



Assessing global-warming induced soil organic matter and iron oxides depletion: Empirical insights into sorption and uptake of atrazine by plants

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ABSTRACT

Recent pesticide use is alarmingly high and unregulated in several parts of the world. Pesticide fate in soil is controlled by sorption processes which affect the subsequent transport and chemical reactivity in the environment, as well as uptake by plants. Sorption processes are dependent on soil composition and properties, but these are beginning to be affected by global warming-linked factors leading to soil depletion. Thus, it is vital to decipher soils' response, especially in the sub-Saharan (SS), to the depletion of some inherent components in the presence of pesticides. This was ascertained by monitoring a model pesticide (atrazine) sorption and desorption on whole SS soil (WS), and the same soil whose organic matter (OMR) and iron oxides (IOR) were substantially depleted, as well as studying atrazine uptake from these soils by fast-growing vegetables. Organic matter depletion enhanced equilibrium in OMR. Sorption was enhanced at lower ambient pH, higher initial atrazine concentration, and higher temperature. Hysteresis was low resulting in high desorption. Overall, atrazine desorption of $\geq 65\%$ was observed; it was higher in OMR ($\geq 95\%$) since SOM enhanced hysteresis. Though sub-Saharan soils are rich in iron oxides, SOM played a significantly higher role in sorption than iron oxides in this soil. This result suggests a high potential for atrazine to leach into the aquifer in the sub-Saharan. Atrazine uptake experiment by waterleaf and spinach showed that it could be detected in soil after 63 d, and its presence significantly affected the growth of both vegetables especially in soils with depleted SOM and iron oxides, and at high (100 $\mu\text{g}/\text{kg}$) atrazine spiking. Spinach may be a higher atrazine accumulator than waterleaf. It may be concluded that waterleaf and spinach grown on atrazine-contaminated soils, especially on SOM/iron oxide-depleted soils, are likely to accumulate atrazine.

1. Introduction

The pervasiveness of environmental chemical contaminants is worrisome, and pesticides are of particular interest due to an ever-increasing input into the environment stemming from the need for higher agricultural yield (Adedayo Adesina et al., 2017; Diagboya et al., 2024a; Gogoi et al., 2018; Wilkinson et al., 2017). Its transport and fate in environmental media (soils and biota) is one issue of serious concern because of the detrimental effects on the health of non-target organisms (Maddalon et al., 2021; Strilbyska et al., 2022). One typical and commonly used pesticide is atrazine (2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine) with a water solubility of ≈ 34 mg/L (at 26 °C) and far lower USEPA portable water permissible limit (≈ 3 $\mu\text{g}/\text{L}$).

Nevertheless, it exhibits some gender bias in toxicity, while continuous exposure to an even lower concentration (0.7 $\mu\text{g}/\text{L}$) in potable water was tied to irregular menstrual cycles in women, missed periods, bleeding between periods, significantly low estrogen levels possibly leading to fertility issues, delayed puberty, pregnancy loss, and low birth weight in newborns (Cragin et al., 2011). Thus, studying the transport or fate of atrazine in under-studied sub-Saharan soil cannot be over-emphasized.

The fate of pesticides in soil is ultimately controlled by sorption processes (adsorption on surfaces and inter-phases, and partitioning within phases in soil), which affect the subsequent transport and chemical reactivity in surface aquatic and groundwater systems, as well as uptake by plants (Junck et al., 2024; Olu-Owolabi et al., 2014). Sorption processes are dependent on soil composition and

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characteristics (including clay/mineral types and percentage compositions, inherent soil organic matter (SOM), and pH) (Diagboya et al., 2015; Martins et al., 2018; Prado et al., 2014; Yue et al., 2017). In this regard, atrazine sorption and desorption were carried out on soils of varying origins including Nigeria (Ololade and Oladoja, 2015), Brazil (Martins et al., 2018), China (Wu et al., 2015), and the United States (Novak et al., 1997). However, the soil's response to the degradation of some of these inherent components especially when induced by global warming-linked factors is still a subject of speculation. Some recent reports suggest that climate change-induced factors are beginning to drastically affect the environmental dynamics of pesticides in many ways. Some of these factors include higher ambient temperatures and erosion of major surface soil components (like SOM and soil iron oxides-SIO) due to increased flooding in the sub-Sahara and several parts of the world (Gaspar et al., 2020; IPCC, 2007). Focus on sub-Saharan soil is important because, even though the region contributes very little to climate change, it is projected to be affected to a disproportionate level (UNFCCC, 2020). In fact, in 2022, the region recorded some of the worst flooding, wash-off of farm crops and vegetation cover, and erosion of top soils, as well as extreme ambient temperatures (Cascais and Mohammad, 2022; Nimi, 2022; Omondi, 2022).

Soils are the key reservoir for pesticides in the environment, as well as a major source of food (Diagboya et al., 2021; Olu-Owolabi et al., 2022). The fate of pesticides in degraded soils is unknown. From field observations and recent reports, the current use of agricultural pesticides, especially atrazine and glyphosate, in the sub-Sahara is alarmingly high and unregulated (Aladesanwa et al., 2001; Owagboriaye et al., 2024). This has resulted in the detection of atrazine in most potable water sources of this region (Owagboriaye et al., 2022) as well as in crops such as Irish potatoes from this region (Fayinminnu et al., 2017). Hence, it is vital to understand the fate of pesticides in a typical whole and degraded soil of this region and the possibility of pesticide uptake from this soil by plants. In this regard, the objective of this study was to sample and treat sub-Sahara soil to eliminate SOM and SIO; this is necessary to disentangle the contributions of major soil constituents. The whole and treated soils were then used for atrazine sorption by varying the ambient factors such as time, solution pH, atrazine concentration, and temperature. A desorption study was also carried out to determine hysteresis. Experimental data obtained were analyzed using various kinetic and adsorption isotherm models. To predict the possibility of atrazine uptake from the soil by plants (spinach- *Spinacia oleracea* and water leaf- *Talinum triangulare*), a plant growth study was carried out on the soil spiked with known concentrations of atrazine.

2. Experimental

2.1. Materials, soil sampling, and treatments

Analytical grade reagents and Milli-Q water were used throughout this study. The chemicals used for the study include sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) (Merck), atrazine (Sigma-Aldrich), 30 % H_2O_2 , Na-citrate (Sigma-Aldrich), NaHCO_3 (Sigma-Aldrich), acetone (HiPerSolv Chromanorm, HPLC gradient), sodium azide (Carl Roth), and acetonitrile (ACN) (HiPerSolv Chromanorm, HPLC gradient).

