

Review Article

Review On a Probabilistic Exposure of Farmers and Biota to Diuron (Herbicide) Used In Santa, North-West Cameroon

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Abstract

Misuse of pesticides in Santa (North-West Region, Cameroon) rural area is obvious since many spraying parameters such as doses, spraying frequencies, time before harvest are not respected. These factors have certainly increased the level of contamination in the environment. Although pesticides are important in controlling pests and diseases proliferation, they have been associated with much adverse effects in humans and ecosystems. Despite their toxic potentials, no scientific experiment has been conducted to characterize herbicides used in these areas. The objective of this review is to critically discuss on diuron, widely used herbicide in Santa. It has been concluded that, diuron probably pollutes the environment and may affect the users health. An assessment on its short and long term effects and risk assessment in food, environment and on humans calls for a great concern.

Keywords: Diuron, health risks, physico-chemical properties, pollution, farmers, contamination

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Introduction

Agriculture is the most practiced activity in the western highlands of Cameroon with about 80 percent of the population involved [1, 2]. Crop production in Santa is practiced at small scale for consumption and to generate family income. Production of vegetables represents about 50% of the total regional production estimated at 185,542 tons from a surface area of 123,769 hectares [3]. Farming facilities have favoured the movement of people towards the zone where many tribes like to develop modern cropping. This is mostly based on excessive use of agro-chemicals to increase the productivity of crops. But, according to Sonchieu et al., Pouokam et al. and Kamga et al. [4-6] the educational level of farmers and pesticide workers remains low. What they do is by experience acquired from general to generation. Their poor knowledge in respect of instructions from manufacturers and technical assistants has led to poor application of spraying parameters (doses, frequencies, packaging materials management, spraying time, attitude during spraying, etc.). In this regard, treatment of pesticide wastes and containers had been seen as not following any safety measures. They are left in the environment, burnt or reuse for domestic purposes [7, 8].

Surveys conducted in this area showed that farmers frequently used three classes of pesticides: herbicides, insecticides and fungicides. Diuron is one of the main herbicides frequently sprayed alongside glyphosate which is the first [4, 5].

Diuron is known to be a broad-spectrum herbicide used for weed, grass, and brush control. It stops photosynthesis, which in turn causes plants to stop growing. It also inhibits seed germination and presents a potential risks to humans, wildlife, and aquatic animals. Evaluating potential risks from pesticides takes into account both toxicity and characteristics for possible exposure [9-11].

It is also known that pesticide misuse causes serious health and environmental problems. Surveys on pesticide application in Santa conducted by Edouard et al. [12] raise growing concern about common symptoms related to pesticide exposure. With this, Sonchieu et al. [4] remarked that pesticides are responsible for symptoms and signs including vomiting, headache, dizziness, etc. which are very common amongst farmers.

Many field studies have been carried out on surveys basis such as on health status and applications conditions [1, 4]; cropping systems and land exploitation [1, 2] and some chemicals characterization [12]. But update review of all these works has been done to facilitate any further study and to give new orientations thereof. This review study aimed at providing information on characteristics of diuron, one of the most applied herbicides in Santa. This information will orientate any further studies to be carried out in the area either in the ecosystems, on agricultural produce or on pesticide workers and farmers.

Presentation of Santa Agricultural Area

The area has two seasons: rainy (from March to September) and dry season (from October to February). The annual rainfall ranges between 2000 and 3000 mm under the altitude of 1000 to 2600 meters giving a mean annual temperature of 19°C, which is favourable for crop production and development of pests [13]. The area is characterized with three types of soil: penevoluted ferrallitic soils, modified orthic soils and the aliotic and penevoluted ferrallitic red soils [1]. The farming focuses on various vegetables and other crops: maize, Irish potatoes, colocassia, cassava, beans, tomatoes, carrots, plantain, soya beans, cabbages, fruits, spices, etc. The most intensive agricultural area includes Mifi, Matazen, Mbufon, Saptsi, Melung, Makemtikong, Achialum, Nephew, Milieus, Njon and Mewungne.

