



Tropical surface water quality studies: Implications for the aquatic fate of *N*-methyl carbamate pesticides

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ABSTRACT

Water quality assessment was conducted on the Ruiru River, a tributary of an important tropical river system in Kenya, to determine baseline river conditions for studies on the aquatic fate of *N*-methyl carbamate (NMC) pesticides. Measurements were taken at the end of the long rainy season in early June 2013. Concentrations of copper (0.21–1.51 ppm), nitrates (2.28–4.89 ppm) and phosphates (0.01–0.50 ppm) were detected at higher values than in uncontaminated waters, and attributed to surface runoff from agricultural activity in the surrounding area. Concentrations of dissolved oxygen (8–10 ppm), ammonia (0.02–0.22 ppm) and phenols (0.19–0.83 ppm) were found to lie within normal ranges. The Ruiru River was found to be slightly basic (pH 7.08–7.70) with a temperature of 17.8–21.2°C. The half-life values for hydrolysis of three NMC pesticides (carbofuran, carbaryl and propoxur) used in the area were measured under laboratory conditions, revealing that rates of decay were influenced by the electronic nature of the NMCs. The hydrolysis half-lives at pH 9 and 18°C decreased in the order carbofuran (57.8 h) > propoxur (38.5 h) > carbaryl (19.3 h). In general, a decrease in the electron density of the NMC aromatic ring increases the acidity of the *N*-bound proton removed in the rate-limiting step of the hydrolysis mechanism. Our results are consistent with this prediction, and the most electron-poor NMC (carbaryl) hydrolyzed fastest, while the most electron-rich NMC (carbofuran) hydrolyzed slowest. Results from this study should provide baseline data for future studies on NMC pesticide chemical fate in the Ruiru River and similar tropical water systems.

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Introduction

The chemical fate of pesticides in tropical aqueous environments remains relatively less well studied than pesticide fate in temperate zones.^[1–3] Higher temperatures, intense sunlight and more frequent pesticide application due to multiple growing seasons, likely cause the fate of pesticides in the tropics to differ from their fate in temperate areas. These variables affect the pesticides' reaction mechanisms, rates of decay and decomposition products. Differences in environmental fate and persistence of pesticides and their degradation products may impact water use and safety, as well as influence recommendations and protocols for remediation of contaminated water. Accurate chemical assessment and description of local environments are essential in understanding the chemical fate of pesticides, and may help inform ecological risk assessment of tropical freshwater ecosystems.^[4–6]

Research in our laboratory focuses on the aquatic chemistry of pesticides in tropical environments. Our recent work has focused on *N*-methyl carbamates (NMCs), which are among the most popular pesticides used globally. First introduced for pesticide use in 1958, NMCs function as acetylcholinesterase inhibitors, and are still valued for their effectiveness against

organophosphate-resistant pests.^[7] In addition, NMCs are chlorine-free and non-ozone-depleting, and favored for their relatively low atmospheric contamination.^[8] Despite these benefits, and with increased application over the past six decades, NMCs increasingly pose risks to human and ecosystem health via contamination of ground and surface water. Water quality characterization and assessment of local aquatic environments are important in gauging the potential impacts of NMCs in tropical areas.

Herein, we report on studies conducted to characterize and assess water quality in a tropical river, and present results from a comparative kinetics study on the relative stability of three popular NMCs. The study site is located in the central highlands of Kenya along the Ruiru River, and within a commercial and subsistence agriculture area that is representative of a heavily cultivated and productive tropical zone. NMCs are used in Kenya in plantation-scale agriculture, small subsistence holdings and on livestock, and the pesticides have been detected in rivers and streams and attributed to agricultural run-off.^[9–13] Results from this study should provide baseline data for future studies on NMC pesticide chemical fate in the Ruiru River and similar tropical water systems.

Materials and methods

The study site

The study site is a 25 km stretch of the Ruiru River near Ruiru town (area: 292 km², population: 238,858) and 50 km north of Nairobi.^[14] Ruiru River is part of a large tropical river system originating in the highlands of central Kenya. The river flows southeast, and is an important tributary of the Athi River, Kenya's second largest river, which drains into the Indian Ocean. The Ruiru region is an important coffee-growing area in a country where agriculture accounts for about one-third of the country's GDP.^[15] Smallholder production is important, accounting for about 75% of the value of agricultural output and providing more than 85% of the employment in agriculture.^[15] The mean annual temperature ranges from 17 to 20°C, and annual rainfall of 1,800–2,000 mm occurs in two rainy seasons: the long rains from March to early June, and the short rains from October to the end of November.^[16–18] The Ruiru River flows through small- and large-scale coffee farms and horticultural gardens, and pesticides are routinely applied to control pests.^[19–21]

Sampling studies

Sampling studies were conducted in June 2013 at the end of the long rainy season. Twelve sites were surveyed along a 25 km segment of the Ruiru River (Fig. 1). Sites 1 and 2 are located at Ruiru dam inlet and outlet, respectively. Site 3 was close to a coffee processing facility. Site 4 was located near a quarry site with little cultivation in the area. Site 5 was close to an access point for use of river water for domestic purposes. Site 6 was near a commercial farming area. Site 7 had flat banks with no agriculture nearby, but with smallholdings about 50 m from the riverbank. Site 8 was situated beside a major highway with no farming activity. Site 9 was close to smallholdings. Sites 10–12 are located on tributaries of the Ruiru

River. Of the 12 locations, 9 are along the Ruiru main stream (sites 1–9) and one was located on each of the three major tributaries (sites 10–12).