Tropical surface soil (0–30 cm) sample was obtained by randomized sampling from Emuhu farming location (6° 16' 57" N; 6° 16' 14" E) in Agbor, Nigeria (annual temperature: 28.9 °C; \approx 298 rainy days/annum with \approx 243 mm of precipitation). The sample was air-dried, crushed, and sieved through a 1.0 mm size sieve and the fine fractions were preserved for the study and labeled whole sample (WS). Using the WS, approximately 370 g each was used for the soil organic matter (SOM) and soil iron oxides (SIO) degradation. For SOM elimination, about 600 mL of 30 % H_2O_2 was poured in 100 mL volumes into one of the weighed samples until the violent frothing stopped. The step-up was heated to 80 °C and excess frothing was stopped by the addition of cold water to avoid sample loss (Diagboya et al., 2021). The sample was washed by

centrifugation (7 times) at 3500 rpm and oven dried at 40 °C overnight. This is the organic matter removed sample (OMR).

The other weighed WS sample was used for the SIO degradation (Mehra and Jackson, 2013). Approximately 400 mL of 0.3 M Na-citrate solution and 50 mL of 1 M NaHCO_3 solution were added and the temperature in the water bath was raised to 80 °C. About 10 g of $\text{Na}_2\text{S}_2\text{O}_4$ was added with constant stirring for 15 min before adding 10 mL of saturated NaCl solution and 10 mL of acetone and left for 24 h before washing the sample as above. This is the iron oxide-removed sample (IOR). The WS, OMR, and IOR samples were characterized by determining the pH in H_2O and 1.0 M KCl (DIN-EN 15933, 2012), organic matter content (DIN-EN-15936, 2012), metals (Varian 720ES ICP OES) (DIN-EN-16174, 2012), carbonates (DIN-EN-ISO-10693, 2014), and soil particle size (DIN-ISO-11277, 2002).

2.2. Atrazine sorption studies on soil and experimental data treatment

Atrazine stock solution (1000 mg/L) was prepared in 20/80 % ACN/ Milli-Q water and stored at 4 °C for this study. Atrazine serial dilutions (in 0.01 CaCl_2 as background electrolyte) for the working solutions were prepared from the stock while using NaN_3 (100 mg/L) as a biocide. Replicate batch atrazine sorption studies were carried out in amber glass vials using 500 mg of the WS, OMR, or IOR, and by employing a 20 mL volume of specific atrazine solution containing the biocide, followed by incubation in an orbital shaker (200 rpm for 24 h examination of the effect of time excluded). To eliminate losses due to photochemical degradation, the vials were wrapped in Al-foil. At equilibrium or stipulated time, the experimental vials were withdrawn, centrifuged at 2000 rpm for 10 min, and filtered using 0.45 μm PES syringe filters.

The rates of atrazine (3.26 mg/L) sorption on these soils' samples were determined at varying times (1–1440 min), the effects of solution pH (3–11), concentration (0.2–4.0 mg/L) as well as the ambient temperature (22–42 °C) on sorption were all determined. All experiments were carried out at the natural soil pH except for the effect of solution pH where pH was adjusted using 0.1 M NaOH or HCl.

Desorption studies were carried out after the equilibrium study to determine desorption and hysteresis at 32 °C which was the temperature where the highest atrazine sorption was observed in this study. This was conducted by carefully decanting the solution in the equilibrium vials and the residual soils in the vials were refilled with the same volume of solution containing the background electrolyte and biocide but no atrazine, then incubating for 1440 min. After the equilibration, the solution was obtained by centrifugation and filtration as above, and the concentration of the atrazine was determined.

The concentrations of atrazine left in the solution were determined by HPLC-UV (1200 Series, Agilent Technologies Inc., USA). The HPLC-UV was fitted with a G1316A column oven, G1329A auto-sampler, G1311A quaternary pump, and G1315B UV detector. The mobile phase was 57:43 ACN (0.5 % H_2O): H_2O (H_2O contains 10 % ACN), the temperature was 35 °C, flow rate of 0.3 mL/min at an injection volume of 40 μL , a wavelength of 223 nm (Ex. of 250 and Em. of 410 nm) and run time was 6 min with the retention time of 2.8 min, while after every 20 samples, the column was cleaned by flushing starting from 53 % ACN up to 90 % ACN. The atrazine calibration curve linear range ($r^2=0.999$) was obtained using 7 concentrations between 0.075 and 8.0 mg/L of atrazine in 0.01 CaCl_2 . Using blank runs (without soil matrices) adsorption on walls and caps of the amber vials was evaluated to be insignificant.

The amounts (mg/g) of atrazine adsorbed (q_e) on soils were calculated using $q_e = (C_o - C_e)v/m$, where the variables C_o , C_e , m , and v are the atrazine concentrations (mg/L) at start and equilibrium, soil mass (mg), and volume (mL) of solution used, respectively. The OriginPro (2015) software (OriginLab Corporation, USA) was used to analyze the experimental data and generate all models' parameters. The models employed for the kinetics and used for predicting the mechanism include nonlinear adsorption kinetics models of Pseudo-First Order (PFO), Pseudo-Second Order (PSO), homogeneous fractal PSO (FPSO) (Sera

et al., 2022), as well as the Weber-Morris (Weber and Morris, 1963) intraparticle diffusion (IPD), while the atrazine equilibrium sorption data were fitted to and described by the simplistic Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) adsorption isotherm models and the more realistic Brouers-Sotolongo fractal (Altenor et al., 2009) and Langmuir–Freundlich (Umpleby et al., 2001) adsorption isotherm models. Thermodynamic parameters were also calculated using equilibrium data at all three temperatures; the equilibrium constants (K_c), Gibbs free energy ΔG° , entropy change ΔS° , and enthalpy change ΔH° were all generated (SI 1).

2.3. Atrazine uptake study in plant

The uptake of atrazine by *Talinum triangulare* (water leaf) and *Spinacia oleracea* (spinach) was studied by spiking the soils (WS, OMR, and IOR) with environmentally feasible concentrations of atrazine (100 and 10 $\mu\text{g}/\text{kg}$). Before planting the seeds, the spiked soils were incubated for 21 d. The time between planting and harvesting was six (6) weeks and the plants were grown in a climate chamber at 75 % light intensity, 13 h daylight at 30 °C, 11 h night time at 24 °C, and 60 % relative humidity. To aid plant growth, NPK fertilizers (N- 12 %; P_2O_5 : 12 %; K- 17 %; Mn- 2 %) were added to the soils at a rate of 2 g NPK to 0.9 kg soil. The final concentrations of atrazine in the soils at harvest and in the harvested plants were determined.

