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The Influence of Fertilizers on the Behavior of Fluoride Fractions in the Alkaline Soil

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The influence of fertilizers on the behavior of fluoride fractions in the alkaline soil

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ABSTRACT

It has been established that fluoride bioavailability in the soil is defined by the form which it exists rather than the amount of total fluoride. In the soil, fluoride exist in different fractions such as water soluble (Ws-F), Exchangeable (Ex-F), bound to iron/manganese (Fe/Mn-F), organic matter bound (Or-F), and the residual (Res-F). All of these fractions are bioavailable however to different extents in an order Ws-F>Ex-F>Fe/Mn-F>Or-F>Res-F. Agricultural practices such as fertilizer application alters the behavior of these fractions which further affects fluoride bioavailability in the soil. This study investigated the influence of the three commonly used fertilizers (Di-ammonium Phosphate (DAP), Urea, and cow-manure) on the bioavailability of soil fluoride in an alkaline soil. The soil was mixed with either one of the fertilizers then incubated for a period of five months. All three fertilizers increased the amount of Ws-F by 7.8 ± 0.6, 4.1 ± 0.2, 9.6 ± 1.1 mg/kg and Fe/Mn-F by 2.24 ± 0.3, 0.44 ± 0.2, and 2.1 ± 0.2 mg/kg, for DAP, Urea, and manure amendments, respectively, but had no impact on the amount of Or-F. All three fertilizers were observed to enhance the bioavailability of fluoride in the soil by increasing the amount of Ws-F. The fertilizers could have increased the bioavailability of fluoride in the soil directly or indirectly through alteration of pH and the soil elemental composition. The three fertilizers might not be suitable for use in fluoride contaminated alkaline soils as they accelerate fluoride release and hence bioavailability in the soil.

1. Introduction

Fluoride is beneficial at low concentrations in preventing dental caries and in the development of stronger bones [1] . However, exposure to higher doses leads to a condition called fluorosis which includes dental caries and brittle bones [2]. Water has long been the known main route of fluoride exposure, but food is identified as another noteworthy exposure path [1]. Studies have investigated fluoride uptake and accumulation by crops from the soil [2-4]. These studies have determined that factors such as type of plant species, soil properties as well as quantity and form with which fluoride exist in the soil influence the amount taken up and accumulated by the plant. The amount of fluoride accumulated by plant finds its way through the food chain thereby prominently affect the top members of the food chain which include human beings [5].

It has been established that mobility, toxicity and bioavailability of fluoride in the soil is defined by the form with which it exists rather than the amount of total fluoride (TF) [2]. Soil fluoride fractions such as water soluble (Ws-F), Exchangeable (Ex-F), bound to iron/-manganese (Fe/Mn-F), bound to organic matter (Or-F) and residual (Res-F) fluoride have been successfully extracted [6, 7]. These forms are considered bioavailable such that they can easily be taken up and accumulated by the soil living forms. Although bioavailable, the extent of their bioavailability decreases in an order Ws-F>Ex-F>Fe/Mn-F>Or-F>Res-F. Therefore, the soil containing high concentrations of Ws-F and Ex-F has high fluoride toxicity compared to the remaining fractions whereas Res-F is considered less bioavailable [5, 8, 9]. These fluoride fractions though, are interchangeable from one another subject to changing soil properties like pH, soil organic matter (SOM), and elemental composition, in so

doing, it modifies the fluoride bioavailability behavior of the soil [8].

Fertilizers have been used for centuries to maintain and increase food production worldwide as they enable farmers to supply the exact nutrients essential to specific soil requirements. Studies have focused on the impact of fertilizers on crop productivity, organic matter, and other soil properties [10, 11] but little attention has been directed towards its influence on the behavior of detrimental ions such as fluoride that exist in the soil. Like other plant nutrients, fluoride uptake by roots and transfer through the plant begins with dissolution into the soil solution, dislocation by soil salts, or by coming into contact with root exudates. The three processes depend on the surface area of the solid phase of the soil and the soil's bonding strength [12]. Regular inputs of fertilizers into the agricultural soils can alter the above-mentioned soil properties which could either accelerate the release of weakly bound fluoride species or increase the bonding strength of the soil which then reduces its release into the soil solution. Therefore, it is of importance to understand the influence of fertilizers on the bioavailability of fluoride in the soil which is the aim of this work. This study investigated the influence of three commonly used fertilizers (Di-ammonium phosphate (DAP), Urea, and cow-manure) on the behavior of five fluoride fractions (Ws-F, Ex-F, Fe/Mn-F, Or-F and the Res-F). It aims to understand as to whether fertilizer application increases or decreases the bioavailability of fluoride in the soil.