River water samples were collected on consecutive days and duplicate sampling was conducted at odd numbered sites 1,3,5,7 and 9 to assess reproducibility of measurements. Four samples were collected at site 5 on consecutive days for assessment of temporal water quality variability. Site 5 was chosen for its central location on the river. Water samples were collected using a Carolina Economy Water Sampler (1.5 L). The sampler was pre-tested by immersing the apparatus into the river to ensure the proper operation of the single-line trigger mechanism that seals the collection tube. Prior to sample collection, the water sampler was thoroughly rinsed with river water at each site, and approximately 1.0 L of river water was collected for analysis. Samples for dissolved oxygen were collected using pre-rinsed 1,000 mL polythene bottles that were submerged in the river and capped.

Field measurements

Photometric analysis was used to measure concentrations of ammonia, copper, dissolved oxygen, nitrate, phenol, phosphate using a CHEMetrics V-2000 Photometer. This field instrument is a portable microprocessor-based LED colorimeter with the capability to automatically test pre-programmed analytes using self-filling, pre-measured vacuum vials. The instrument was tested in the laboratory using standard solutions to gauge accuracy and precision of field measurements. Copper standards (NIST traceable) were obtained from Hach Co. as 100 ppm solutions. Ammonia, nitrate, phosphate, and phenol standards (NIST traceable) were obtained from Lab Chem as 1,000 ppm solutions. The standards were used to prepare the following concentrations: ammonia: 2 ppm; copper: 10 ppm; nitrate: 25 ppm; phenol: 5 ppm; and phosphate: 5 ppm. Calibration results are presented in the Supporting Information.

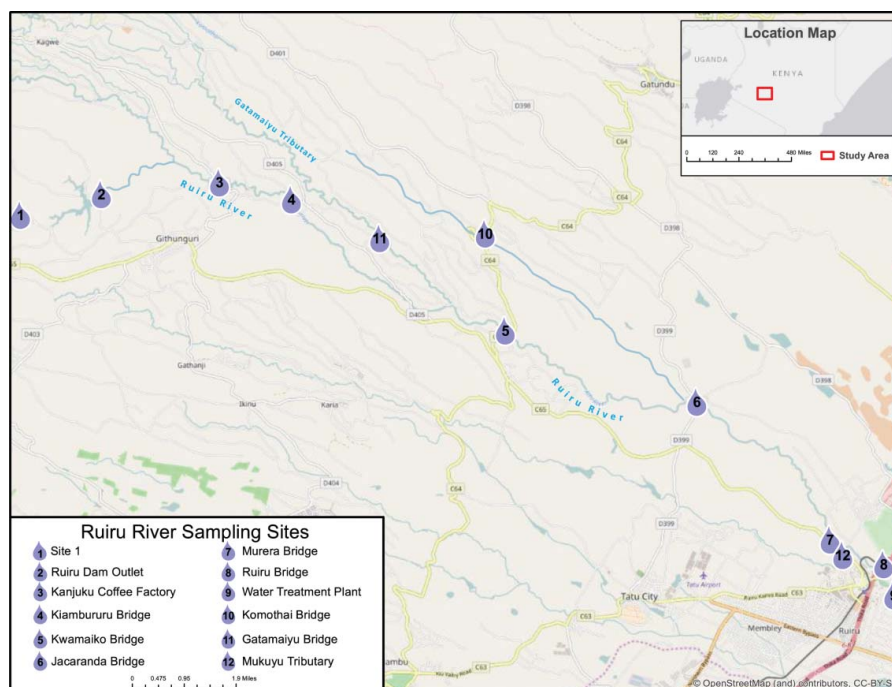


Figure 1. Sampling sites along the Ruiru River.

Dissolved oxygen, ammonia, nitrate, phosphate, phenol and copper were measured at field sites using the portable V-2000 Multi-Analyte Photometer and CHEMetrics colorimetric indicator tests provided by the manufacturer in self-filling, pre-measured vacuum vials. Dissolved oxygen measurements were obtained with minimum exposure to air. All measurements were made within 1 h of sample retrieval. ChemMetrics colorimetric tests were performed in vials of reagents provided by the manufacturer to generate colored solutions for analysis. The concentrations of the colored complexes generated in the reactions are directly proportional to the concentrations of each analyte. All colored complexes were generated in the vials provided by the manufacturer using the protocol provided. These reactions are presented in the Supporting Information.

All pH measurements were made using an Oakton 35634 pH Testr 10 m with a pH range of -1.0 to 15.0 . Measurements of pH were performed by dipping the electrode of the pH meter directly into the river water and allowing the reading to stabilize before recording. The instrument had a resolution of 1.0 pH and accuracy of ± 0.1 pH. The Oakton pH meter was pre-calibrated by immersing the electrode about 2 to 3 cm into Fisher Scientific certified buffer solutions of pH 4, 7 and 10.

Temperature was measured using a Fisher Scientific temperature probe inserted directly into the river. The temperature probe was calibrated by immersing in a beaker of water and comparing readings with an Enviro-safe 76 mm (3") immersion thermometer. The probe and thermometer were left in the same water and checked several times a day. Measurements typically differed by no more than $\pm 1^\circ\text{C}$. GPS coordinates and altitudes were determined using a Magellan eXplorist 200 handheld GPS receiver, and confirmed by cross-referencing with Google Earth-generated maps.