2.4. Atrazine extraction from plant and soil

Atrazine extraction from the vegetables and roots followed a slight modification of the reported QuEChERS procedures (Montiel-León et al., 2019; Negussie et al., 2021). Thoroughly washed, freeze-dried, and homogenized biomass was weighed to obtain a known dry mass. The sample was dispersed in 20 mL ACN in a 50 mL polypropylene tube, followed by the addition of 2.0 g of MgSO_4 (to eliminate water from the organic phase), 0.5 g NaCl (to induce separation of the layers), 0.5 g sodium citrate tribasic dihydrate, and 0.25 g sodium citrate dibasic sesquihydrate. The tube was vortexed for 1 min, agitated at 200 rpm for 10 min, and centrifuged for 20 min at 4000 rpm. The extract which was the upper layer of the three phases (the middle was plant residue while the lower was salt solution) was carefully collected. The extract was mixed with 1.0 g MgSO_4 and 0.2 g PSA (primary and secondary amines) for clean-up, vortexed for 30 sec, agitated for 10 min, centrifuged as above, and the final extract was carefully collected. Dispersive liquid-liquid micro-extraction (DLLME) was performed on the extract by mixing it with 5 mL NaCl solution (12 %, w/v) at pH 7. This was quickly followed by a 2 mL tetrachloroethene addition, vortexed for 1 min, and centrifuged. The sediment phase was collected and heated under a stream of nitrogen at 40 °C on a water bath until dry and re-constituted in 1.0 mL acetonitrile before HPLC-UV analysis.

Freeze-dried soil samples (5.0 g) were used to extract atrazine. The soils were transferred into 20 mL amber glass vials with 10 mL 0.01 M CaCl_2 solution (using 100 mg/L NaN_3 as biocide). This was mechanically agitated at 200 rpm for 24 h, centrifuged at 2000 rpm for 10 min, and filtered using 0.45 μm PES syringe filters. Atrazine in the solution was extracted into ethyl acetate as a cleanup step, separated and dried

under a stream of nitrogen at 40 °C on a water bath, and re-dissolved in 1.0 mL ACN before HPLC-UV analysis. The limit of detection was 0.03 mg/kg while the limit quantification was 0.1 mg/kg (He et al., 2022).

3. Results and discussion

3.1. Physico-chemical properties of whole and treated soils

The physicochemical properties of the whole and treated soils are reported in Table 1. The percentages of SOM remaining in the samples were well correlated with the treatments employed; the OMR had far less (0.13 %) SOM (≈ 94 % inherent SOM removed) compared to the IOR sample (1.66 %; viz. lost ≈ 21 % of inherent SOM during treatment). Conversely, the OMR had far higher (75 %) iron content (compared to inherent iron in WS) than the IOR sample which had ≈ 29 % iron. Sub-Saharan soils are reportedly high in iron oxide contents, and a possible reason for the non-complete removal of SOM from the WS would be due to the high iron oxide minerals content such as gibbsite, hematite, and goethite, which forms stable organic-mineral complexes with SOM (Diagboya et al., 2015; Prado et al., 2014). This is chemical protection of the SOM, and it limits the efficiency of H_2O_2 to oxidize SOM (Martins et al., 2018). Similarly, organic-mineral complexes result in some form of chemical protection for the iron oxides, thus lowering the sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) efficacy for iron oxide destruction.

The WS pH in water is neutral, and the removal of the soil iron oxides (in IOR) did not seem to affect this neutral pH in water, however, on the removal of SOM (in OMR), the soil pH became slightly acidic. The pH values of the WS and OMR in the KCl solution were both slightly acidic, but the IOR sample remained neutral. This suggests that the presence of SOM in this soil contributes to its pH neutrality (buffering), while the presence of mainly soil iron oxides (and lower SOM content) drives the pH towards acid values. Similar data has been reported for other sub-Saharan soils (Diagboya et al., 2021).

From the granulometric measurements, the soils expressed ≥ 86 % sand content, and this implied that the bulk of the SOM was associated with the silt fraction of WS because removal of the SOM resulted in ≥ 50 % loss of OMR silt fraction. Similarly, the removal of SOM resulted in significant losses (≥ 50 %) of the inherent Na, K, Mg, Ca, and Al contents; since these cations contribute to the soil cation exchange capacity (CEC) loss of SOM invariably leads to reduced CEC (Diagboya et al., 2015). Conversely, iron oxide removal resulted in exponential increases in the amounts of Na and S in the IOR sample (Table 1). This observation may be a common feature of sub-Saharan soils because a similar result has been reported for several soils from this same region (Diagboya et al., 2015). This was attributed to the unmasking of inherent Na^+ ions within other soil components such as soil minerals, clays, and organic matter upon the removal of iron oxides. In general, SOM removal resulted in the loss of essential plant micro/nutrients in comparison to iron oxide removal, and this may lead to lower agricultural productivity.

3.1.1. Sorption kinetics for atrazine and influence of pH

To predict the time to attain equilibrium atrazine sorption and

Table 1
Soil physicochemical properties pre- and post-treatment.

Soil	pH (H_2O)	pH (KCl)	SOM (%)	CaCO_3 (%)	CEC (meq/100 g)	PSA (%)			Metals (mg/kg)									
						*Sand	*Silt	Clay	Fe	Na	K	Mg	Ca	Al	Mn	P	S	Zn
WS	7.46	5.68	2.08 \pm 0.01	0.15	7.96	87.6	5.7	6.7	18948.1	21.5	184.1	391.5	825.6	16755.3	256.6	242.8	131.4	28.0
OMR	5.86	4.01	0.10 \pm 0.19	0.17	2.23	92.8	2.7	4.6	14277.8	13.8	64.7	158.3	137.1	7543.7	77.8	136.8	54.5	10.8
IOR	7.27	7.04	1.66 \pm 0.01	0.03	13.75	86.5	4.5	9.0	5565.3	2085.6	129.4	223.3	498.7	13127.9	52.7	160.2	1498.1	14.4

* PSA = Particle size analysis; *% sand = sum of the coarse, medium, and fine sand; *% silt = sum of the coarse, medium, and fine silt

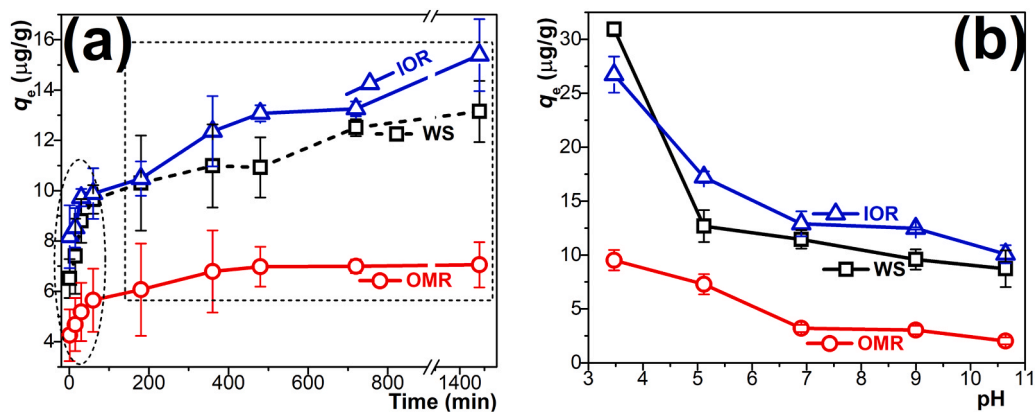


Fig. 1. (a) Atrazine sorption kinetics for the WS, OMR, and IOR samples; (b) sorption trends at varying soil solution pH values.

