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SUFFERING OCEANS OF ABUSE: A MARINE TOXICOLOGIST'S ASSESSMENT OF CHANGE

AN INAUGURAL LECTURE

By

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Dedication

TO THE MEMORY OF MY LATE PARENTS

ORD. RANSOME A. DAKA

AND

MRS LADY R. DAKA

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I would like to appreciate God for my late parents Ord. Ransome A. Daka and Mrs Lady R. Daka who ensured that all their children attained enviable academic heights. Ma would have danced and danced on a day like this. To all my brothers and sisters (Tamunoigbeinbia, Osesiyechinma, Owutamunopiri, Tamunonengiyeofori, Asigo, Otonye, Iyaeneomi, Ibinabo and Miebaka), I say, thanks for being there for me. Thanks also to Dr Graham Kalio, Elder E. Amabipi, Sir E.D. Kalio and Sir I Amabipi.

To my wife Blessing and children, Emediong and Ibifuaba, I say thank you so much for keeping the home front adorable and supportive.

My special gratitude goes to my spiritual father, Pastor David Ibiyeomie, the presiding pastor of Salvation Ministries. I thank God for directing me to his ministry as my place of spiritual nourishment and growth. Thank you for the great privilege to serve as a part-time pastor in Salvation Ministries.

I started by acknowledging the almighty God as the source of my promotion and success. The Lord is my light and my salvation. He has done all things well and to Him I give all the glory. Please join me to sing the following hymn to glorify Him:

To God be the glory, great things He hath done,
So loved He the world that He gave us His Son,
Who yielded His life our redemption to win,
And opened the life-gate that all may go in.

Praise the Lord, praise the Lord,
Let the earth hear His voice;
Praise the Lord, praise the Lord,
Let the people rejoice;
Oh, come to the Father, through Jesus the Son,
And give Him the glory; great things He hath done.

THANK YOU FOR LISTENING AND GOD BLESS YOU.

PROTOCOL

The Vice-Chancellor

Deputy Vice-Chancellor

Registrar and other Principal Officers

Provost of College of Medicine; Dean of PG School and Deans of Faculties

Directors of Institutes and Heads of Departments

Distinguished Professors and Emeritus Scholars

Staff and Students of Rivers State University

Distinguished Ladies and Gentlemen

1.0 INTRODUCTION

But whatever I am now, it is all because God poured out His special favour on me and not without results(1 Corinthians 15:10 New Living Translation). I am deeply grateful to the almighty God for making this day a reality. I wish to also thank the Vice-Chancellor, Professor Blessing Didia and the Chairman, Senate Lectures Committee, Prof. I.K.E. Ekweozor for providing the platform for this inaugural lecture, the 61st in this University and 1st in the Department of Animal and Environmental Biology.

Mr Vice-Chancellor, Sir, My academic career took a defined trajectory when in 1984, Prof Kumar,Head of the then Department of Biological Sciences of this University directed me to take my final year research topic from Dr Richard Snowden, the coordinator of the Marine Biology

Programme. I chose the topics'Oil Pollution in the Nigerian Marine and Estuarine Waters' and 'The Toxicity of Nigerian Crude Oil to the Mangrove Oyster Crassostrea gasar' for seminar and project respectively. My interest naturally gravitated towards Marine Biology and I carried out 'Studies on the Fouling Organisms of the upper Bonny Estuary' for a Master's degree in Marine Biology also from Rivers State University of Science and Technology under the supervision of Dr N.J. Abby-Kalio. My PhD work (in Marine Biology Ecotoxicology)was supervised by Prof. S.J. Hawkins at the University of Liverpool (now an Emeritus Professor of the University of Southampton and a Lankester Research Fellow at the Marine Biological Association, United Kingdom) on Population Differences in the Toxic Effects of heavy metals to Littorina saxatilis in the Isle of Man. I rose through the ranks from graduate Assistant in 1986 to Professor of Marine Toxicology in 2013

Aquatic toxicology is the study of the effects of manufactured chemicals and other anthropogenic and natural materials and activities on aquatic organisms at various levels of organization, from subcellular through individual organisms to communities and ecosystems(Rand and Petrocelli, (1985). It is a multidisciplinary field which integrates toxicology, aquatic ecology and aquatic chemistry. The topic of this lecture was adapted from a quote by Mark Hertsgaard (2007): 'Suffering oceans of abuse / We can't kill all sea life, but we're steadily' poisoning it’

The ocean is vast, covering 140 million square miles, some 72 per cent of the earth's surface. Not only has the oceans always been a prime source of nourishment for life, but from earliest recorded history it has served for trade and commerce, adventure and discovery. It has kept people apart and brought them together. Even now, when the continents have been mapped and their interiors made accessible by road, river and air, most of the world's people live no more than 200 miles from the sea and relate closely to it. For centuries it was