2. Materials and methods

2.1. Soil Sampling and fertilizer treatments

The soil used in this experiment was collected from a farm in an area known to contain high fluoride in water and soil. The area is located at the slopes of Mount Meru, Arusha, Tanzania with coordinates 3°10'35" S 36°51'35" E. The farming practices involve maize and beans cultivation during the rainy season and horticultural production (Tomato, kale, cabbage, and onions) under irrigation during the dry season. The soil has regularly been supplied with DAP, Urea, and manure fertilizers for more than 2 decades to supply plant nutrients.

The area receives rainfall range from 90 to 1000 mm per annum and the temperatures range between 12 - 30°C [13]. The topsoil (0-20 cm), was randomly collected on the same farm using a hand spade during the dry season to represent the root zone of most cultivated crops in the area. The soil was then mixed thoroughly, air-dried for 2 days, and then passed through a 2 mm sieve to eliminate grit and other debris. The soil was stored in the plastic containers that were cleaned with nitric acid (HNO₃) before laboratory analysis. Soil aliquots were later mixed with the selected fertilizers; (Di-ammonium phosphate (DAP) which contains 46% P_2O_5, 18 % N; Urea with 46 % N; or cow-manure. The selected three fertilizers are commonly used in the area to enhance crop production in both seasons. The synthetic fertilizers were commercially obtained whereas manure was collected from the household's animal yards of the same village where the soil was sampled.

2.2. Analytical procedure

In the laboratory, the selected soil properties were quantified. The soil particle size distribution was determined according to DIN ISO 11277, 2002. The cation exchange capacity (CEC) was examined using the ammonium acetate (pH 8.2) extraction method by Schollenberger and Dreibelbis (1930) [14]. The pH and electric conductivity (EC) were measured using a pH meter (orionVersASTAR pro) in a 1:2.5 soil-water suspension. The elemental composition was determined using atomic absorption spectrophotometer (AAS) [15]. The Walkley-Black acid digestion method was used to quantify the soil organic matter (SOM) [16]. Fluoride concentration was measured using a potentiometric method (ISE- Thermo Scientific Orion 164 9609BNWP). The reagents used were of analytical grade and distilled water was used wherever needed throughout the experiment.

2.3. Experimental setup

To investigate the influence of fertilizer on the forms of fluoride in the soil, the three different fertilizers were mixed with the experimental soil at the laboratory scale. A 100 g sample of soil was thoroughly mixed with 80 mg of DAP or Urea or 500 mg of cow manure. The samples were then incubated in a shaded area at room temperature (27 ± 2 °C) and 70 % moisture. The experiment was conducted in a completely randomized design. The blank samples were prepared within each series of sampling and analysis for quality assurance and detection of possible contaminations. The analysis of the amount of Ws-F, Ex-F, Fe/Mn-F, and Or-F on the soil-fertilizer mixtures together with pH was monitored every 30 days for a period of 5 months. For analysis, the small amount of soil was taken, oven-dried at 40°C then stored in a desiccator. When the soil samples cooled to room temperature, the soil was measured and analyzed according to section 2.4

2.4. Fluoride determination

2.4.1. Total fluoride (TF) determination

Total fluoride was determined according to McQuaker and Gurney (1977) procedure [17]. The 0.5 g of the soil sample was weighed into the crucibles and then moistened with 5 ml of distilled water. A 6 ml of concentrated NaOH (17 M) was then added and placed into the oven set to 150 °C for 1 h. After 1 h the samples were moved into the muffle furnace set at 600 °C for 30 min and then left to cool to room temperature. Distilled water was added to allow for the dissolution of the NaOH cake then moved to the 50 ml centrifuge tubes where the pH was adjusted to around 8 by using HCl. Subsequently, the samples were shaken, centrifuged and the supernatant was collected for analysis using a fluoride ion-selective electrode (F-ISE) mixing with TISAB II as an ionic strength adjustment buffer at 1:1.

2.4.2. Extraction of various species of fluoride

Species of fluoride were extracted sequentially following a procedure reported by Chen et al. (2013) [18]. A 2.5 g of soil sample was sieved using 0.2 mm mesh and placed into a 50 ml centrifuge tube and various species of fluoride were extracted by adding 25 ml of the extracting solutions as summarized in table 1. The sequential extractions were also used to extract the forms of fluoride present in the fertilizers.