Kinetic studies of N-methylcarbamate hydrolysis

Kinetic studies were conducted on the three NMCs under laboratory conditions at pH 9. These conditions were not expected to replicate the Ruiru River water matrix, but rather were conducted to initially gauge the relative stability of the three NMCs and to examine how NMC structure can be used to predict NMC longevity. Future studies will simulate the river matrix to measure the stability of the NMCs under field conditions.

Solutions of each NMC in deionized water were prepared by weighing out the appropriate mass of each NMC (carbaryl 5.0 mg; propoxur 5.2 mg; carbofuran 5.5 mg) into three separate 25 mL volumetric flasks to yield solutions with concentrations of 1×10^{-3} M. About 15 mL deionized water was added to each volumetric flask and pH adjusted to pH 9 using monophosphate/diphosphate buffer. Deionized water was added to each volumetric flask to make up the volume to 25 mL. Approximately 4 mL of the solvent was transferred into 4.5 mL capacity UV-grade methacrylate cuvettes and loaded into a Cary 50 UV-visible spectrophotometer. The change in concentration of the NMC was monitored by measuring λ_{max} at 15 min intervals for at least three half-lives (see Supporting Information for UV-vis spectra of NMCs).

Results and discussion

Research in our group focuses on the aquatic chemical fate of NMC pesticides in tropical environments. We have previously

reported on the aquatic chemical fate of the NMC pesticide for-metanate in the Guayas River basin of Ecuador. Decomposition studies under pre-determined field conditions showed that for-metanate would hydrolyze in the slightly alkaline (pH 7.6 and 33°C) environment of the Guayas River. We determined $t_{1/2}$ (formetanate) to be 14.4 h and predicted that the carbamate hydrolysis product would persist for over 6 months and be itself potentially active as an NMC.^[22,23] Our studies showed that formetanate hydrolyzed more rapidly at higher tropical-zone temperatures (33°C : $t_{1/2}$ 14.4 h at pH 7.6) than at cooler temperate-zone ones (25°C : $t_{1/2}$ 4.5 days at pH 8 and $t_{1/2}$ 45.2 days at pH 7).^[24] These results illustrate the importance of precisely characterizing environmental conditions to accurately assess chemical fate of pesticides in tropical surface water.

Field studies and water quality assessment

The Ruiru River in Kenya is a second field site under investigation by our group. Like the Guayas River (1.9575° S, 79.9193° W), the Ruiru River (1.1457° S, 36.9649° E) traverses an agriculturally productive region close to the Equator. Water quality assessment of the Ruiru River is an important first step toward understanding pesticide aquatic fate in this important river. Assessment was conducted over a 25 km stretch of the river and measured water temperature, pH, nitrates, phosphates, ammonia, copper, phenol and dissolved oxygen. Water temperature and pH dictate reaction rates and mechanisms of hydrolysis as determined in previous studies.^[23] Nitrates, phosphates and ammonia are important indicators of water quality and are an indication of surface run-off and/or migration of nutrients originating from fertilizer, animal manure, and sewage. Copper content was measured because water-soluble copper oxychloride fungicides are heavily used on coffee trees in the study area. The presence of copper in the Ruiru River would be a proxy indicator of pesticide run-off. The measurement of phenols was performed because the compounds are a product of NMC pesticide decomposition, and therefore a possible indicator of pesticide use. Dissolved oxygen was tested to indicate the suitability of the river for aquatic life. A map of the study site is presented in Figure 1.

Sampling was conducted at 12 sites along the river. Sites were selected in order to capture a broad description of the river's environment, represent zones with different anthropogenic activities, compare the main river's water quality to that of tributaries and provide efficient and safe access to sites by land. Parameters measured at each site are plotted in Figures 2 and 3.

In general, concentrations of all chemical species measured tended to be higher in the tributaries (sites 10–12) than on the main river. Site 10 had the highest concentrations of phosphate, ammonia, copper and phenol overall. Nitrate concentration was highest at site 12. The higher concentrations in the tributaries may be the result of the greater extent of agricultural activity in adjacent areas. Also notable was a decrease in most parameter readings at the Ruiru Dam outlet relative to the dam's inlet, indicating that the dam may play an important filtration or deposition role in nutrient removal. Dissolved oxygen was found to be normal and close to the range of healthy surface water (8–10 ppm)^[25] at all sites. The temperature of the river was determined to be between 17.8 and 21.2°C , and pH values were determined to lie between 7.08 and 7.70.

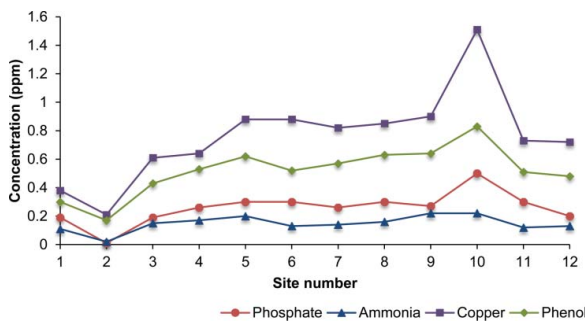


Figure 2. Concentrations of ammonia, phosphate, copper and phenol (ppm) at sites along the 25 km stretch of the Ruiru River; temp = 17.8–21.2°C.