Diuron's Formulations used in Santa Agricultural Area

A good number of surveys carried out on the types of pesticides (formulations) used in Santa agricultural area [4, 12, 6] revealed that glyphosate and diuron are the main two active ingredients used in more than seven formulations. Diuron, a systemic pesticide, is sold in one main powder formulation (Action 80) in dry flowable state. It belongs to class III toxicity and is authorized to be used in cotton cultivation [13].

Formulating Agents

Caroline [9] described some inert ingredient found in diuron formulations like in many other pesticide formulations. Its formulations contain inert ingredients that include: Sodium salt of lingo-sulfonic acid mostly found in DF with no toxicity observed; Ethylene glycol which has shown to be toxic with various symptoms like throat and respiratory tract irritation, kidney and liver disturbances, and even induces fetal malformations; Sodium polyphosphate which can cause irritation of eye, skin and respiratory tract, nausea, vomiting and diarrhea; and Kaolin (clay) which can lead for long term effect and increase lung cancer risk [14].

Overview on Diuron

Diuron is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds [11]. It is also used to control weeds and mosses on non-crop areas and among many agricultural crops such as fruit, cotton, sugar cane, corn, tomato, and other vegetables and legumes [13]. Diuron works by inhibiting photosynthesis [9]. It is applied for pre-emergent herbicide. It is moderately mobile, and minor residues have been found in groundwater after applications [10, 15]. It contains microbes which contribute on its breaking down inside water [16, 17]. It may persist for more than one year when applied at high rates. It has low leaching potential and is slowly degraded in coarse-textured soils. The plant can retake it through roots and translocates it to the edible parts [18].

Identification of Diuron

Chemical Association Society (CAS) registered diuron under the number 330-54-1. Its formula is $C_9H_{10}Cl_2N_2$ with the Structure shown on **Figure 1**. The molecular Weight is 233.10 g/mol. It has been identified by IUPAC as 3-(3,4-dichlorophenyl)-1,1-dimethylurea while CAS named it as N'-(3,4-dichlorophenyl)-N,N-dimethylurea [19, 20].

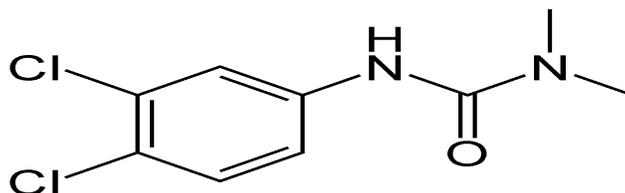


Figure 1 Chemical structure of Diuron

Some Properties of Diuron influencing Environmental Contamination

The persistence of diuron in the environment, as of other chemicals, is based on their physic-chemical properties and chemical structures. All properties do not contribute to environmental contamination. Listed below are those with direct link to environmental pollution by diuron.

Hydrolysis

Under hydrolysis control, diuron presents no observable degradation at 25°C in the pH 7 and 9 solutions, and only slight degradation at pH 4 - 5 with half-lives of 798 and 313 days are observed respectively (Caroline 2003) [9]. However, at a higher temperature of 50°C hydrolysis happens for pH 4, 5 and 9 with half-lives of 26, 56 and 109 days respectively. It leads to the generation of two degradation products and the half-life is greater than 500 days. They are: N'-(3, 4-dichlorophenyl)-N-methyl urea (DCPMU) and 3,4-dichloroaniline (DCA) [21].