2.4.3. The amount of fluoride was calculated as

Fluoride concentration = C x (V/1000) x (1000/W)
Where; C - measured reading in mg/l
V - Volume of the extracted solution
W - Amount of the soil used

2.5. Statistical analysis

Statistical data analysis was computed using Origin Pro 8.5 software.

Table 1
Extraction processes of various species of fluoride in soil adapted from Chen et al. (2013) [18]

Fluoride specie	Extraction process
Water-soluble fluoride (Ws-F)	distilled water Shake for 30 min at 60 °C
Exchangeable fluoride (Ex-F)	1mol/l MgCl₂ Shake for 1 h at 25 °C
Fe/Mn bound fluoride (Fe/Mn-F)	0.04 mol/l NH₄.HCl Shake for 1 h at 60 °C
Organic matter bound fluoride (Or-F)	Step 1: 3 ml of 0.02 mol/l HNO₃ + 10 ml 30 % H₂O₂ Step 2: 12 ml of 3.2 mol/l NH₄ acetate Shake for 30 min at 25 °C
Residual fluoride (Res-F)	TF minus the above for species of fluoride

For quality assurance, the experiment was conducted in triplicates and two samples were drawn from each replicate for analysis. Values are given as mean ± standard deviation. To calculate the statistical significance levels of the three fertilizers on fluoride forms, ANOVA tests were conducted using XLSTAT followed by Tukey's multiple pairwise comparison tests. Replicates of soil-fertilizer samples were used for the ANOVA test, and a significant level of 5 % was used in the statistics.

3. Results and discussion

3.1. Soil properties

3.1.1. Soil characterization
The average values of soil properties are presented in table 2. The soil properties observed are in concordance with those obtained by Rizzu et al., (2020) who used the same agricultural soil to investigate fluoride uptake by maize and bean plants [5]. The soil is characterized as sandy loam with a total fluoride (TF) concentration of 422 ± 52.9 mg/kg containing Ws-F of one order of magnitude less than TF and therefore very likely to cause toxicity to fluoride-sensitive plants and animals. The behavior and quantity of fluoride in the soil have been linked to many soil properties [5]. However, the fluoride concentration observed in the experimental soil could be associated with exchangeable sodium percentage (ESP), clay content, pH, irrigation, and contamination from long-term use of phosphate fertilizers.

The soil is characterized by high ESP (76.9 %) which discloses an imbalance between the exchangeable sodium and other cations which in turn affects the behavior and quantity of fluoride in the soil. High ESP lessens the degree of water percolation through the soil [19]. When water percolates into the ground it leaches down fluoride that is present at the topsoil, thereby reducing the amount present for plant uptake. High ESP, contributes to high fluoride retention at the topsoil solution by reducing the soil's ability to percolation. During the dry season, most of the fluoride will likely accumulate at the topsoil compared to the wet season because the evaporation rate is expected to be higher.

Soils with low clay content contain fluoride that is readily available to plants due to the incapability of soil to retain large amounts of fluoride [12]. Alternatively, a coarse soil with small clay content such as the one used for this study with 6.4 % clay, limits the fluoride bonding surface of the soil because it does not provide a wide surface area to hold the available free fluoride.

Furthermore, the strong alkaline property of the soil (pH of 9.3) could be associated with the amount of fluoride in the soil. This is because fluoride is strongly held by the soil at pH 6 and desorbed intensely at one unit higher or lower [20]. For example, if the soil contains significant amounts of Al at low pH, Al and F react from AlF_x complexes thereby reducing the free fluoride in the soil solution [9]. High pH increases the electrostatic potential of the soil thus decreasing its fluoride retention capacity. Moreover, high pH increases the concentration of OH^- ions in the soil solution which then displaces the adsorbed fluoride [12]. Therefore, the high pH characteristic of the experimental soil could be among the reason for the high fluoride concentrations observed.