Ammonia

Ammonia was detected in the Ruiru River at concentrations of 0.02–0.22 ppm with an average concentration of 0.14 ppm. The highest two concentrations reported, 0.20 ppm and 0.22 ppm, occurred at site 5 and site 10, respectively (Fig. 2). In general, ammonia levels in temperate rivers and bays are usually less than 6 ppm, though a total N concentration above 1 ppm is considered a high eutrophication potential.^[26] Ammonia contamination of surface water can occur via biodegradation of organic matter, agricultural run-off, animal farming, industrial wastes and urban sewage effluents.^[27–31] High concentrations of ammonia in water can be detrimental to aquatic life, because most cellular membranes are permeable to ammonia.^[32] The Ruiru River water appeared to be healthy with respect to ammonia contamination. The higher concentrations of ammonia at sites 5 and 10 could be attributed to anthropogenic and agricultural activity, respectively, since site 5 was an access point for water collection for domestic use, and site 10 was located on a tributary in a heavily cultivated area.

Copper

Copper concentrations in the Ruiru River ranged between 0.21 and 1.51 ppm and the average concentration was 0.77 ppm (Fig. 2). The highest concentration of copper (1.51 ppm) was detected at site 10 on a tributary and located downstream of a heavily cultivated area and in close proximity to coffee farms, smallholdings horticulture and several coffee processing plants. The field test for copper measured fully ionized solubilized copper and did not measure suspended, insoluble particulate copper, or chelated copper.

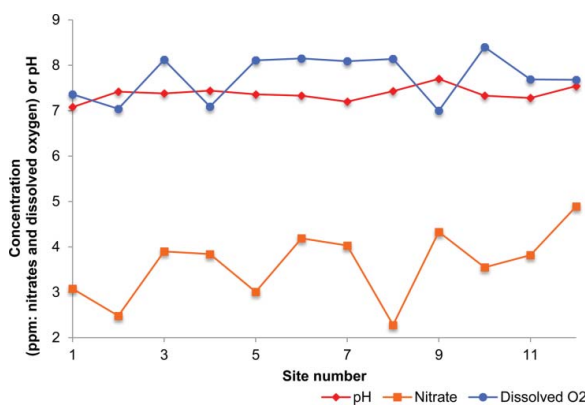


Figure 3. Concentrations of nitrate and dissolved oxygen (ppm) and pH at sites along the 25 km stretch of the Ruiru River; temp = 17.8–21.2°C.

Thus, copper values measured in the field and reported in this work represent fully ionized dissolved copper (Cu (II) and Cu (I)) in the river.^[33]

The concentrations of copper in the study site are significantly higher than naturally occurring concentrations of copper in surface freshwater systems, and higher than the mean dissolved copper in surface waters of the US.^[34] Copper concentrations in lakes and rivers typically vary between 5×10^{-4} to 1 ppm with an average concentration of 0.01 ppm.^[35] A study by Mwamburi found copper levels in surface water in lake systems in western Kenya to be between 0.002 and 0.02 ppm.^[36] The high levels of copper in the Ruiru River are likely a result of surface run-off from coffee farms in the vicinity. Copper (II) oxychloride is a well-known fungicide that has been used in Ruiru coffee plantations for over 60 years to protect coffee trees from fungal diseases.^[37] Application rates are reported at 10–12 sprays per year on large-scale plantations using 50% solutions of copper (II) oxychloride or copper (II) sulfate at 5 kg/ha.^[38] Estimates place the application rates of copper fungicides by mass in Ruiru at 29.7 kg Cu/ha/year.^[39]

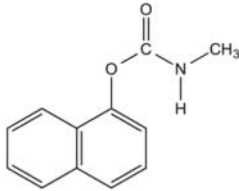
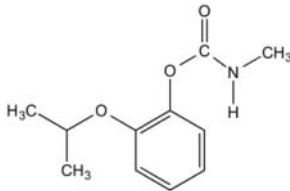
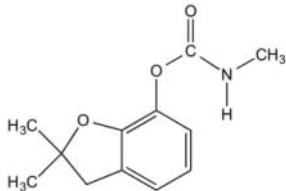
Surface run-off or leaching of soils from farms with high levels of copper is likely the source of copper in the Ruiru River. Dickinson et al. have reported on the retention and loss of copper fungicides in coffee stands in central Kenya.^[38] The authors found that in 4-year old coffee stands, only 45.5% of the copper sprayed could be accounted for, and that the remainder was likely to have leached through the soil or in surface run-off.

Nitrates

Nitrate concentrations (Fig. 3) in the study site ranged between 2.28 and 4.89 ppm with an average concentration of 3.62 ppm. The highest concentration of nitrates was detected at site 12 located downstream of numerous coffee large farms. These values are similar to those determined in other agriculturally productive areas on Kenya. For example, a recent study by Onyando et al. conducted within during the long rains in a similar river system in Kenya determined nitrate levels to be between 1 and 7 ppm.^[40] These high levels of nitrate were attributed to surface run-off from intensively cultivated areas that had little riparian vegetation.