Photodegradation

The chemical decomposition or breaking down of materials under the influence of light is referred as photolysis [22]. Sunlight photodegradation (photophysical and photochemical Processes) is one of the most destructive pathways for pesticides after their release into the environment. Photodegradation of diuron was found to be one of the most important factors in dissipation process except for evaporation, rainfall elution, and growth dilution. The extent of sunlight photolysis is highly dependent on UV absorption profiles of the pesticide, the surrounding medium, and the emission spectrum of sunlight [18, 22, 23]. Braun et al. [15] reported that under neutral pH at 25° C, diuron in an aqueous medium the photolysis undergone by diuron leads to a relatively long half-live ranging from 44 to 108 days. The photolysis of diuron followed first order kinetics and is pH-dependent with degradation at pH 7 slower than at pH 5 or 9 (Boule et al. 2002). Under the sunlight, [20] researchers found that diuron undergoes direct photolysis because it absorbs UV light at wavelengths greater than 290nanometers.

Photolysis in the soil is relatively slow with 90% of the applied diuron recovered after 30 days of irradiation. The half-life of diuron is 173 days using first order kinetics. N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU) is the main degradation product noted. Photodegradation in soil is very slow and unlikely to be a significant contribution to environmental degradation of diuron [15].

Volatilization factors

Vapour pressure (P°) is a dependent factor for vaporization. It depends strongly on the temperature and varies widely with compounds because of interactions [24]. This intrinsic physical property plays a crucial role in determining its distribution in environment. It is important in predicting the equilibrium distribution coefficients such as Henry's Law constant (KH) [25]. Diuron is non-volatile, as indicated by its low vapour pressure of 6.90×10^{-8} mm Hg (25° C), and a low Henry's law constant (5.10×10^{-10} atm.m³ mol⁻¹). Its low vapour pressure and low Henry's law constant are indicator that diuron is unlikely to be distributed in air over a large area and has a low capacity of volatilizing from water or wet soils. Volatilization can be significant only when diuron is exposed under hot and dry conditions [26].

Solubility in water and K_{OC} tan Water Partition Coefficient at 25°C

Diuron in water has a solubility of 4.2×10^{-4} gram /litter at 25 °C and very slightly soluble in many organic solvents as glyphosate [11].

The diuron has K_{OC} tan Water Partition Coefficient of 2.85 at 25°C [11]. This relatively low K_{OC} indicates a relatively low tendency to sorb to soils and sediments. Consequently diuron is both mobile and relatively persistent, and is therefore prone to off-site movement in surface runoff, and migration to ground water [27].

Diffusivity

Diffusivity or diffusion coefficient is the proportionality constant between the molar flux due to molecular diffusion and the gradient in the concentration of the species. It can also be assimilated to a driving force for diffusion. It depends on the temperature of the medium and varies according to the nature of the material [11]. Diffusibility of diuron in the air is estimated at $2.77 \cdot 10^{-02}$ cm²/s while in water it is known to be 7.293×10^{-06} cm²/s.

Soil Adsorption Coefficient

Reports indicate that there is high adsorption of diuron in the soil which is dependent on organic carbon in the soil but also on the silt or clay component due to the high adsorption in the soil with low organic carbon [28]. The adsorption was considered to be reversible as the distribution coefficients since adsorption and desorption are close in values. The K_{ocs} indicate that DCPU is moderately adsorbed to the soils and is rated as being low to medium mobility (McCall classification).

Toxicological Properties of Diuron and Metabolites

Maximum Residues Limit (MRL)

The amount of residues available in raw commodities put in the market will influence the health risk of exposure of consumers. It is generally collected on on-going monitoring programmes put in place by governments to ensure the quality. **Table 1** presents the various MRL in various crop cultivated in the area according to Sonchieu et al. [4].