subsequently, the mechanism of uptake, the rates of atrazine sorption on the WS, OMR, and IOR soil samples were determined over a 1440 min time, and the sorption rate trends are presented in Fig. 1a. Under the experimental conditions, the trends expressed a rapid uptake of atrazine from solution for all soils within the initial 180 min (higher uptake below 60 min) of commencing the sorption process as observed in the steep rise of the curve in Fig. 1a (circled portion). After this point, the sorption was steady or almost insignificantly varied, signaling equilibrium. The equilibrium sorption was attained at 180 min for the WS; this was faster for the OMR sample at 30 min but much slower for the IOR samples at 360 min: $IOR_{360\text{ min}} < WS_{180\text{ min}} < OMR_{30\text{ min}}$. These variations in sorption rates may not be unrelated to the exposed sorption surfaces upon the sample treatment; removal of organic matter led to

exposure of charged, less porous, and non-aromatic (non-humic) mineral surfaces resulting in comparatively (to WS) lower sorption and faster equilibrium. However, the removal of iron oxides exposed more aromatic and porous humic materials resulting in comparatively (to WS) higher sorption and slower equilibrium time especially due to the slow sorption within bulk pore phases. Similar sorption trends have been reported for pyrene sorption on SOM and iron oxide degraded soil, though the speed of attaining equilibrium times was reversed in that case (Diagboya et al., 2021). Notwithstanding these varying equilibria, 1440 min equilibrium time was employed for subsequent experiments. The expressed experimental trend exhibiting a steep rise in the curve and then a plateau (Fig. 1a) may be attributed to the presence of unoccupied sorption sites with high atrazine affinity resulting in a fast

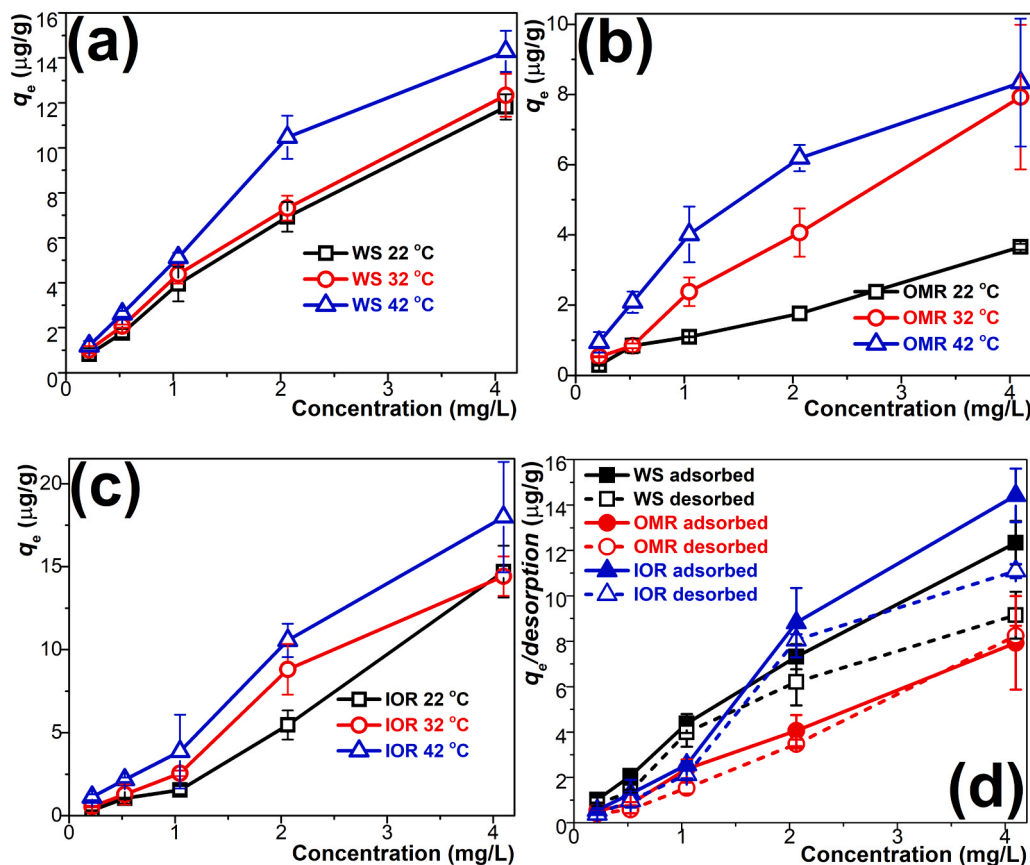


Fig. 2. Atrazine equilibrium sorption at different temperatures (22, 32, and 42 °C) for (a) WS, (b) OMR, and (c) IOR; (d) comparison of atrazine sorption and desorption trends of all samples at 32 °C.

sorption process at the beginning of the process (steep region). Once ≈75 % of the sites are filled, the steep starts leveling towards a plateau (at equilibrium) where most sites are occupied and the sorption rate is stabilized with insignificantly varied sorption/desorption (Olu-Owolabi et al., 2021).

An important factor that affects sorbent and contaminant's nature, charge density, and ionization, and ultimately influences sorption is the ambient solution pH (Akpotu et al., 2022; Diagboya et al., 2024b). Sorption trends over varying solution pH range of 3–11 are shown in Fig. 1b; the trends exhibited a decrease in atrazine sorption as pH increased, with the highest sorption recorded at pH 3 (acidic region). This observation is consistent with reported trends showing that atrazine sorption in the soil is favoured at lower ambient pH (Prado et al., 2014; Yue et al., 2017). This trend may be attributed to the nature and responses of the atrazine molecules and soil surfaces to changing ambient solution pH (Prado et al., 2014). For instance, atrazine is a weak base with pKa of 1.68, thus when ambient pH is close to pKa, about half of the molecules in the solution exist in the cationic form while the others are in the non-ionic form. Therefore, there is a high possibility of sorption via electrostatic interaction between cationic atrazine and negatively charged soil surfaces, in addition to possible hydrogen bonding, hydrophobic interactions with humic substances, and π–π interactions between aromatic atrazine rings with humic substances which are protonated at lower pH, as well as π–π interactions between aromatic atrazine rings and other surface adsorbed atrazine molecules (Diagboya et al., 2016). However, increasing ambient pH leads to deprotonation (hydrolysis) of the functional groups of the humic substances, subsequently reducing the atrazine cationic fraction, and thus sorption could mainly be ascribed to hydrogen bonding, hydrophobic interactions with humic substances, and lower π–π interactions (compared to at lower pH).