The concentrations of nitrates detected at the study site are consistent with the abundance of agricultural activity in surrounding areas and the application of N-fertilizers. Antao et al. studied the contamination potential of agricultural activities in Ruiru and reported nitrate concentrations in the Ruiru River of up to 4.6 ppm and within the range reported by others.^[40,41] The researchers attribute the high nitrate concentration to agricultural run-off from coffee farms and flower farms. This correlation is also reported by Ribbe et al. for a study on the extent of agricultural contribution to nitrate pollution in the Pochay watershed of the Aconcagua River, Chile. This study showed that when agriculture is the only significant source of nitrogen contamination, nitrate-N content in surface water averaged 4.5 ppm.^[42] Thus, the higher nitrate loading at site 12 may be the result of larger volumes of application of N-fertilizers on the commercial farms relative to the smaller holdings. Conversely, the lowest concentration of nitrates was measured at site 8, a point at which the river was situated beside a local highway with no visible agricultural activity nearby.

Table 1. Half-life values of representative *N*-methyl carbamates at pH 9 and 18°C.

Representative <i>N</i> -methyl carbamates (NMCs)			
			
carbaryl	propoxur	carbofuran	
$t_{1/2}$ pH 9, 18°C	19.3 h	38.5 h	57.8 h

Phenols

The goal of the phenol analysis was to measure the baseline phenol levels in the Ruiru River. The analytical method used in this study does not differentiate between structurally distinct phenols and could not therefore determine whether phenols detected were products of NMC hydrolysis.¹ Thus, phenol concentrations reported for the Ruiru River included a wide variety of substituted phenols and may have originated from wide range of sources, both natural and anthropogenic.^[43,44]

Phenols were detected between 0.19 and 0.83 ppm with an average concentration of 0.52 ppm (Fig. 2). The variations in phenol concentrations are likely due to variations in the content of dissolved organic matter (DOM), an important natural source of phenol, and itself determined by surrounding geology and vegetation. Indeed, tropical river systems have been shown to have large variations in DOM values of between 1 and 10 ppm due to multiple sources of DOM.^[45] In our study, dense riparian vegetation at the sampling sites was likely responsible for phenols detected in the Ruiru River e.g., site 10 located on a tributary with heavy vegetation close to the sampling point had the highest phenol reading (0.83 ppm). Notably, site 2 located downstream of the Ruiru dam, showed the lowest value of phenol at 0.19 ppm. This lower concentration of phenol may be due to a natural filtration or deposition of DOM by the dam. In addition to natural sources, anthropogenic activity may contribute to phenols including those generated from NMC hydrolysis because pesticides are routinely applied in Ruiru, and the NMC carbofuran has been detected in surface water by other researchers.^[9,46] However, it is yet to be determined whether NMCs make any significant contribution to phenol concentrations in the Ruiru River, and future studies by our group will focus on exploring possible correlation between phenols detected in river water and NMCs that are used in the area.

Phosphates

The levels of phosphates measured at the Ruiru River (Fig. 2) were between 0.01 and 0.5 ppm with an average concentration of 0.23 ppm. These values are higher than natural surface water levels,

which typically range from 0.005 to 0.05 ppm.^[47] Most values measured by our group fall within the range of 0.12–0.32 ppm reported by others working on a similar tropical stream system in Kenya.^[40] Natural sources of phosphorus such as the natural weathering of submerged soil and rock, the atmosphere, riparian vegetation and riverbank erosion may minimally contribute to the observed phosphate concentration.^[48–50] However, there is likely significant contribution from anthropogenic sources such as fertilizer run-off, domestic waste water drainage^[41] and septic tank discharge.^[51,52] It was noteworthy that the Ruiru River was free of algal blooms, despite having phosphate concentrations greater than 0.1 ppm, which typically trigger algae growth.^[48] This anomaly may be due to presence of copper in the river (vide supra), which is known to inhibit photosynthesis and restrict growth of algae.^[53]

