PCDD/F AND PER- & POLYFLUOROALKYL SUBSTANCES CONTAMINATION IN SELECTED SEWAGE SLUDGES IN NIGERIA

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Introduction

Sewage sludge as solid residues from waste water treatment that contains in addition to nutrients such as phosphorous and nitrogen compounds also a range of toxic by-products[1]. Therefore it is a question if sewage sludges should be applied as bio-solids to agricultural soil or if you should be disposed to landfills or thermally treated. For industrial countries and for economies in transition sewage sludge contain a wide variety of organic pollutants which could have adverse effects on the soils, plant, animals and finally human health if bioaccumulating in the food chain.[1].One class of persistent organic pollutants (POPs) measured in sewage sludge are the polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) which are regulated in some countries in sewage sludge.. A more recent POPs found as contaminant in sewage sludge is PFOS and other per- and polyfluoroalkyl substances (PFASs). PCDD/Fs and PFOS levels in sewage sludge are a subject of concern because they bioaccumulate if e.g. cattle is grazing on pasture contaminated by PCDD/F or PFAS/PFAS, that large amounts of sludges are generated each year, and furthermore one of the alternatives to disposal is the application to agricultural land such as soil conditioners and fertilisers, with the risk that hazardous compounds, such as PCDD/Fs, enter the food chain and bio-accumulate in it[2].

PCDD/F has been included within the dirty dozen as initial POPs in the convention. PFOS and related precursor substances were added in May 2009 as the first fluorinated POPs in the Stockholm Convention[4].

In addition, sewage sludge is an important sink that can lead to the concentration of these persistent organic pollutants (POPs). A range of studies have monitored PCDD/Fs and PFASs in sewage treatment plants in industrialized countries[7,8] and in China[9,10] . For many years, PCDD/PCDF has been reported in sewage sludge of many countries[13]. Decreasing trends have been reported in countries such as Germany and Austria, as well as in Spain[12,13].

For developing and economy in transition countries the monitoring of PCDD/Fs and PFASs is a particular challenge and currently not feasible in almost all developing countries due to the lack of analytical capacity[5,6]. However considering the lack of PCDD/F and PFAS data in most developing countries and the need to understand the fate of these substance classes, data need to be generated in developing county regions such as African countries for a preliminary understanding of the environmental pollution status and fate of PFASs.

It is also important to monitor sewage sludge for chemical pollutants as the purpose of wastewater treatment is to contain and prevent pollutants from being re-released into the environment. The aim of this study was to determine the levels PCDD/Fs and PFASs in sewage sludge from industrial, municipal, and hospital wastewater treatment plants in Nigeria.

Materials and methods

Sampling: Sewage sludge was sampled in three municipal wastewater treatment plants (WWTPs), two industrial effluent treatment plants and one hospital wastewater treatment plant from January – April 2012 at different locations in Lagos, Oyo and Ogun state, all in South West Nigeria.

Extraction and clean up: For PCDD/F the samples were extracted by pressurized Liquid extraction method using two subsequent solvents, toluene and n-hexane, to efficiently recover the target compounds. The sample was spiked with 40 µl each of Internal Standard of PCDD/Fs prior to extraction. The extracts were purified and fractionated on two different open chromatographic columns consisting of multilayered silica and Carbon column. For PFASs, sludge samples were extracted according to an established method[9,14] with a few modifications. The extracts were then dried using a gentle stream of N_2 gas before dilution with HPLC grade water for SPE extraction (using Oasis WAX cartridges (Waters, 6 cc/150 mg)). The elute from SPE was dried by passing a gentle stream of N_2 gas, and subsequently reconstituted using 1:1 volume ratio of MeOH and 4 mM

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The Dissipation of Carbofuran in Two Soils with Different Pesticide Application Histories within Nzoia River Drainage Basin, Kenya

Selly Jemutai-Kimosop · Francis O. Orata · Isaac O. K'Owino · Zachary M. Getenga

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Abstract The dissipation of carbofuran from soils within the Nzoia River Drainage Basin in Kenya was studied under real field conditions for 112 days. Results showed significantly enhanced dissipation of carbofuran with half life (DT_{50}) values of 8 days ($p = 0.038$) in soils with prior exposure to carbofuran compared to 19 days in soils with no application history. At the end of the experiment, residues of 2.57 % and 9.36 % of the initial carbofuran applied were recorded in the two types of soil, respectively. Carbofuran metabolites identified in the study were 3-keto carbofuran and carbofuran phenol with 5.84 % and 15.0 % remaining in soils with prior exposure, respectively. Soils with no application history recorded 16.05 % and 12.82 % of 3-keto carbofuran and carbofuran phenol metabolites, respectively.