Table 1 Maximum Residues Limit of diuron for various vegetables cultivated in Santa agricultural area

S/N	crop/water	scientific name	diuron: MRL UE (ppm)
1	carrot	<i>Daucus carota</i>	0.01
2	cabbage	<i>Brassica oleracea</i>	0.01
3	leeks	<i>Allium porrum</i>	0.01
4	onion	<i>Allium cepa</i>	0.01
5	huckleberry	<i>Solanum nigrum</i>	0.05
6	tomatoes	<i>Lycopersicon esculentum</i>	0.01
7	irish potato	<i>Solanum tuberosum</i>	0.01
8	celery	<i>Apium graveolens</i>	0.02
9	okra	<i>Hibiscus esculentus</i>	0.01
10	parsley	<i>Petroselinum crispum</i>	0.02
11	pepper	<i>Capsicum frutescens</i>	0.01
12	green beans	<i>Phaseolus vulgaris</i>	0.01
13	lettuce	<i>Lactuca sativa</i>	0.01
14	garden egg	<i>Solanum melongena</i>	0.01
15	drinking water	-	0.07

Source: [4, 29-32], Toxicity of diuron active constituent has been proved [20]

Effects on Human Health

Diuron is herbicide commonly used in Santa may have long/ short term adverse effects on farmers, workers and consumers. They are exposed to contaminated air, water and food which can get into their systems through any of the following routes: skin contact, inhalation, eating and drinking and may find itself in metabolites or parent form in various biological liquid [33-36]. Diuron has slight toxicity if an individual absorbs it in moderate amount. It is moderately irritating to the eyes and slightly irritating to the skin. It has been shown to cause slight anemia, enlarged spleen, bone marrow changes, and abnormal blood pigments [4, 36-38].

Continuous exposure has led in developing signs and symptoms such as itching and burning of oral and nasal mucosa and conjunctiva, small ulceration in the skin area affected, chest discomfort with cough and mucoid sputum, headache, muscle twitching and throat soreness [17, 25]. Much symptoms linked to diuron exposure including methemoglobin, and irritation of skin, eye, nose and throat where observed among pesticide sellers in Santa [39].

In poisoning cases involving ingestion of diuron, parents products and metabolites [3-(3,4-dichlorophenyl)-1-methyl urea, 3-(3,4-dichlorophenyl) urea and/or 3,4-dichloraniline] were detected in the blood and urine, [38, 40].

The US-EPA [10] classifies diuron as a “known/likely” human carcinogen. Under maximum exposure conditions, diuron poses potentially low to high adverse non-cancer risk to the public with a hazard quotients ranging from 8.6 to 12[41]. However, no reproductive harmful effect has been reported from diuron user [42].

Effects on Ecosystems

Diuron is slightly toxic to mammals and birds. Fish and water insect exposure to diuron occurs primarily through direct contact with contaminated surface waters and it does not build up in aquatic organisms. Diuron has been reported to be moderately toxic to fish and highly toxic to aquatic life. So the LC50 (48 hours) values ranges from 4.3 to 42 mg/L in fish, and from 1 to 2.5 mg/L for aquatic invertebrates. However, Diuron is rated as non-toxic to bees and earthworms [9, 15]

Fate and Metabolites of Diuron

The degradation of pesticides can be induced by several phenomena such as photolysis, microorganisms, hydrolysis,

biochemical reactions, etc. These processes can be influenced by many environmental factors as reported by Toshiyuki [27]. There are: illumination conditions, effect of formulation, anatomy of the leaf, wax structure, photo-induced reactions, soil components, environmental factors affecting soil properties, mass transport in soil, photic depth in soil, effects of soil properties on photolysis, photophysical and photochemical processes of soil components and atmospheric oxygen species, micro-organisms, etc. Their action will contribute to the transformation of parent compounds to metabolites (degradation products). They vary according to structure of the molecule [43].

Global fate of diuron

Microorganisms are the primary agents in the degradation of diuron in aquatic environments [44]. The aerobic biodegradation pathway for diuron is well established (**Figure 2**), proceeding by successive demethylation process to form DCPMU [3-(3,4-dichlorophenyl)-1-methyl urea], DCPU [1-(3,4-dichlorophenyl)urea] and DCA (3,4-dichloroaniline) (Cabrera et al. 2007; ePM 2003). Reductive dechlorination has been observed in anaerobic pond sediments and leads to the formation of the dechlorinated product, 3-(3-chlorophenyl)-1,1 dimethylurea [25]. Boule et al. [22] reported that [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is the major photoproduct obtained during photolysis of diuron.