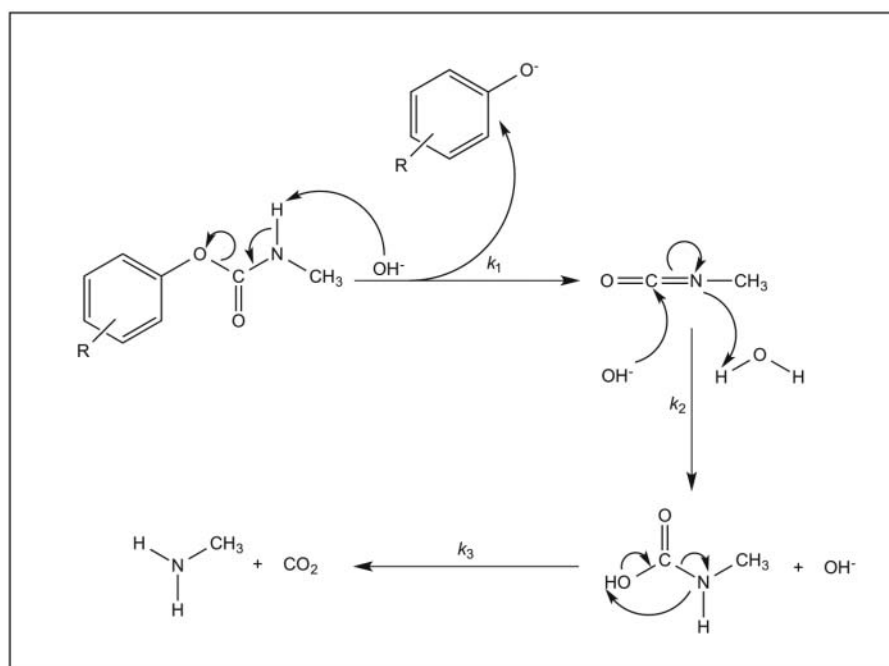
Kinetic studies on NMC degradation

The relative rates of degradation of three NMCs (carbaryl, propoxur, carbofuran) used in Kenya were investigated (Table 1). To our knowledge, there are no other reports that compare the half-lives of these three specific NMCs under identical conditions.^[13,54–56] Carbaryl (Sevin) is a broad spectrum pesticide^[57] that is moderately toxic to aquatic organisms and highly toxic to many non-target insects, such as honeybees.^[58] The compound has the potential to migrate to groundwater ($K_{ow} = 71$).^[57,58] Propoxur (Baygon) possesses tumorigenic activity in experimental animals,^[59] and is moderately soluble in water ($K_{ow} = 33.11$).^[60] Carbofuran (Furadan), an insecticide and nematicide, is classified as a restricted-use pesticide in temperate zones.^[61,62] It is highly toxic to mammals, has been shown to be mutagenic after metabolic activation,^[63,64] and is partially soluble in water ($K_{ow} = 209$).^[61]

Linear first-order kinetics of NMC hydrolytic decay

The hydrolytic decay of NMCs has been well studied, and under basic conditions shown to proceed via an E_{1cb} mechanism to yield phenolic products (Scheme 1).^[65,66] The degradation follows first-order kinetics with respect to the concentration of the NMC ($k_1 \ll k_2 \sim k_3$); the rate-limiting step is the initial deprotonation of the *N*-bound hydrogen. The Ruiru River was found to be mildly basic, and kinetic studies were conducted under alkaline conditions to determine the relative stability of the three NMCs. Experiments were performed to determine the half-life values of the NMCs at pH 9 and 18°C (Figs. 4–6). The pH, although not environmentally relevant, was selected to provide accurate data on the relative

¹The method used involves the reaction of phenol and other phenolic compounds with 4-aminoantipyrine in alkaline solution to produce a red-colored complex. This reaction is initiated by potassium ferricyanide which is coated on the tip of the ampoule. This chemistry detects ortho- and meta-substituted phenols and under certain pH conditions will detect phenols substituted in the para-position with a carboxyl, halogen, hydroxyl, methoxyl or sulfonic acid group. Results are expressed in ppm (mg/L) "equivalent phenol" as C₆H₅OH and represent the minimum concentration of phenolic compounds in the sample.



Scheme 1. Mechanism of base-catalyzed hydrolysis of *N*-methylcarbamate.

stability of the three NMCs in reasonable time frames at room temperature. NMC half-lives at the lower pH of the study site (pH 7.08–7.70) are expected to be longer than the values reported in our kinetic studies conducted at pH 9. For example, a separate study found that at pH 9 (20°C), $t_{1/2}$ for carbaryl is 3.2 h, but this value increases to 10.5 days at pH 7 (20°C).^[58]

Under the reaction conditions, NMC concentrations of 1×10^{-3} M were used, and rate measurements were determined by monitoring the disappearance of λ_{max} in UV-vis spectrum of NMC solutions for at least three half-lives. First-order kinetics should give linear plots of $\ln [\text{NMC}]$ vs. time (Eq. 1), and linear first-order plots were obtained from integrated decay plots of the concentrations of the NMCs, and are provided in Figures 4–6. The results confirm that hydrolysis of all three NMCs was first order, and that carbaryl hydrolyzed most rapidly ($t_{1/2} = 19.3$ h) followed by propoxur ($t_{1/2} = 38.5$ h). Carbofuran underwent the slowest hydrolysis ($t_{1/2} = 57.8$ h)

$$\ln [\text{NMC}]_t = -kt + \ln[\text{NMC}]_0. \quad (1)$$

Our relative rankings of hydrolysis rates for the three NMCs are consistent with relative hydrolysis rates reported by others, albeit under different alkaline pH and temperature conditions. For example, one group reports that at pH 9 and 20–25°C, the half-life for carbaryl was faster ($t_{1/2} = 2.5$ –3.2 h) than that of

carbofuran ($t_{1/2} = 12.96$ h).^[67] In a separate study at pH 9 and an unspecified temperature, $t_{1/2}$ propoxur was reported as 38.4 h close to the half-life value of 38.5 h determined in our experiments.^[60]

Effects of NMC structure on rates of hydrolysis

The relative rates of NMC hydrolysis may be rationalized by considering the chemical structure of the NMCs. The rate-determining step of the hydrolysis is the deprotonation of the *N*-bound hydrogen, and more acidic *N*-bound protons will undergo this reaction faster. The electron density in the

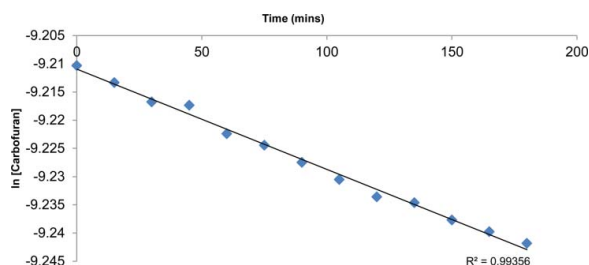


Figure 5. Hydrolysis of carbofuran at pH 9 and temperature of 18°C; $t_{1/2} = 57.8$ h.