3.1.2. Fluoride fractionation in the soil
The various forms of fluoride present in the soil were extracted sequentially according to table 1. The soil contained an average TF of 422 ± 52.9 mg/kg containing Ws-F of 39.5 mg/kg which was the largest

quantity extracted followed by Or-F (9.1 ± 2.1 mg/kg), then Ex-F (3.5 ± 0.5 mg/kg), and the smallest being Fe/Mn-F (3.1 ± 1.0 mg/kg). The extracted fluoride accounted for 13.5 % of the TF whereas 86.5 % remains quantified as the residual amount. In the soil, fluoride is found attached to minerals and inorganic compounds [4]. Each of these fluoride fractions exhibits a unique behavior dictated by factors such as; the place it is attached, soil properties, human activities, and the climate of the area [9]. The mobility, availability, and toxicity of fluoride to plants and animals is not a function of TF but the form in which it exists [4].

The Ws-F and Ex-F are the two fractions easily available for plant uptake and therefore mostly associated with the bioavailability and the extent of toxicity. The high quantity of Ws-F in the soil compared to the other fractions indicate that most of the bioavailable fluoride in this particular soil exists as NaF, SiF_4, or HF which are readily soluble fluorinated compounds [21]. When sodium is freely available and abundant in the soil (317 mg/kg in this case), it bounds to the clay particles through displacing other cations. Being highly electro-positive, sodium easily reacts with fluoride ion which is also highly electro-negative. But because sodium is simply soluble, it releases fluoride back into the soil solution. The displacement of exchangeable cations with sodium also contributes to a lesser quantity Ex-F observed, existing as sparingly soluble in forms of CaF_2 and MgF_2.

The Fe/Mn-F is the amount of fluoride held by the oxides and hydroxides of Fe, Al, and Mn. The small concentrations of Fe/Mn-F observed could be related to pH. This is because, pH is known to dictate the behavior of elements such as aluminum and iron (Fe) in the soil. In this case, although the soil contained significant amounts of aluminum (81.3 g/kg), its reaction with fluoride is rated impossible at high pH [9] whereas, at the same high pH, Fe (65.4 g/kg) exists as Fe (III) a form which is not reactive leading to less quantity of Fe/Mn-F [22].

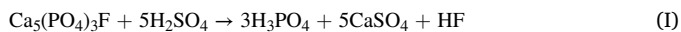### 3.2. The fluoride fractions in the fertilizers
Various forms of fluoride existing in the fertilizers were quantified according to table 1 and the results are presented in Table 3. There was a significant difference ($p<0.05$) between fertilizers on the amount of fluoride fractions. DAP contained the extremely high concentration of all fluoride fractions whereas manure and Urea contained less quantities, Urea exhibiting the least. The Ws-F concentration was found to be 1.5 ± 0.1 mg/kg for Urea, 2.4 ± 0.5 g/kg for DAP, and 8.2 ± 1.9 mg/kg for manure. Other forms of fluoride were minimal (< 0.5 mg/kg) in Urea whereas manure contained 1.9 ± 1, 6.8 ± 0.4, 6.1 ± 0.6 mg/kg, and DAP contained 52.8 ± 19.7, 370 ± 22.5 and 570 ± 44.0 mg/kg; Ex-F, Fe/Mn-F and Or-F, respectively.

The high fluoride concentration observed in the DAP fertilizer is principal because it is derived from the phosphate rock. Phosphate-rock is known to contain fluorapatite ($Ca_5(PO_4)_3F$) and fluorite (CaF_2) which are fluoride-containing rocks [4, 23]. DAP is synthesized during the

Table 3
Average concentration of the forms of fluoride in the Fertilizers

	TF (mg/kg)	Ws-F (mg/kg)	Ex-F (mg/kg)	Fe/Mn-F (mg/kg)	Or-F (mg/kg)
DAP	8,760 ± 246	2,410 ± 53.3	52.8 ± 19.7	370 ± 22.5	570 ± 44
Manure	98 ± 7	8.2 ± 1.9	1.92 ± 1	6.8 ± 0.43	6.12 ± 0.6
Urea	1.98 ± 0.9	1.5 ± 0.12	0.27 ± 0.1	N/A	N/A

Table 2
Baseline soil properties

Depth (cm)	CEC (mmol/g)	Clay (%)	Silt ((%)	Sand (%)	Ca (mg/kg)	Mg (mg/kg)	K (mg/kg)	Na (mg/kg)	ESP (%)	O.M (g/kg)	EC (µS/cm)	pH(H2O)
0-15	0.097	6.4	18.2	75.4	34	7	98	317	76.9	11.2	208.6	9.3

reaction between ammonia and phosphoric acid formed by a wet process (Eq I, III). Although during this process fluoride is lost as HF, yet some of it precipitates as CaF_2 (Eq II) accounting for 2-3 % of the phosphate-fertilizer [24].