Keywords Pesticides · Persistence · Tropical region · Metabolites

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad spectrum carbamate insecticide and nematicide that has been used worldwide for control of pests in sugarcane, sugar beet, rice and coffee farms (Trabue et al. 2001). In spite of its efficacy in pest control, carbofuran is acutely toxic and has been linked to wildlife mortalities in many countries (Gupta 1994; Otieno et al. 2010). As a result, carbofuran use has been banned in several countries (Khuntong et al. 2010). However, this chemical is still imported into Kenya for restrictive use to control foliar feeding insects in rice paddy fields including the Bunyala rice irrigation scheme (Mohanty et al. 2009). Consequently, carbofuran is among the leading surface and ground water contaminants in Kenya (Otieno et al. 2010). Its detection in various matrices has raised a lot of environmental concerns based on its persistence in the environment (Bermúdez-Couso et al. 2011).

Dissipation of carbofuran in the environment occurs through both abiotic and biotic processes (Kim et al. 2004). Biomineralization of carbofuran results in complete detoxification of a contaminated environment (Chung 2000). However, pesticides that are newly introduced into soils are usually resistant to biodegradation by indigenous soil microflora (Krishna and Philip 2008). Nevertheless, studies have shown that repeated applications of the same pesticide or its analogues may result in selective build up of microbial populations capable of utilizing the compound as a source of carbon, nitrogen and/or energy (Getenga et al. 2009). For example Trabue et al. (2001) reported accelerated degradation of carbofuran in soils with prior exposure to the same pesticide. Rozo et al. (2013) recorded increased microbial population of carbofuran-degrading bacteria in soils with 8 years of carbofuran application compared to soils having three or 1 year of carbofuran exposure. A similar trend was observed by Plangklang and Reungsang (2013). Most of these studies have been conducted in temperate regions; however, there are limited studies detailing the degradation of carbofuran in soils with prior exposure in tropical regions, particularly the Nzoia River Drainage Basin (NRDB) where it is frequently used.

These soils have a good potential for enhanced degradation of carbofuran arising from the long exposure to the chemical (Mohanty et al. 2009). This phenomenon reduces the level of persistence of carbofuran in the soil and its

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Chlorpyrifos Degradation in Soils with Different Treatment Regimes Within Nzoia River Drainage Basin, Kenya

Gershom Kyalo Mutua, Anastasiah Njoki Ngigi & Zachary Moranga Getenga

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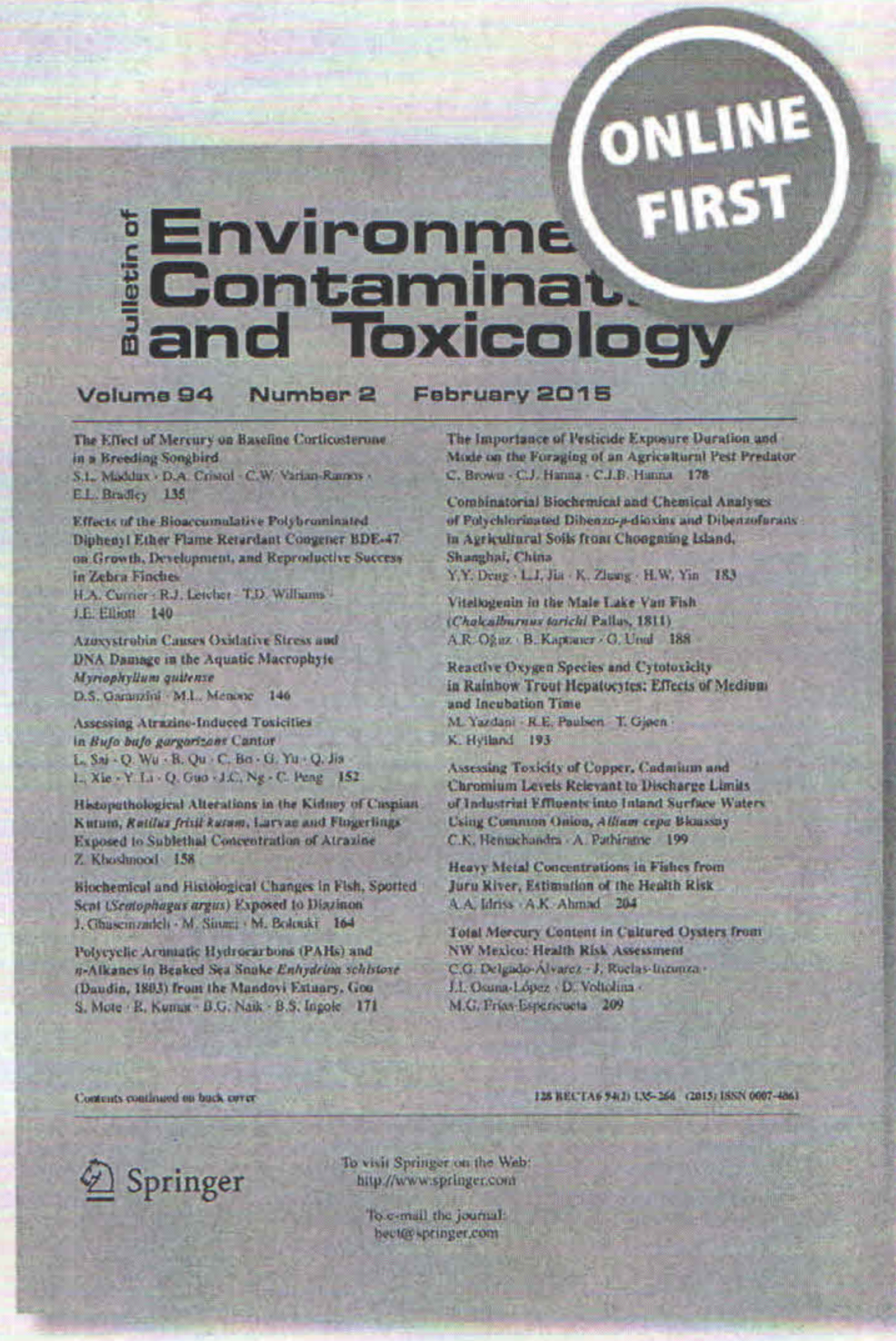