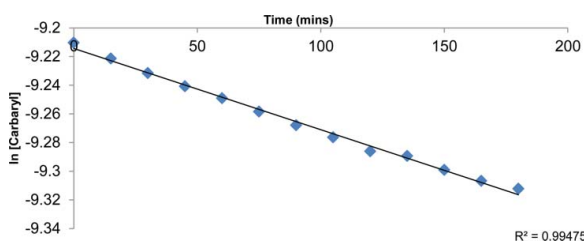


Figure 4. Hydrolysis of carbaryl at pH 9 and temperature of 18°C; $t_{1/2} = 19.3$ h.

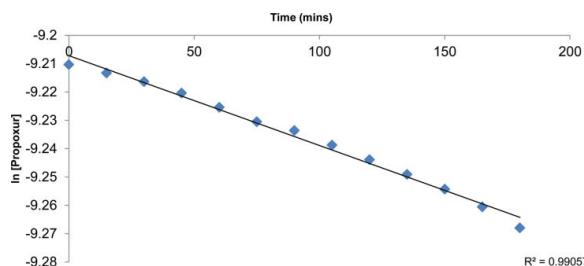


Figure 6. Hydrolysis of propoxur at pH 9 and temperature of 18°C; $t_{1/2} = 38.5$ h.

aromatic ring is influenced by the electronic nature of the substituents and affects the acidity of the *N*-bound hydrogen. The acidity of substituted benzoic acids has been long known to depend on the electronic nature of substituents on the aromatic ring, and a similar effect can be expected in other systems bearing substituents with acidic protons.^[68] Thus, in our NMC systems, electron-releasing substituents should increase electron density in the aromatic ring and reduce acidity of the *N*-bound proton. Conversely, electron-withdrawing substituents should decrease electron density in the aromatic ring and increase acidity of the *N*-bound proton.

Both propoxur and carbofuran bear electron-donating alkoxy groups, which should increase the aromatic ring's electron density. Carbofuran bears an additional hydrocarbon group that increases electron density further in this NMC. The fused aromatic ring in carbaryl does not significantly alter overall electron density of the carbamate-bearing aromatic ring.^[68] Thus, the electron density in the aromatic rings of the NMCs is expected to *decrease* in the order: carbofuran > propoxur > carbaryl. By extension, the acidity of the *N*-bound hydrogen is expected to *increase* in the order carbofuran < propoxur < carbaryl. The rate of NMC hydrolysis should increase in the same order as the proton acidity.

Results of our kinetics experiments are consistent with this prediction and with the expected first-order decay for all three NMCs. Carbaryl, predicted to have the most acidic *N*-bound proton, hydrolyzed fastest ($t_{1/2} = 19.3$ h). Carbofuran, predicted to have the least acidic *N*-bound proton, hydrolyzed slowest ($t_{1/2} = 57.8$ h). Propoxur, predicted to have an *N*-bound proton of intermediate acidity, hydrolyzed slower than carbaryl, but faster than carbofuran ($t_{1/2} = 38.5$ h).

An important implication of the findings is that, with the longest half-life, carbofuran may be the most persistent NMC. This outcome may be consequential as carbofuran is also the most toxic of the three NMCs to aquatic life.^[69,70] Future studies will investigate the decay rates of the three NMCs under conditions determined in the fieldwork, and will further explore the relationship between NMC chemical structure and tropical environmental fate of NMCs in general.

Conclusion

This study focused on determining baseline conditions of the Ruiru River, an important river in the agriculturally productive central highlands of Kenya. The assessment was conducted at the end of the long rains season in June 2013. Results showed that concentrations of nitrates, phosphates and copper in Ruiru River were higher than those in uncontaminated freshwater.^[47] Surface run-off during the long rains is the likely source of the contamination. Notably, Ruiru dam inlet had higher concentrations than the outlet, and the dam appeared to naturally filter or deposit contaminants.

Importantly, copper concentrations in the Ruiru River were much higher than naturally occurring concentrations in surface freshwater systems and indicate an anthropogenic source. Widespread and long-term use of copper fungicides on coffee farms in the study area and their subsequent migration into the river is the likely cause of this contamination. Phenols were detected in the water at normal ranges and may be attributed

to DOM from the dense riparian vegetation. Ammonia values were within the normal range for uncontaminated water and indicated a probable absence of contamination from sewage and industrial effluence.

Preliminary kinetics studies on NMC decay revealed that the relative rates of decomposition increased in the order carbofuran < propoxur < carbaryl, following the trend of decreasing electron density in the aromatic ring of the NMCs. This decrease in electron density causes an increase in acidity of the *N*-bound proton, and more acidic *N*-bound protons cause NMCs to decompose at a faster rate. Future studies will involve simulation of the Ruiru River water matrix to investigate the chemical fate of a broad range of NMC pesticides.

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Supplementary Materials

Colorimetric Reactions

The following are the chemical reactions occurring in vials provided by the manufacturer, and used to measure each of the analytes in this study.