$$Ca_5(PO_4)_3F + 5H_2SO_4 \rightarrow 3H_3PO_4 + 5CaSO_4 + HF \qquad (I)$$

$$Ca^{2+} + 2HF \rightarrow CaF_2 + 2H^+ \qquad (II)$$

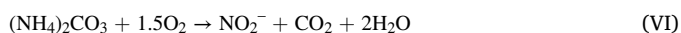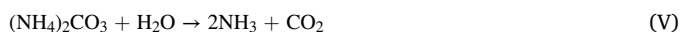$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4 \qquad (III)$$

The 2-3 % fluoride introduced into the soil each time the phosphate-fertilizer is applied into agricultural soils is significant especially when the application is regular and long-term.

Conversely, fluoride in the manure attests to the fluoride exposure to herbivorous in the area. The probable paths for fluoride exposure to the animals are through grazing, soil ingestion, and/or drinking water [25]. Apart from water, fluoride exposure to animals through grazing is reported to be low compared to soil ingestion [2]. Regardless, acute fluorosis has been observed in domestic animals after short-term ingestion of feed containing fluoride levels higher than 3000 mg/kg [23]. Even further, deaths have been observed due to the ingestion of fluoride-containing volcanic ash deposited on pastures [26].

3.3. Impact of fertilizers on pH

Table 4 shows the influence of fertilizers on the pH of the soil. There was a significant difference ($p < 0.05$) in the influence of the three fertilizers on pH of the soil. The pH change exhibited a slight positive correlation with the control (0.31) and manure (0.38), a weak positive correlation with DAP (0.19), and a strong negative correlation with Urea (-0.88). The negative correlation with Urea could be facilitated by the presence of nitrogen (46 %) in the fertilizer. Once Urea dissolves into the soil solution, it releases ammonium which rises the soil pH (in the first 14 days). Depending on the soil microbial activity, ammonium will progressively be converted to nitrate (nitrification) resulting in consequent acidification (Eq. IV to VIII). Alternatively, at high pH and temperature, ammonium can be converted into ammonia-nitrogen which is lost into the atmosphere through the ammonia volatilization process (Eq. V), this results into the pH rise observed on the 90th day [27]. The initial pH rise could have taken place in the first few days as the initial data were collected from day 30.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \qquad (IV)$$

$$(NH_4)_2CO_3 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (V)$$

$$(NH_4)_2CO_3 + 1.5O_2 \rightarrow NO_2^- + CO_2 + 2H_2O \qquad (VI)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad (VII)$$

$$4NO_3^- + 5C + 2H_2O \rightarrow 2N_2 + 4HCO^- + CO_2 \qquad (VIII)$$

Unlike Urea, the sudden pH sink and rise observed in DAP-amended soils could be the result of a simultaneous impact of transformations of both nitrogen (18 %) and phosphorus pent-oxide (46 %). While nitrogen undergoes revolutions in Eq. IV-VIII, phosphorus also undergoes its chain of conversions. In the soil, Phosphorus pent-oxide dissociates into phosphoric acid which is its temporal intermediate product. The

formation of phosphoric acid lowers the soil pH before its disintegration to hydrogen and phosphate ions (Eq. IX-XI). The two ions are further neutralized by the hydroxyl ions from the soil solution endorsing the pH rise again.

$$(NH_4)_2HPO_4 \rightleftharpoons NH_3 + (NH_4)H_2PO_4 \qquad (IX)$$

$$(NH_4)H_2PO_4 \rightleftharpoons NH_4^+ + H_2PO_4 \qquad (X)$$

$$H_2PO_4 \rightleftharpoons PO_4^- + 2H^+ \qquad (XI)$$

The soil ions normally react with the ions introduced by the fertilizers to establish an equilibrium. Through this process, the soil stabilizes most of the fluoride from fertilizers but the stabilization capacity is dictated by soil factors including pH [28]. The pH transforms the ionic species existing in the soil and the electrostatic potential of adjustable charge surfaces with which the ionic species react. At low pH, for example, the soils containing Al^{x+} species will retain most of the fluoride through the formation of AlF_x compounds whereas at high pH the soil's retention capacity will be dictated by Ca^{2+} through the formation of CaF_2 precipitate [28].

