspension, in mineral or organic state [30]. Orthophosphate concentrations in undisturbed natural environments are around 10 µg/L [31].

The analysis of Fig. 3 shows that phosphate levels exceed the WHO standard (0.5 mg/L) but also natural concentrations. These high values above natural levels show that there is a contribution other than natural of these ions in the waters. These levels also show that this element constitutes a risk of pollution for all waters in the Maga area. Observation of the graph shows peaks during campaigns 1 and 4, which confirms that the phosphorus in the waters does not have a single source. In addition to agriculture, with the use of phosphate fertilizers, phosphates can also come from exchanges between inorganic particulate forms of phosphorus. It is known that only 10% to 15% of the phosphorus provided by fertilizers is used and transformed into plant or microbial organic matter after one year of burial [32]. The other part remains attached to the surface of the soil particles. This extremely strong adsorption depends on the composition of the soil and its clay and oxyhydroxide content (iron, aluminum, limestone). However, it is known that an increase in temperature in a natural environment amplifies the biological activity of mineralization, which consumes oxygen. The oxygen level thus reduced following biological activity lowers the Redox potential and can cause a release of orthophosphates linked to Iron by reduction of Fe^{3+} to Fe^{2+} [33]. In the study area high concentrations of total iron are obtained. This process of releasing orthophosphates can, therefore, also justify the various contributions of PO_4^{3-} ions in the water analyzed.

4. CONCLUSION

The mineralization of the waters of the rice-growing area of Maga by nitrogen and phosphorus has various sources. For nitrates, fertilizers used for rice cultivation have significant contributions to subsurface waters. The clayey nature of the roof of the aquifer in the area favors the fixation of these ions, which translates into their reduction in deep waters. The reduction of nitrates to ammonium ions is not the only way of bringing ammonium into water. The hydrolysis of ammonium fixed in clay is another important source of these ions in the waters studied. The non-correlation between nitrate and ammonium ions justifies this double contribution. Phosphates also have a diverse source of intake. The phosphate fertilizers used for soil amendment, on the one hand, and the release of orthophosphates linked to iron by oxidation-reduction phenomena, on the other hand, explain the presence of these ions in the waters of the study area. A slight fluctuation in the concentrations of different nitrogen and phosphate ions is noted throughout the study area. The water from wells and boreholes studied in the rice-growing area of Maga is used by the population for food and domestic use; therefore, the concentrations of nitrogenous and phosphate substances must be monitored because of their concentrations.

CONFLICT OF INTEREST

The authors declare that they do not have any conflict of interest.

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