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Stability and Kinetics Studies Using an RP- HPLC-UV Method Developed for Assays of Salvianolic Acid A Degradation as a Therapeutic

Were L. L. Munyendo[1,2*], Lilechi D. Baraza[3] and George Sowayi[2]

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Authors' contributions

This work was carried out in collaboration between all authors. Author WLLM designed the study, mobilized resources, engaged in laboratory activities and wrote the first draft of the manuscript. Authors LDB and GS wrote the protocols and managed the analyses of the study. All authors read, reviewed and approved the final manuscript.

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Original Research Article

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ABSTRACT

Aims: To evaluate the stability of Salvianolic acid A (SAA), a promising cardiovascular drug candidate. Additionally avail an archetype in-vitro therapeutic monitoring from SAA degradation profile for characteristic oral gavages.
Study Design: Experimental by laboratory analysis.
Place and Duration of Study: Department of Chemistry & Biochemistry, Moi University; Department of Pure & Applied Chemistry and Department of Medical Laboratory Sciences of Masinde Muliro University of Science & Technology, between June 2013 and September 2014.
Methodology: Drug stability was studied according to ICH guidelines. A stability-indicating

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Perfluoroalkyl acids in selected wastewater treatment plants and their discharge load within the Lake Victoria basin in Kenya

Florah Chirikona · Marko Filipovic · Seline Ooko · Francis Orata

Received: 21 September 2014 / Accepted: 10 March 2015

Abstract A major ecological challenge facing Lake Victoria basin is the influx of chemical contaminants from domestic, hospital, and industrial effluents. Determined levels of perfluoroalkyl acids (PFAAs) in wastewater and sludge from selected wastewater treatment plants (WWTPs) in Kenya are presented and their daily discharge loads calculated for the first time within the Lake Victoria basin. Samples were extracted and separated using solid-phase extraction and ultra-performance liquid chromatography (UPLC)-MS/MS or LC-MS/MS methodology. All sewage sludge and wastewater samples obtained from the WWTPs contained detectable levels of PFAAs in picogram per gram dry weight (d.w.) and in nanogram per liter, respectively. There was variability in distribution of PFAAs in domestic, hospital, and industrial waste with domestic WWPTs observed to contain higher levels. Almost all PFAA homologues of chain length C-6 and above were detected in samples analyzed, with long-chain PFAAs (C-8 and above chain length) being dominant. The discharge from hospital contributes significantly to the amounts of PFAAs released to the municipal water systems and the lake catchment. Using the average output of wastewater from the five WWTPs, a mass load of 1013 mg day^{-1} PFAAs per day discharged has been calculated, with the highest discharge obtained at Kisumu City (656 mg day^{-1}). The concentration range of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in wastewater was 1.3–28 and 0.9–9.8 ng L^{-1} and in sludge samples were 117–673 and 98–683 pg g^{-1}, respectively.