3.4. Impact of fertilizers on the fractions of fluoride in the soil

The dynamics of the fractions of fluoride in the soil after adding fertilizers are presented in figure 1. There was a significant difference ($p < 0.05$) between the influence of the three fertilizer-amended soils and the control on the increase of Ws-F in the soil. The difference between Manure and DAP was not significant ($p > 0.05$) while DAP and Urea were not significantly different ($p > 0.05$) during the incubation period. The increase in the amount of Ws-F was instant during the first 30 days followed by the insignificant deviations thereafter in all samples. Supplementing the soil with the fertilizers contributed to a rise in the average amount of Ws-F from 39.5 to 42.7 ± 2.0, 46.4 ± 2.6, and 48.2 ± 3.2 mg/kg for Urea, DAP, and manure, respectively whereas in the control this amount decreased to 38.6 ± 1.7 mg/kg over 150 days. There was no significant difference observed in Ws-F from day 90 to 150 on all soil samples pointing to the establishment of the equilibrium of fluoride in the soil. When compared to the control, Ws-F concentration in the soils treated with fertilizers increased by 4.1 ± 0.2, 7.8 ± 0.6, and 9.6 ± 1.1 mg/kg for Urea, DAP, and manure, respectively. The increment in the amount of Ws-F observed when Urea was added into the soil is similar to the results obtained by Chen et al., (2010) on both fluvo-aquic and paddy soil [8].

There was similarly a significant difference ($p < 0.05$) observed between the fertilizer-amended soils on the behavior of Ex-F. Urea amended soil did not reveal a noteworthy impact on the amount of Ex-F whereas manure exhibited a rise of 1.8 ± 0.5 mg/kg and DAP of 0.7 ± 0.5 mg/kg equated to the control soils as shown in figure 1 (b). The Ex-F exhibited a zigzag rise and fall changes which could be associated with the trivial pH changes that were taking place in the soil-fertilizer solution however the zigzag pattern came to an end from the 90th day where the concentration of Ex-F in both samples became constant all the way to the 150th day.