I have benefitted from the counsel and support of a number of other academics: Prof. I.K.E Ekweozor has made tremendous contribution to my academic growth. I also appreciate Professors J. Ajienka (former VC of Uniport), S.D. Abbey, E.N. Amadi, S.A. Braide (Late), G. K. Fekarurhobo, T.K.S. Abam, S.C. Teme, Eunice Nwachukwu (Uniport), ER Akpan (Unical), A.E. Ogbeibu (Uniben), E.T. Jaja, C. Israel-Cookey, F. B. Sigalo, N. Ukoima, C.K. Wachukwu, E. Chukwu, N. Ukoinma, U. U. Gabriel, D.N. Ogbonna, B. Nwauzoma, B. Green, C. Obunwo, A.E.Gobo, N. Ngah, P. Ede, T.J.K Ideriah, I Jack, S. Orupabo, J. Isodiki, K. Akaninwor, R. Amaewhule, C.O Ahiakwo and M.J. Ahiakwo.

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As a 'student of destiny', I owe a debt of gratitude to the entire Departmental Board of Biological Sciences in my undergraduate days. The department led by the then HOD, Prof Kumar made a case for my conversion, straight from University Diploma for which I was admitted into the third year BSc programme after the second year in UD. I therefore graduated with a DIP matric number (instead of DE), perhaps the first and only student to have had such a privilege in this University. Prof Kumar also gave me the inspired advice to take Zoology option and a project in Marine Biology in my final undergraduate year, which set a clear career path for me. I am grateful to Dr R. J. Snowden and Dr N.J. Abby-Kalio who supervised my BSc and MPhil projects respectively, and gave me a sound background in research. Prof SJ Hawkins (Steve as his students call him) was my quintessential PhD supervisor; even after my graduation at the University of Liverpool, he sponsored me on a one-month trip to Southampton in 1999 to sharpen my skills in scientific writing and publication. He also part-financed my attendance of the Aquatic Biodiversity and Ecosystems conference in Liverpool in 2015.

thought that the oceans were so vast that nothing people could do could possibly have an impact on it. It was on this premise that the ocean has suffered abuse from anthropogenic activities. These may be pollution activities at sea (such as shipping, fishing, and oil or gas offshore production) or land-based pollution (waste, sewage water, coastal development activities, and inland activities). According to World Ocean Network (2019), 80% of marine pollution comes from land-based sources. In many developing countries, 90% of wastewater and 70% of industrial waste is discharged without treatment; More than 100,000 chemicals are produced commercially and they represent a threat for oceans through accidents or transport; they can also be emitted in the atmosphere, soil or water and reach the ocean.

In the context of this lecture, the ocean covers not only the marine environment, but estuaries (which are areas where seawater is diluted with freshwater coming from rivers and streams). Much of the pollution is concentrated in these shallow coastal areas, which are often next to urban centres and other concentrations of humans who are responsible for the pollution. Our studies have mostly focussed on coastal areas and estuaries.

2.0 CONCEPTS

Definition of Marine Pollution

According to the Group of Experts on the Scientific Aspects of Marine Environmental Protection- GESAMP (1991), marine pollution is the introduction by man, directly or indirectly, of substances or energy to the marine environment (including estuaries) resulting in deleterious effects such as hazards to human health, hindrance of marine activities, including fishing; impairment of water quality for the use of seawater and the reduction of amenities.

Measuring Change

Clark (1998) has an elaborate discussion of the ways to measure change arising from marine pollution and the presentation in this section was largely from that source. Any material discharged into the sea inevitably causes some change in the environment. The change may be great or small, long-lasting or transient, widespread or localized. If the change can be detected and is regarded as damaging, it constitutes pollution. Much effort is devoted to measuring the levels of contamination of sediments and organisms by chemical analysis, but to determine if the observed level of contamination causes pollution generally requires a study of its biological effects. These effects may be detected at the level of the individual, or by changes in the population or the community, and a variety of techniques are available to identify and measure the responses.

Impact on the individual

Individual organisms may suffer some form of impairment or damage as a result of exposure to a pollutant. In extreme cases it results in death.

Measurement of toxicity

Paracelsus (Father of Modern Toxicology): "All things are poisons, for there is nothing without poisonous qualities. It is only the dose which makes a thing poison."

Conclusion AND Recommendations

Pollution of the marine environment remains a serious global concern and the oceans continue to suffer abuse from human activities. Monitoring of heavy metals with biological organisms require understanding of responses by local species and history of contamination. Consumption of fish and crab contaminated by heavy metals and PAH pose some risks to human in heavily industrialized and urbanized areas in the Niger Delta. Continuous monitoring of the environment is recommended and modern equipment are required. Fortunately, our forward-looking Vice-Chancellor has placed an order for an Atomic Absorption Spectrophotometer AAS (which should arrive in the next couple of weeks!). The AAS package includes a Hydride Generator and Cold-Vapour Unit to handle a wide range of metals at high sensitivity levels. We hereby call on multinationals and other corporate organizations to support research with the provision of modern equipmentand funds. Plastic pollution is an issue of grave concern and requires institutional intervention in the Nigerian context, as well as behavioural change.There is need for studies of microplastics in the Nigerian coastal and marine environment. It is our responsibility to stem the tide of abuse to end the suffering of the oceans, so that we can bequeath a sustainable environment to future generations.