- Copper:** Total soluble copper reacted with bathocuproine ligand to form an orange colored chelate in direct proportion to the copper concentration.
- Ammonia:** Free ammonia reacts with hypochlorite to form monochloramine which further reacts with salicylate in the presence of sodium nitroferricyanide to form a green colored complex called 5-aminosalicylate in direct proportion to ammonia concentration.
- Phenols:** Phenols react with 4-aminoantipyrine in alkaline solution to produce a red colored complex in direct proportion to phenol concentration. This reaction is initiated by potassium ferricyanide, which is coated on the tip of the ampoule.
- Nitrate:** Nitrates are reduced to nitrite with cadmium. The nitrite diazotizes with a primary aromatic amine in an acidic solution, then couples with another organic molecule to produce a highly colored azo dye in direct proportion to nitrate concentration.
- Phosphate:** Phosphates react with ammonium molybdate in an acidic solution to form molybdophosphoric acid. This acid is then reduced by stannous chloride to the intensely colored molybdenum blue in direct proportion to phosphate concentration.
- Dissolved Oxygen:** In an acidic solution, oxygen oxidizes the yellow-green colored leuco-form of indigo carmine to generate a highly colored blue dye in direct proportion to oxygen concentration.

Table 15. Photometric measurements using certified standards.

Analyte	Prepared Concentration	1st reading (ppm)	2nd reading (ppm)	Standard deviation
Ammonia	2 ppm	2.11	2.19	0.0565
Copper	10 ppm	9.82	10.28	0.325
Nitrate	25 ppm	20.9	19.1	1.22
Phenol	5 ppm	4.63	4.50	0.0919
Phosphate	5 ppm	4.76	4.73	0.0212

Photometric analysis using a CHEMetrics V-2000 Photometer. Samples diluted from certified standards with the following concentrations: [NH₃] 1000 ppm; [Cu] 100 ppm; [Fe] 100 ppm; [NO₃] 1000 ppm; [phenol] 1000ppm; [phosphate] 1000ppm

Table 25. Measurements along Ruiru River in ppm.

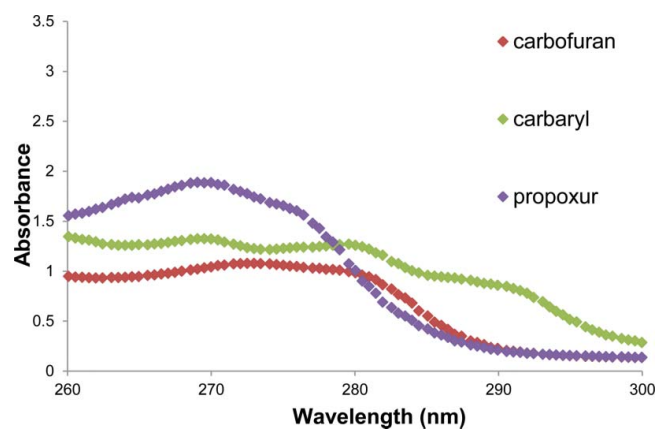
Sampling Site	pH	Nitrate	Phosphate	Ammonia	Copper	Phenol	Dissolved O ₂
1. Ruiru Dam inlet	7.08	3.08	0.19	0.11	0.38	0.30	7.36
2. Ruiru Dam outlet	7.42	2.48	0.01	0.02	0.21	0.17	7.04
3. Kanjuku coffee factory	7.38	3.90	0.19	0.15	0.61	0.43	8.12
4. Kiambururu bridge	7.44	3.84	0.26	0.17	0.64	0.53	7.09
5. Kwamaiko bridge	7.36	3.01	0.30	0.20	0.88	0.62	8.11
6. Jacaranda bridge	7.33	4.19	0.30	0.13	0.88	0.52	8.15
7. Murera bridge	7.20	4.03	0.26	0.14	0.82	0.57	8.09
8. Ruiru bridge	7.43	2.28	0.30	0.16	0.85	0.63	8.14
9. Water treatment plant	7.70	4.33	0.27	0.22	0.90	0.64	7.00
10. Komothai bridge	7.33	3.55	0.50	0.22	1.51	0.83	8.40
11. Garamaiyu bridge	7.28	3.82	0.30	0.12	0.73	0.51	7.69
12. Mukuyu tributary	7.54	4.89	0.20	0.13	0.72	0.48	7.68

Table 35. Replicate measurements at site 5 over four-day period. Concentrations in ppm. Temperature in °C.

Sample	pH	Temp	Nitrates	Phosphates	Ammonia	Copper	Phenols	Dissolved O ₂
1	7.36	20.60	3.01	0.30	0.20	0.88	0.62	8.11
2	7.32	19.30	3.54	0.20	0.15	0.71	0.40	7.75
3	7.57	19.60	3.70	0.20	0.06	0.39	0.43	7.63
4	7.60	18.50	4.21	0.20	0.20	0.70	0.48	7.85
Avg	7.46	19.50	3.62	0.23	0.15	0.67	0.48	7.84

Table 45. Duplicate measurements (in ppm) at odd-numbered sites along The Ruiru River.

Site	Nitrates	Phosphates	Ammonia	Copper	Phenols	Dissolved O ₂
1	2.45	0.13	0.13	0.53	0.28	7.80
1	3.66	0.25	0.09	0.23	0.32	8.06
3	4.26	0.16	0.13	0.59	0.36	7.45
3	3.56	0.22	0.17	0.46	0.33	7.69
5	4.30	0.16	0.22	0.69	0.42	7.95
5	4.11	0.23	0.18	0.71	0.54	7.74
7	4.46	0.27	0.23	0.73	0.56	8.18
7	2.84	0.24	0.04	0.68	0.56	7.44
9	3.86	0.27	0.21	0.86	0.57	8.29
9	3.90	0.27	0.22	0.71	0.58	8.71

**Figure 15.** UV-vis spectra of carbofuran, carbaryl and propoxur.

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