Inversely, no significant difference ($p > 0.05$) observed on the impact of fertilizer-amended soils and the control to the amount of Fe/Mn-F. The initial concentration of Fe/Mn-F in the soil before addition of fertilizers was 3.1 ± 0.9 mg/kg which increased to 4.0 ± 2.1, 6.2 ± 1.7, 3.5 ± 0.7, and 6.1 ± 1.9 mg/kg for control, DAP, Urea, and manure (figure 1 (c)). These values are equivalent to an increase by 2.2 ± 0.3 and 2.1 ± 0.2 mg/kg for DAP and manure and a decrease by 0.4 ± 0.2 mg/kg for Urea equated to the variations in the control sample. Although the impact exerted by fertilizers on Fe/Mn-F was different from one another, the difference was not significant. The difference in the amount of Fe/Mn-F from day 90 to 150 was not significant. Furthermore, the fractions of fluoride were found to correlate to each other such that Ws-F-Ex-F showed a strong positive correlation (0.697), Ex-F-Fe/Mn-F a
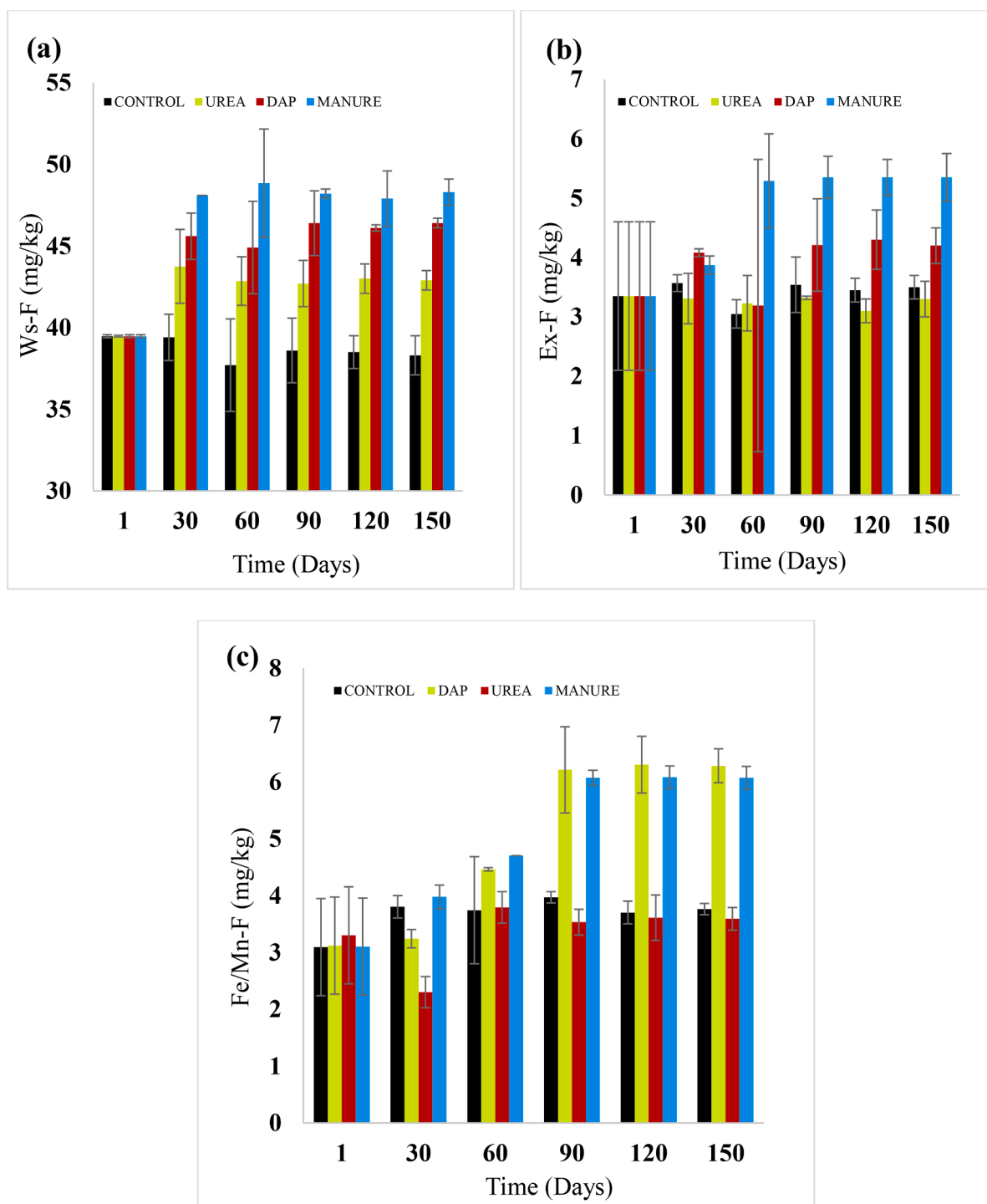
Table 4
The influence of fertilizers on pH of the soil

Day	Control	DAP	Urea	Manure
0	9.3 ± 0.1	9.3 ± 0.1	9.3 ± 0.1	9.3 ± 0.1
30	9.1 ± 0.3	8.0 ± 0.3	8.8 ± 0.3	9.7 ± 0.3
60	9.6 ± 0.04	9.3 ± 0.5	8.8 ± 0.3	9.6 ± 0.0
90	9.4 ± 0.0	8.9 ± 0.2	9.6 ± 0.2	9.8 ± 0.1
120	9.3 ± 0.2	9.2 ± 0.3	9.3 ± 0.3	9.5 ± 0.2
150	9.3 ± 0.2	9.3 ± 0.2	9.4 ± 0.2	9.6 ± 0.3

Figure 1. Influence of fertilizers on (a) Water-soluble-fluoride (Ws-F) (b) Exchangeable-fluoride (Ex-F) (c) iron and manganese oxides bound-fluoride (Fe/Mn-F) in the soil

moderate positive correlation (0.449), and Ws-F-Fe/Mn-F a weak positive correlation (0.173).

There was no significant change in the amount of all fluoride fractions from day 90 to 150, this behavior can be observed to resemble the pH change which remained fairly constant from day 90 to 150. This is the point where the soil establishes its new fluoride fractionation equilibrium succeeding fertilizer application. Each time a fertilizer is introduced into the soil, the soil undergoes through these fluctuations until its equilibrium is established. Fertilizers interferes the fluoride cycle in the soil through introduction of new ions, changes pH and direct

introduction of fluoride. New ions presented take part in chemical reactions in the soil to gain its stability which further affects the soil pH. The ability of the ions to participate in the chemical reactions in the soil can either accelerate fluoride release or enhance fluoride holding capacity of the soil the same case being applied to pH changes. Although DAP and manure contained fluoride, the amount that gets into the soil directly is minimal depending on the amount of fertilizer added and the application period. This is attested by no significant change on the amount of TF observed after fertilizers amendments. Therefore, although the fertilizers could have accelerated the bioavailability of

fluoride in the soil directly, its impact is fairly low compared to its indirect impact through alteration of the soil elemental composition and pH.