Keywords Perfluoroalkyl acids · Discharge · WWTPs · Wastewater · Sludge · UPLC-MS/MS · Lake Victoria

Introduction

Perfluoroalkyl acids (PFAAs) belong to the commercially important family of perfluoroalkyl and polyfluoroalkyl substances (PFASs). They are highly fluorinated substances that contain one or more carbon atoms on which all hydrogen substituents have been replaced with fluorine (Buck et al. 2011). PFAAs are widely used due to their unique amphophilic properties that find beneficial application in both the commercial market and industry as protective coating of paper and textile fabrics and the electric industry in the production of semiconductors or as a component of fire fighting foams (Lindstrom et al. 2011; Brooke et al. 2004; Tsai et al. 2002), among other uses. The carbon-fluorine bond of PFAA is strong, and it therefore resists breakdown in the environment (Kissa 2001). The observed PFAA concentrations in the

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Biodegradation of carbofuran in soils within Nzoia River Basin, Kenya

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Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) has been used within the Nzoia River Basin (NRB), especially in Bunyala Rice Irrigation Schemes, in Kenya for the control of pests. In this study, the capacity of native bacteria to degrade carbofuran in soils from NRB was investigated. A gram positive, rod-shaped bacteria capable of degrading carbofuran was isolated through liquid cultures with carbofuran as the only carbon and nitrogen source. The isolate degraded 98% of 100-μg mL^{-1} carbofuran within 10 days with the formation of carbofuran phenol as the only detectable metabolite. The degradation of carbofuran was followed by measuring its residues in liquid cultures using high performance liquid chromatography (HPLC). Physical and morphological characteristics as well as molecular characterization confirmed the bacterial isolate to be a member of *Bacillus* species. The results indicate that this strain of *Bacillus sp.* could be considered as *Bacillus cereus* or *Bacillus thuringiensis* with a bootstrap value of 100% similar to the 16S rRNA gene sequences. The biodegradation capability of the native strains in this study indicates that they have great potential for application in bioremediation of carbofuran-contaminated soil sites.

Keywords: Carbofuran, biodegradation, bioremediation, *Bacillus thurigiensis*, *Bacillus cereus*.

Introduction

Carbofuran (2, 3-dihydro-2, 2 dimethyl-7-benzofuranoyl N-methylcarbamate) is a broad-spectrum carbamate insecticide, acaricide and nematicide.[1–2] It belongs to the N-methylcarbamate class that is extensively used in pest control. It is widely used in the control of pests such as corn root worm, wire worms, boll weevils, mosquitoes, alfalfa weevils and white grubs.[3] It has been also used worldwide for the control of rice pests such as green leafhoppers, brown planthoppers, stem-borers and whorl maggots.[1] For example, in South Korea, this pesticide was used as early as 1975 to control brown hoppers, green rice leaf hoppers and rice stem borers in rice paddies.[4] It has been reported that Carbofuran has rapid action against both nymphs and adults, killing them within 20 min.[1] However, accidental exposure of carbofuran can result in acute toxicities and fatalities even to human beings, thereby making it highly hazardous.[1,3]

As in 2010, commercial carbofuran (Furadan®) with 10% active ingredient was allowed for restrictive use by informed users in Kenya.[1] Studies showed that carbofuran was still being imported mainly for use in seed dressing at the rate of 0.5–4 kg a.i. ha^{-1} (active ingredient per hectare) for control of soil-dwelling and foliar-feeding insects. It was used in Isiolo and Laikipia districts to control agricultural pests and its residues were found in the soils, plants and water sources in such areas.[2] Carbofuran has also been used in Nzoia River Drainage Basin, especially in Bunyala Rice Irrigation Schemes nuclear estates.[5] A study done by Kimosop[6] in the same area on the dissipation behavior of carbofuran in the soil established that residual levels of carbofuran ranged from 0.01–1.08 μg g^{-1} in the soils, indicating environmental contamination. Therefore, the detoxification of the contaminated sites is necessary.

Conventional (chemical) methods of carbofuran detoxification, such as oxidation with ozone, photodegradation, fenton degradation, ozonation, membrane filtration and adsorption,[7] have been used. However, these methods, including pyrolysis of carbofuran, are more cumbersome, less effective and more costly to set up and run than

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lesb.