3.1.2. Equilibrium atrazine sorption

Equilibrium sorption trends on the whole and treated soils using atrazine concentrations between 0.2–4.0 mg/L at 22 °C are depicted in Fig. 2a–c (black curves). A concentration-dependent sorption process was observed with more atrazine sorption recorded as the initial solution concentration was gradually increased. This observation is consistent with reported trends showing that atrazine sorption on heterogeneous soil surfaces is favoured as concentration gradually increases (Martins et al., 2018; Prado et al., 2014; Yue et al., 2017). This sorption trend may be ascribed to the presence of multi-layer sorption which was facilitated by π–π interactions (Olu-Owolabi et al., 2022), as suggested earlier; thus allowing further sorption on surfaces of the adsorbates. In addition, as the solution concentration increases, there is the possibility of transfer of atrazine molecules from the saturated soil surfaces to the inner surfaces or soil pores (Olu-Owolabi et al., 2021).

Comparing the amount of atrazine adsorbed on each treatment, sorption was dependent on the SOM present (Martins et al., 2018) and the overall trend was IOR >WS >OMR (Fig. 2a–d). This means that the degradation of iron oxides from the soil (as in IOR) exposed more atrazine sorption sites (probably originating from the SOM) which enhanced the sorption process. On the other hand, degradation of the SOM (as in OMR) resulted in the loss of the rich sorption surfaces ascribed to the SOM and subsequently, a significant loss in atrazine sorption was observed. This implied that for this sub-Saharan soil, SOM

Table 2
Thermodynamics parameters for atrazine sorption on all soils.

Parameter		WS	OMR	IOR
ΔH°	kJ/mol	16.35	46.62	50.57
ΔS°	J/mol/K	67.19	160.63	174.10
ΔG° (kJ/mol)	288.15 K	-3.49	-0.90	-0.79
	298.15 K	-4.09	-2.07	-2.49
	307.15 K	-4.84	-4.13	-4.27

played a significantly higher role in atrazine sorption than the iron oxides, though sub-Saharan soils are reportedly rich in iron oxides (Diagboya et al., 2016; Towett et al., 2015).

Accessibility of SOM sorption sites in the WS is another important factor in the contaminant sorption process, because SOM may form stable organo-mineral complexes with iron oxides and allophanes which are inaccessible for sorption processes (Prado et al., 2014). This was probably the case for the WS having both SOM and IOR intact, but exhibited lower atrazine sorption in comparison to the IOR sample; iron oxides formed stable complexes with SOM in WS which reduced the accessibility of SOM for sorption reactions, but the degradation of iron oxides in IOR eliminated the oxides masking humic substances and exposed its sorption surfaces, hence the observed trend between WS and IOR. This result highlights the importance of the nature of the interactions between soil constituents in pesticide sorption, and it is consistent with the report of Prado et al. (Prado et al., 2014) for Andosols from Mexico.

Equilibrium sorption trends at varying temperatures between 22–42 °C were compared as depicted in Fig. 2a–c (black, red, and blue curves). It was observed that increasing ambient temperature generally led to higher atrazine sorption on both the whole and treated soils. This trend is an indication of an endothermic process, and this theory was tested by evaluating the thermodynamic parameters which are presented in Table 2. Generally, the negative ΔG° values indicate the spontaneity and feasibility (Yue et al., 2017) of the atrazine sorption process in the WS and its variants within the experimental temperature range (22–42 °C). In alignment with the endothermic nature of the sorption process, the ΔG° values decreased with increasing temperature; $\Delta G^\circ_{288.15\text{ K}} > \Delta G^\circ_{298.15\text{ K}} > \Delta G^\circ_{307.15\text{ K}}$ (Table 2), confirming that the sorption process is better favored at higher temperatures (Yue et al., 2017). The positive ΔH° values confirmed the fact that higher temperatures favoured the sorption process and the increasing values suggested that higher heat energy was needed for the transfer of the contaminant from the aqueous phase to the bulk soil phase. The low values of the ΔH° (average of ≈40 kJ/mol) indicated that weak forces of interactions (such as electrostatic interaction, hydrogen bonding, π–π interactions, and hydrophobic interactions) were mainly involved in the atrazine sorption processes (Olu-Owolabi et al., 2022). The positive values of ΔS° suggested increased randomness of atrazine at the soil/solution boundary.

Atrazine desorption trends (and isotherms: SI Fig. 1) after a single desorption step for 1440 min depicted in Fig. 2d suggest high average desorption of the initial atrazine sorption (≥65 %) at any concentration point irrespective of the soil treatment. This was far higher in OMR (≥95 %), while the presence of SOM in the soil enhanced hysteresis (Martins et al., 2018). Overall, there was very low hysteresis with high

Table 3
Atrazine adsorption kinetics models parameters for the whole and treated soils.

Model of kinetics	Parameter	WS	OMR	IOR	
PFO	q_e (μg/g)	10.47	6.17	11.59	
	$q_t = q_e(1 - e^{-k_1 t})$	k_1 (/min)	0.973	1.170	1.222
		r^2	0.269	0.261	0.107
		χ^2	3.535	0.854	5.288
PSO	q_e (μg/g)	10.68	6.26	11.76	
	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	k_2 (g/μg/min)	0.109	0.274	0.152
		r^2	0.380	0.362	0.182
		χ^2	2.998	0.737	4.842
FPSO	q_e (μg/g)	224.7	60.6	561.87	
	$q_t = \frac{k_f q_e^2 t^\alpha}{1 + k_f q_e t^\alpha}$	k_f	1.24×10^{-4}	1.12×10^{-3}	2.19×10^{-5}
		α	0.108	0.091	0.104
		r^2	0.949	0.937	0.866
IPD	χ^2	0.249	0.073	0.791	
	C (μg/g)	7.43	4.75	8.21	
	$q_e = k_{IPD} t^{1/2} + C$	k_i (g/μg min ^{1/2})	0.170	0.079	0.197
r^2		0.882	0.797	0.971	
χ^2		0.570	0.235	0.175	
Experimental q_e	μg/g	12.2	7.0	13.9	

Table 4
Atrazine adsorption isotherm models fitting parameters at 42 °C.