The impact of fertilizer on the increment of the fractions of fluoride was highly pronounced on the Ws-F fraction compared to the other fractions. The Ws-F is the highest bioavailable over the rest of fractions, and was reported to directly correlate with fluoride uptake by *Trifolium repens* and *Lolium multiflorium* [9]. The accumulation of fluoride in tea leaves was also reported to linearly correlate with its amount in the soil [29]. The Ws-F is the form of fluoride that dissolves in soil solution, one that has weakly been attached to the soil solid phase. The higher the amount of Ws-F, the higher its availability for plants and animals and the higher the toxicity exposure levels [7]. The three fertilizers contained Ws-F, which could have released it directly into the soil solution after amendment. But considering the amount of fertilizers mixed into the soil, the amount released directly into the soil could be estimated to be as low as around 0.2 ± 0.7 mg/kg for DAP and 0.004 ± 0.02 mg/kg for manure and negligible for urea. The amount of Ws-F increased could be originating from conversion of the Res-F since there was no significant changes observed on the quantity of other fractions. The fertilizers could have acted indirectly through alteration of the soil's pH (discussed in section 3.3) and/or elemental composition. Since they contain anions such as ammonium, nitrite, nitrate, and phosphate, it could easily replace fluoride ions attached to the soil particles they have a high affinity to the exchange site. Through this process, fluoride attached to the Res-F can be replaced accelerating its release into the soil solution.

The Ex-F is held by exchangeable cations (Ca, Mg, Al, K, and H) present in the soil [30]. These cations balance charges of unstable clay minerals and are interchangeable with one another. Clay ordinarily comprises an electrical charge caused by the imbalance of the quantity of electronegative and electropositive ion layers within the crystals. The imbalance is generated by the impurities integrated into the clay minerals during its development. The presence of an electrical charge attracts ions such as exchangeable cations to gain stability. Consequently, exchangeable cations are held by the negatively charged clay minerals in the soil [31]. Therefore, the number of exchangeable cations and hence Ex-F is limited by the quantity of negatively charged clay particles. The presence of a substantial amount of permanently negative charged clay minerals increases the number of exchangeable cations and vice versa.

The exposed surface of the Fe/Mn-OH group has an amphoteric character which enables it to lose or accept hydrogen ions depending on the pH of the soil solution. At low pH, anions are strongly held and the soil will participate in anion exchange capacity (AEC) whereas, at high pH, cations are strongly held and become part of the soil CEC [18, 31]. Also, the carboxyl group associated with the surface of the oxide/-hydroxide takes part in anion exchange with the fluoride-containing ligands interchanging the F^- and OH^- depending on pH, the amount of Fe/Mn-OH, and fluoride present in the soil. This explains the increase in the amount of Fe/Mn-F in the experimental soil. The increase in the amount of Fe/Mn-F could be beneficial since this form of fluoride is mostly unavailable for plant uptake [8].

4. Conclusion

This study investigated the influence of the three fertilizers on the bioavailability of fluoride fractions in the alkaline soil. the three fertilizers used for this study contained different concentrations of the bioavailable fluoride the highest being di-ammonium phosphate (DAP) followed by manure. All three types of fertilizers increased the amount of water soluble fluoride (Ws-F) as well as the amount of iron/manganese bound fluoride (Fe/Mn-F) but had no observable impact on organic matter bound fluoride (Or-F). The findings observed fertilizer application practice to contribute to the availability of fluoride through direct fluoride input, and alteration of soil pH. These three fertilizers might not be suitable for use in alkaline soils especially those with high fluoride concentrations as they accelerate fluoride release into the soil solution.

DAP and manure contained significant fluoride quantity and therefore its addition to the fluoride-contaminated soil with high exchangeable sodium percentage (ESP) may result in further fluoride accumulation on the topsoil however this entails further investigations. This study recommends further investigation of the influence of these fertilizers on fluoride fractions in a wider variety of soil or employment of different fluoride locking mechanisms equivalent with the fertilizers to prevent its further fluoride release into the soil.

Declaration of competing interest

The authors declare that there are no conflicts of interest whatsoever in publishing this article

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