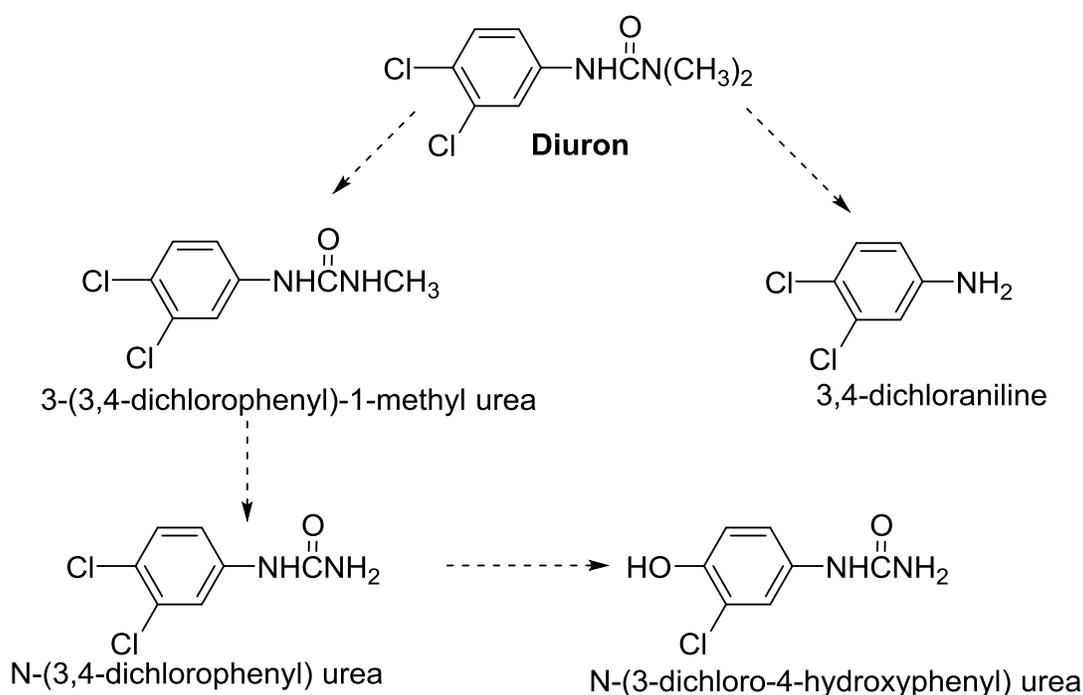


Figure 2 Common degradation pathway of diuron

Fate of diuron in Soil

In the soil, persistence of diuron varies from moderate to high according to its characteristics. The commonly reported average field dissipation half-life is 90 days, although such half-lives are typically highly variable [15]. Phytotoxic residues generally dissipate within a season when applied at low selective rates. At higher application rates, residues may persist for more than one year [26]. Diuron is mobile in soil. As many other pesticides, diuron sorption is highly correlated with organic matter [11]. Consequently leaching is the greatest in low organic matter soils. Other soil conditions that favor diuron leaching include high soil permeability to water [37].

Fate of diuron in plants, Mammals and Air

Diuron is readily absorbed through the root system of plants and less readily through the leaves and stems. Diuron rapidly translocates from roots to shoots via the xylem. Very little or no diuron moves from the apex downward toward the base of a treated leaf via the phloem [16]. It is metabolized via N-demethylation of the nitrogen atom and hydroxylation of the benzene ring. Once diuron is ingested, it is excreted through feces and urine of test animals. Little tissue storage under field conditions is anticipated. Hydroxylation and dealkylation are the main pathways of diuron metabolism [27].

Persistence of Diuron in The Environment

Diuron's relatively low K_{oc} indicates a relatively low tendency to sorb to soils and sediments, while its hydrolysis and aqueous photolysis half-lives are relatively long. Consequently diuron is both mobile and relatively persistent, and is therefore prone to off-site movement in surface runoff, and migration to ground water [20, 45].