Adsorption isotherm	Parameter	WS@42 °C	OMR@42 °C	IOR@42 °C
Langmuir model $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q_o (mg/g)	29.9	13.4	196.8
	b	0.256	0.436	0.03
	r^2	0.980	0.997	0.980
	χ^2	0.611	0.027	0.996
Freundlich model $q_e = k_f C_e^n$	k_f	5.81	3.82	5.21
	n	0.715	0.602	0.971
	r^2	0.956	0.968	0.979
	χ^2	1.328	0.286	1.07
Fractal Brouers-Sotolongo model $Q_e = Q_{max}(1 - \exp(-K_w C_e^n))$	Q_{max} (mg/g)	15.1	9.16	20.5
	K_w	0.515	0.587	0.276
	α	1.35	1.04	1.57
	r^2	0.993	0.999	0.986
Langmuir-Freundlich model $q_e = \frac{Q_{max}(K_{LF} C_e)^n}{1 + (K_{LF} C_e)^n}$	Q_{max} (mg/g)	18.4	11.3	28.2
	K_{LF}	0.502	0.570	0.216
	n	1.497	1.17	1.63
	r^2	0.989	0.999	0.984
Experimental	χ^2	0.341	0.009	0.786
	q_e (mg/g)	14.3	8.3	18.0

desorption. A similar trend has been reported in the literature (Martins et al., 2018; Prado et al., 2014; Yue et al., 2017). This result correlates well with the low magnitude of the ΔH° values calculated for the thermodynamics of the sorption process: it connotes weak interactive forces that are easy to break during the desorption process. This result suggests a high potential for atrazine to leach into the aquifer from the sub-Saharan soil. Considering the unregulated usage of pesticides in the

sub-Sahara, and the fact that most potable water is obtained from the groundwater without further treatment, there is a high potential for atrazine (and similar pesticides) poisoning in the sub-Sahara population. This is confirmed by the values of the Groundwater Ubiquity Score (GUS index)(Hale et al., 2022) which were greater than 2.9 using K_{OC} of 100 and DT_{50} ranging between 29 and 75 (Lewis et al., 2024), thus atrazine is considered a groundwater leacher by this value.

3.1.3. Atrazine sorption data modeling

Predictive sorption models are usually applied to sorption data to suggest the plausible mechanism(s) controlling the contaminant(s) uptake process on soils. In this regard, several kinetics models (Table 3) and adsorption isotherm (Table 4; Fig. 3a–c) models were fitted to the obtained experimental sorption data. The chi-square (χ^2) (small values preferable) and correlation coefficient (r^2) (closer to unity) values were used to determine the appropriateness of the model, as well as the closeness of the model calculated soil maximum sorption capacity (Q_o) to the experimentally sorbed amount (q_e) values.

A comparison of the χ^2 and r^2 values for the fitting of the PFO, PSO, and FPSO (Table 3) to the experimental rates data showed that the PFO and PSO were deficient with large χ^2 (≥ 0.737) and small r^2 (≤ 0.380) values. However, the FPSO exhibited better fits with comparatively smaller χ^2 (≤ 0.791) and higher r^2 (≥ 0.866) values, while rate constant k values aligned with increasing equilibrium time: $OMR > WS > IOR$. A comparison of the calculated q_e values to the experimental values showed that the better-fitting FPSO expressed an overestimation of the sorption process, while the poor-fitting PFO and PSO expressed values that were more in alignment with experimental values. These models buttress the fact that sorption on heterogeneous surfaces like soils is difficult to describe using the simplistic PFO or the PSO models, and are

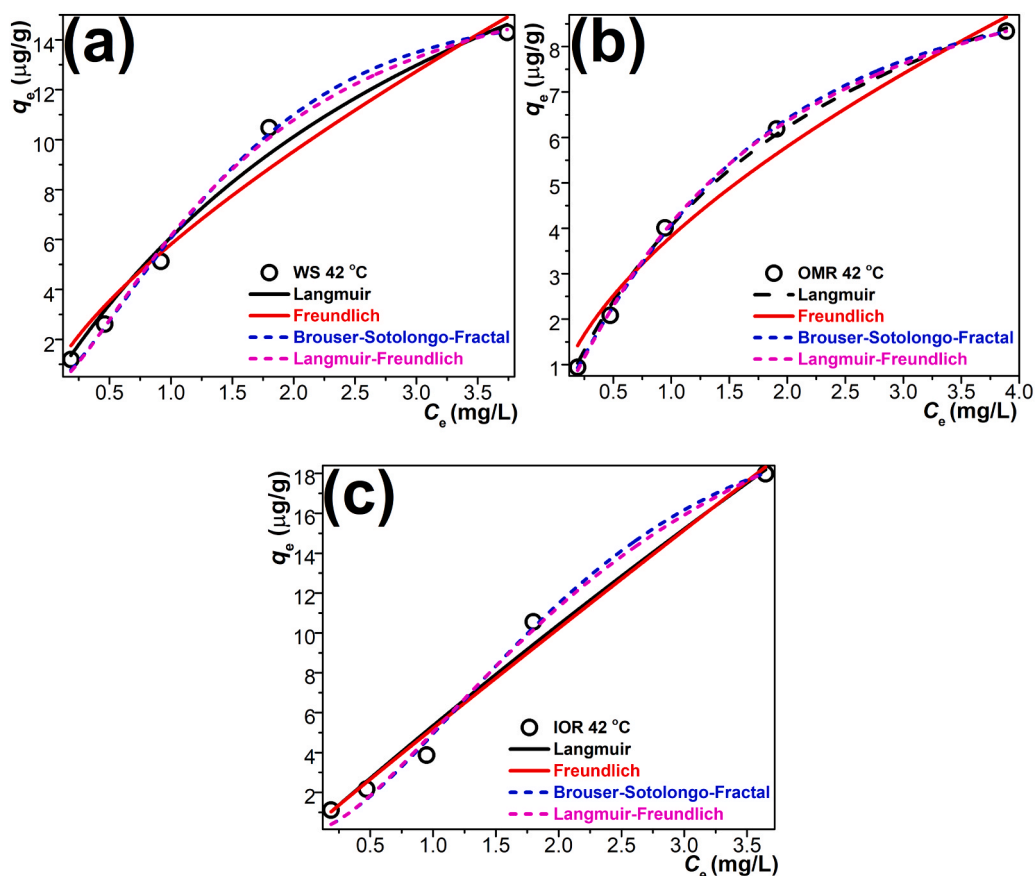


Fig. 3. Comparison of experimental equilibrium data to the fittings of the Langmuir, Freundlich, fractal Brouser-Sotolongo, and Langmuir-Freundlich adsorption isotherm models for (a) WS, (b) OMR, and (c) IOR soils.

better described by a combination of sorption models or more complex models such as the FPSO (Diagboya et al., 2023; Diagboya et al., 2018). The PFO describes a very fast sorption process occurring within a few minutes of commencing the experiment when atrazine molecules in solution outnumber the vacant sorption sites, while the PSO describes a process mainly dominated by electron transfer between surfaces or electrostatic interactions (Olu-Owolabi et al., 2022), but neither of these is solely the case. The experimental data appropriately fits the homogeneous FPSO and suggests that the atrazine sorption mechanism on the soil and its treatments involved complex forces of interactions such as electrostatic interactions, soil phase trapping, multi-layer adsorption of atrazine on already sorbed atrazine via π - π interactions, and various van der Waals interactions (Altenor et al., 2009; Diagboya et al., 2021; Olu-Owolabi et al., 2021).