This book discusses understanding of chemical bonding which is a principle concept in chemistry. It is a key area in secondary school chemistry and even at higher levels of learning. The book highlights that students in secondary schools have some learning difficulties and lack a proper understanding of structure and chemical bonding concepts, and also clearly provides evidence that learners' attitude towards structure and chemical bonding concepts is positive. It suggests that teachers should try to identify learners' conceptions in their classes in order to correctly assist them acquire scientific knowledge. It enlightens teachers on the difficulties that their learners encounter and as a result, it therefore helps them improve on their teaching approach to the subject matter as well as other related topics. This provides invaluable information for the understanding of student learning difficulties, and insight into how they might be addressed. In general, it generates knowledge and helps improve the practice of teaching of these concepts in schools.

Mr. Wanyonyi is a Kenyan born in 1982. He holds B.Ed (Sci) from Moi University and MSc (Sci Ed) (Chemistry) from Masinde Muliro University of Science and Technology (MMUST). He is currently works as a Lecturer, Department of Pure and Applied Chemistry, MMUST. His current research interests include Natural Products Chemistry and Chemical Education.

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Chemical concepts in schools

Wanyonyi

Mark Wanyonyi

Understanding of Chemical Bonding in Secondary Schools in Kenya

Learning of structure and chemical bonding concepts in secondary schools

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MINUTES FOR PHD PROPOSAL DEFENCE HELD ON 12TH FEBRUARY 2015 IN SPD 314

Members present

1. Dr. Francis Orata
2. Prof. Maurice Omollo
3. Prof. Paul Tarus
4. Dr. Benard Juma
5. Dr. Danstone Barasa
6. Ms. Regina Bwire
7. Dr. Veronicah Okello
8. Ms. Selly Kimosop
9. Mr. Mark Wanyonyi
10. Mr. Gershom Mutua
11. Ms. Roselyne Ongulu
12. Dr. Selline Ooko
13. Ms. Emily Ngeno
14. Mr. Ibrahim Sande
15. Dr. John Muoma
16. Mr. Anthony Sifuna
17. Dr. Dennis Ochieno
18. Mr. Peter Gudo

Min1/15: Preliminaries

The defense was called into order by the departmental postgraduate chair Ms. R. Ongulu at 10.30 am and opened with a word of prayer from Dr. B. Juma.

Min 2/15: Presentations/Defense

Min 2/15/1 Presentation by Mark Wanyonyi SCH/H/02/12

Topic: Chemical composition, antimicrobial and antioxidant properties of Meliponula stingless bee propolis.

1. Title: Antimosquito to be included

2. Abbreviations page should be included

3. In introduction the candidate should talk more about compounds and the composition of propolis

4. Statement of the problem should be reframed to include the word 'compound'

5. Specific objectives should be reduced to 4 as well as the hypotheses

Literature review

6. Some information about propolis should be added as well as on antioxidant activities.

7. Novelty of the work should come out clearly.

8. Isolated compounds from propolis and their quantities from different areas should be included in the proposal

Methodology

10. "To be send to icipe" to be removed

11. Schematic diagrams can describe the methodology better in presentation

12. "If necessary' be removed after x-ray crystallography

13. In references, one format should be adopted.

Work plan

14. Calendar months should be included

Budget

15. Travelled to collection of samples (10,000) should be amended.

16. Additional comments are in the reviewed proposal

General comments

The proposal was good and well presented with advancement of natural products chemistry

Reviewers' comments should be given to candidates before the presentation of proposals

Min 2/15/2 Presentation by Selly Kimosop SCH/H/01/13

Topic: Mass flow of pharmaceuticals in Lake Victoria Basin, Kenya. "Their phytoremediation and sorption kinetics using nanoparticle- impregnated adsorbents."

1. Topic- to be amended into one statement

2. Abstract- should be narrowed down

3. The study area should be specific. Nzoia River Drainage Basin/ Lake Victoria Basin

4. Applicability/ importance of the work should come out clearly

5. General comments; several long sentences were noted. The candidate was advised to correct them.

6. There should be differentiation between problem statement and justification

7. Literature review: the student to include information on the presence and problems caused by pharmaceutical and personal care products in Kenya.

8. It was noted that the student was using contaminants and pollutants interchangeable which may not be correct.

9. The status of the sampling areas should looked at: towns/ municipalities/ cities

10. It was observed that analytical methods were shallow

11. General suggestions: Organic chemists should be included in future studies

12. The candidate should explain why sampling in different areas was done. The sampling areas should be enhanced or the title changed to NRDB.

14. The third objectives should be amended

15. Additional comments are in the reviewed proposal

Adjournment

The meeting was closed with a word of prayer from Prof. Omollo and adjourned at 2.30 pm.

Ag. DGSC Chair

Signature.....