Water Quality

Diuron is a non-ionic compound with moderate water solubility of 22 to 42 mg/L at 20°C. Based on evaluations by the Food Directorate of the Department of National Health and Welfare, the acceptable daily intake (ADI) for diuron is 0.0156 mg/kg body weight per day while the maximum acceptable concentration (MAC) is derived from the ADI is 0.15mg/L [17, 46].

Analytical Methods

Diuron may be monitored in water or food by extraction into hexane, hydrolysis to the aniline derivative, quantification by gas/liquid chromatography and Hall conductivity detection. Granular activated carbon and powdered activated carbon are effective in removing up to 90% of diuron from drinking water. Other method involved in extraction of the herbicide includes low temperature precipitation and solid phase extraction techniques, and high performance liquid chromatography-ultra violet (HPLC-UV) for detection [46, 47].

Critical Analysis of Risks in Santa Agricultural Area

Most formulations used by farmers of Santa are not indicated by Cameroonian authorities (MINADER) [48] for vegetables while they are frequently applied. The utilization of diuron seems to be inadequate according to instructions of national authorities.

The following enterprises are involved in manufacturing, importation and distribution, of those herbicides in particular and pesticides in general: Fimex International SA (Douala-Cameroon), Ader Cameroon (Douala-Cameroon), Syngenta (Douala-Cameroon), Agrochem (Douala-Cameroon), Jaco (Yaounde), Africaware (Douala-Cameroon), Arysta LifeScience (France), Nordox (Norway) and Yara (Douala-Cameroon) [48].

However photolysis and micro-organisms are the main factors responsible for molecules degradation. Its action depends on climate factors since it is directly linked to the sunlight. Considering these parameters, it is showing that, during the months of December, January, February and March the photodegradation of the herbicides will be greater, compared to other period which will be obviously low because of low temperature [49].

The contamination of atmosphere by pesticides can be done through three main ways which are period of application, volatilization potentiality and wind speed. The low volatilization factors such as vapour pressure and Henry's law constant shows that diuron is unlikely to be dispersed in air over the large area of Santa agricultural area. So the tendency to volatilize from water or soils may happen only when the compound is exposed to sun light for long time. Under dry and hot conditions, slight evaporation will happen and contaminate the air. This, as indicated, will obviously happen between dry seasons (December-March). During this period, agricultural activities are intensified around irrigable sites. More farmers and pesticides workers are highly exposed since they ignorantly spray under hot time of the day and at time when wind speed is high [13].

The stability of diuron in the soil and poor ability of moving in the soil and water following the solubility in water will be responsible for plant uptake activity during cropping. This will lead in increasing the amount of residues in plant which at time are stored in edible parts. This fact may lead to level above MRL either in water or in food. This has not yet been estimated to assess the related risk. In addition, the leaching with runoff water will facilitate the contamination of other zone since weather indicates heavy rains for seven months [50, 51].

The stability of diuron in water constitutes a high threat for the population in the sense that the same water is used for herbicides preparation for spraying around streams, for domestic activities, food preparation and as drinking water [52] This expresses the exposure of workers, farmers, consumers and all other related food chain members[43, 52, 53]. This will also affect the aquatic and terrestrial fauna. In addition, the excessive use of these pesticides may affect the nutrient content of vegetables cultivated in that area as shown by the study conducted by Akono et al. [54].

Conclusions

Looking at the above factors attributed to diuron, it is clear that pesticides workers, farmers and consumers are

effectively exposed since former studies showed abusive spraying. Despite the intensive farming activities carried out in Santa, no control on the safety of foodstuffs produced and put in markets is done. The following aspects can be done to bring more light: level of residues in agricultural produce, contamination of the environment, residues load in operators systems and deep health status, and other concerns on pesticides effects.

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