The IPD values (Table 3) of the χ^2 (≤ 0.570) and r^2 (≥ 0.797) suggest that the experimental data may be explained by this model. The model curves (similar to Fig. 1a) were dual-linear which implied a two-step control mechanism including an initial fast film diffusion step (circled portion of Fig. 1a), and a slower intra-particle diffusion step (squared portion of Fig. 1a). A concentration-dependent external mass transfer most likely controlled the sorption process because the model plots did not pass through the origins (Weber and Morris, 1963). The C ($\mu\text{g/g}$) values of the model which is an estimate of surface layer atrazine thickness were $\approx 38\%$ less than the experimental q_e values and suggest that $\approx 62\%$ of atrazine sorption occurred on the soils' surfaces, while the rest sorption occurred within the soil phases. This confirms the theory that soil phase trapping is a mechanism for atrazine sorption on these soils.

Atrazine equilibrium sorption data at 42°C were evaluated with two classical and two more realistic nonlinear adsorption isotherm models: the Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906), and Brouers-Sotolongo fractal (Altenor et al., 2009) and Langmuir-Freundlich (Umpleby et al., 2001) adsorption isotherm models, respectively. The model fittings and parameters are presented in Fig. 3a-c and Table 4, respectively. The same model parameters as in the kinetics models were used in determining the appropriateness of each model. The Langmuir adsorption isotherm model assumes that uniform adsorption occurs at a finite amount of sites that are structurally and energetically identical (Langmuir, 1916), while the Freundlich suggests sorption occurs at non-identical sites that are energetically distinct, and unlike the Langmuir, multilayer adsorption can occur on the initial adsorbates (Freundlich, 1906). The Langmuir-Freundlich model assumes a strict combination of both models (Umpleby et al., 2001), while the Brouers-Sotolongo fractal presupposes a more complex and environmentally realistic model (Altenor et al., 2009).

A comparative evaluation of all four models' parameters showed that the fractal Brouers-Sotolongo model fits the data better for all soils with smaller χ^2 (≤ 0.695) and higher r^2 (≥ 0.986) values, while the Q_{max} values were better correlated to the experimental q_e values. However, the χ^2 and r^2 values of the Langmuir-Freundlich adsorption isotherm model showed that the model could describe the data reasonably well. Thus, the Langmuir-Freundlich non-linearity parameter n which was greater than unity is an indication that at higher concentrations, atrazine sorption tends toward linearity, and this may be a confirmation of an effective formation of multi-layer stacking at higher concentration (Martins et al., 2018; Olu-Owolabi et al., 2014). Considering that the sorbents (soils) are heterogeneous, the better fits of the FPSO and fractal Brouers-Sotolongo as well as the Langmuir-Freundlich models to the experimental data are complementary and buttress the idea that the complex interactions earlier suggested (such as electrostatic interaction, hydrogen bonding, hydrophobic interactions with humic substances, and π - π interactions between aromatic atrazine ring and humic substances) were chiefly involved in the atrazine sorption.

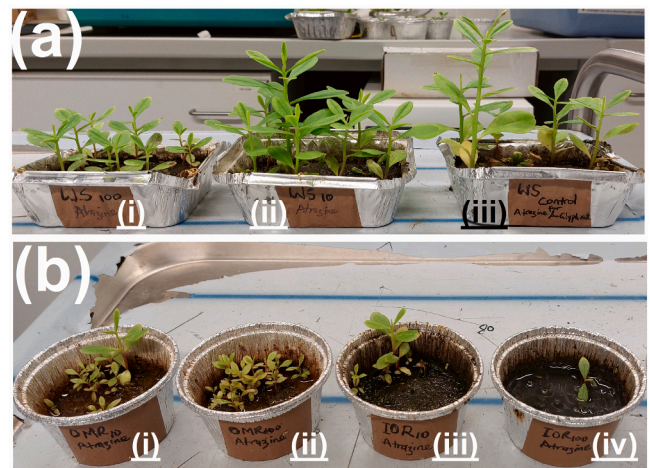


Fig. 4. (a) Plant growth in (i) WS-100, (ii) WS-10, (iii) WS; (b) growth in (i) OMR-10, (ii) OMR-100, (iii) IOR-10, (iv) IOR-100 (number attached to the soil treatment indicates the concentration of atrazine in $\mu\text{g/kg}$).

3.2. Atrazine uptake by plants

Environmentally feasible concentrations (10 and $100\ \mu\text{g/kg}$) of atrazine (which are within the field application range of 2.2 – $4.5\ \text{kg/ha}$ (Mudhoo and Garg, 2011)) were spiked on the soils, and incubated for 21 d before planting the fast-growing vegetables: *Talinum triangulare* (waterleaf- WL) and *Spinacia oleracea* (spinach- SP). The plants were grown for 6 weeks before harvesting; the final concentrations of atrazine in the soils and harvested plants were determined. The results are depicted in Fig. 4 and 5.

The plants grown in the control pots and the WS pot with $10\ \mu\text{g/kg}$ atrazine (WS-10) exhibited normal growth (Fig. 4a ii-iii), but growth was reduced in the WS with $100\ \mu\text{g/kg}$ atrazine (WS-100) pot (Fig. 4a i). Thus, the higher the amount of atrazine in the soil the more reduction in growth was recorded. Depletion of inherent soil constituents such as organic matter and iron oxides with a simultaneous presence of atrazine resulted in significantly lower growth of these vegetables (Fig. 4b); the reduction was higher in iron oxides depleted soils (Fig. 4b iii-iv). This later observation was congruent with the experimental sorption results above which shows that SOM adsorbs more atrazine; the adsorbed atrazine is evenly distributed within the organic matter phase (of the IOR soils) making it easily bio-available to disrupt growth. For the organic matter depleted soils (OMR soils) (Fig. 4b i-ii), it is assumed that since iron oxides adsorb less atrazine (as observed in the sorption data above), the bulk is transported deeper into the soil, away from surface soil; if the roots do not get to the lower depth, the plants will interact with less atrazine in the soil with a resultant lower effect on growth.

Atrazine applied to the soils before planting could be detected in the soils after 63 d (9 weeks). The concentrations of atrazine determined in the soils at harvest were proportional to the amounts spiked on the soils (Fig. 5a). The amounts observed for the OMR soils were higher than for the WS soil, suggesting that inherent SOM reduces the availability of atrazine in soil solution, while its absence might result in higher availability. In contrast to the WS and OMR soils, the amounts of atrazine observed in IOR soils were not proportional to the spiked concentrations: this soil contained higher SOM but exhibited lower atrazine amounts at higher spiking after harvesting. This was not expected and may imply that SOM effectively traps the atrazine at higher concentrations (in agreement with the sorption data above).

The concentrations of atrazine in the harvested vegetables are depicted in Fig. 5b. The presence of atrazine on the soils significantly affected the growth of waterleaf (WL) and spinach (SP), especially in soils with depleted SOM and iron oxides. The results showed that atrazine was almost not detected in the roots and leaves of the waterleaf

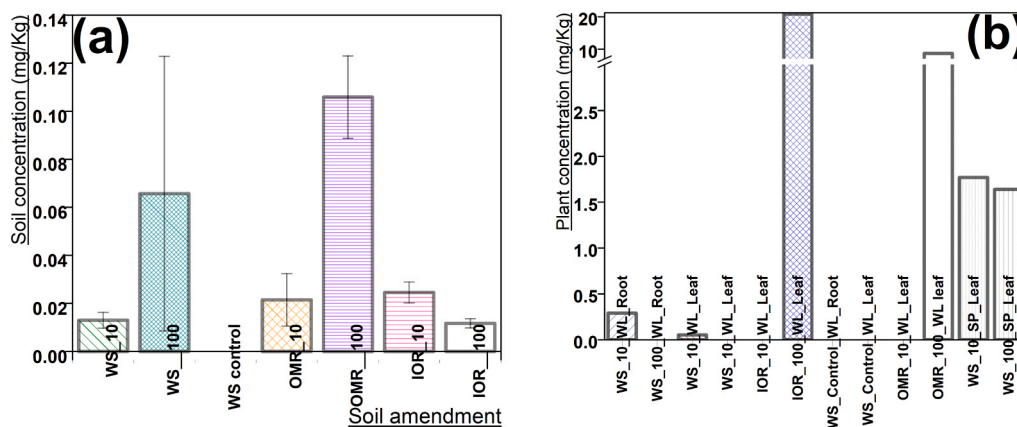


Fig. 5. (a) concentrations of atrazine in soil and treatments; (b) concentrations of atrazine in the harvested fast-growing vegetables: *Talinum triangulare* (waterleaf-WL) and *Spinacia oleracea* (spinach-SP).

grown in both the WS-control and the WS soils with low (10 $\mu\text{g}/\text{kg}$) and higher (100 $\mu\text{g}/\text{kg}$) atrazine spiking. Similarly, for the OMR and IOR soils with low atrazine spiking (10 $\mu\text{g}/\text{kg}$), it was not detected. However, for both OMR and IOR soils at higher (100 $\mu\text{g}/\text{kg}$) spiking, atrazine was detected; with a significantly higher concentration in IOR-100 than OMR-100 soil. Specifically, the result observed for the waterleaf grown in IOR-100 soil may be related to the high amount of atrazine detected in the IOR-100 soil; it is plausible that the high atrazine adsorbed on the SOM-rich IOR-100 soil is evenly distributed and results in high bioavailability, and the consequent high atrazine detection in the waterleaf (Fig. 5a-b). For the OMR-100 soil (low SOM, iron oxide-rich) with lower sorption, the atrazine may be washed to the lower part of the growing pot, resulting in less atrazine getting to the plant and hence the observed lower detection.

Interestingly, it was observed that spinach (SP) grown in WS with both low (10 $\mu\text{g}/\text{kg}$) and high (100 $\mu\text{g}/\text{kg}$) atrazine spiking accumulated atrazine (Fig. 5b). This may imply that spinach is a higher atrazine accumulator than waterleaf. Generally, this result suggests that leafy vegetables, especially waterleaf, grown in either SOM-/iron oxides-depleted soils that were treated with atrazine *ab initio* are likely to accumulate atrazine. Due to the limited quantities of plant biomass obtained during the growth period, it is recommended that further atrazine absorption studies be carried out on these plants and in a mesocosm, using a more sensitive atrazine detection instrument.

4. Conclusion

The influences of major sub-Sahara soil constituents on a model pesticide (atrazine) sorption were quantified using the whole soil (WS), and soils whose organic matter (OMR) and iron oxides (IOR) have been significantly depleted, and the extent of plant uptake of atrazine on these soils was investigated. The WS pH is neutral and unaffected by the depletion of the soil iron oxides (in IOR), but on depletion of SOM (in OMR), it becomes acidic. Generally, the depletion of SOM resulted in the loss of essential plant micro/nutrients in comparison to the depletion of iron oxides.

Depletion of SOM accelerated equilibrium atrazine sorption, while depletion of iron oxides only decelerated equilibrium: $\text{IOR}_{360 \text{ min}} < \text{WS}_{180 \text{ min}} < \text{OMR}_{30 \text{ min}}$. Atrazine sorption was enhanced at lower ambient pH, high initial atrazine concentration, and higher temperature. The sorption process was endothermic, spontaneous, and feasible, and involved weak forces of interactions. Atrazine desorption was $\geq 65\%$ of initial sorption in all soils; SOM depletion enhanced desorption and lowered hysteresis. The sorption process was controlled by complex mechanisms and data was better described by the more realistic (FPSO and Brouers-Sotongo fractal) predictive sorption models. There is a high potential for atrazine to leach into the aquifer from the sub-

Saharan soil, this is more so with the depletion of organic matter. Considering the unregulated usage of atrazine in the sub-Sahara, and the fact that most potable water is obtained from groundwater for consumption without further treatment, there is a high potential for atrazine (given its moderate persistence) poisoning in the sub-Sahara area.

Atrazine is persistent in the soil and significantly affected the growth of *Talinum triangulare* (waterleaf- WL) and *Spinacia oleracea* (spinach-SP), especially in soils with depleted SOM and iron oxides. In whole soil and at low atrazine spiking, the effect on growth was unnoticed. Atrazine was not detected in the roots and leaves of the waterleaf grown on both the WS-control and WS-soils spiked with atrazine. But plants grown in the depleted soils spiked with atrazine expressed significant atrazine uptake in the leaves especially at higher spiking. Spinach may be a higher atrazine accumulator than waterleaf. It may be concluded that waterleaf and spinach grown on atrazine-treated soils, especially on either SOM-/iron oxides-depleted soils, are likely to accumulate atrazine.

Ethical Approval and Consent to Participate

We declare that we have no human participants or data.

CRedit authorship contribution statement

Rolf-Alexander Düring: Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition. **Paul N. Diagboya:** Writing – original draft, Software, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2024.116794](https://doi.org/10.1016/j.ecoenv.2024.116794).

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