Table 18: Quantification of different waste types based on the DAFOR (dominant, abundant, frequent, occasional, rare) scale at the different locations

Waste type	Locations				
	Nweja Creek	Ntawogba	Amadi	Azuabie	Miniokoro
Plastic cans/bottles	D	D	D	D	D
Pure water sachet	D	D	D	D	D
Cork/food raps	A	A	A	A	A
Poly-ethylene bags	D	D	D	D	D
Bottles/Glass wares	F	F	F	F	F
Foam	R	R	O	O	O
Tyres	O	O	O	O	O
Paper cardboard	F	F	F	F	F
Textiles	F	F	F	F	F
Batteries	O	O	R	R	O
Bones	R	R	R	F	R
Ferrous metal	F	F	F	F	F
Leather	O	O	O	O	O
Ceramics	O	O	R	O	O
Electronic wastes	O	O	R	R	O
Sac bags	O	O	F	F	O
Baby pampers	F	F	F	F	F

The application of efficient, cost effective and practical methods such as the modified drag net technique, scoop net technique, debris barriers and direct picking techniques are effective solutions that will tremendously clean up our creeks and river systems.The simplest, yet highly effective, action is the manual cleanup of the beaches, coasts, rivers, lands and estuaries. Nationaland international manual clean-up operations of shorelines are in existence. For example, the Japan Environmental Action Network (JEAN) has been organizing a yearly beach clean-up and survey for about 20 years; the Marine Conservation Society of the United Kingdom has organized annual beach cleanup/ survey since 1994.The International Coastal Cleanup (ICC) engages the public to remove trash and debris from the world's beaches and waterways, to identify the sources of debris, and to change the behaviors that cause pollution.

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A toxic substance is one that harms living things at low concentrations. Toxic effects have been studied primarily in laboratory experiments (bioassays). Early studies of pollutant effects relied on tests that measured lethality (death). The LC50 the concentration of chemical that caused 50% of the test animals to die (typically in 96 hours) was the benchmark. It may also be expressed as LT50 the time taken to kill 50% of the test animals in a given concentration. Even today acute toxicity bioassays are still considered amongst the most useful in a regulatory context. For instance, acute toxicity bioassays (toxicity testing) are required for the specific operations by the guideline and standards of the Department of Petroleum Resources (DPR, 2002).

Synergism and Antagonism

In the natural environment, toxins are rarely present in isolation and they may interact with other substances. The combined effect of several toxins may be additive (the addition of one mortality to another), synergetic (one increases the mortality caused by the other) or antagonistic (one reduces the mortality caused by the other).

Sublethal effects

It is often possible to detect responses in organisms to toxins at far lower concentrations than those that kill them. Sublethal responses vary widely but may include major physiological stress, tumours, or developmental abnormalities that could likely result to early death.

Population change

From the biological point of view, when pollution causes death, what matters is not the initial mortality, but the numbers and fate of the survivors. Mortality that results in a prolonged reduction in the population of a species is obviously regarded more seriously than a loss that is rapidly made good. Population changes in particular species, of course, have some impact on the community of which they are part, and the pollution impact may be measured at the level of population or communities. Population change may be assessed on the basis of key species, for instance, indicator species known to be particularly resistant or particularly sensitive to pollutants. The presence or absence of these indicators may provide a warning signal in the existence of pollution effects. The abundance of a species is measured by population density or biomass. Whatever parameter is measured, it is necessary to demonstrate that a change is related to pollution by comparison with controls. This may be by comparing the population density at the same site before and after introduction of a supposed pollutant or by using a comparable but unaffected area as a control site.

Community response

A more realistic approach than the study of the fate of selected species is to examine the response of the whole community; that is, the whole assemblage of species in an area. This is now the most popular approach in pollution impact studies. Generally, community studies involve taking samples of organisms from polluted and control sites, identifying and enumerating the species and then analysing the resulting data to determine if significant changes have occurred. The data may be analysed by univariate or multivariate methods.

Univariate analysis

A single numerical index is calculated to characterize the community. Generally, indices are calculated for each replicate sample, allowing statistical comparison of means between polluted and control sites. These indices are usually an expression of diversity, which may simply be the number of species present per unit area (species richness) or a much more complex quantity such as Shannon-Weiner diversity index. Some univariate indicessuch as Margalef richness index (d),

Figure 31: Solid wastes gradually taking over the creeks (Amadi-Nwaja creek by NLNG).

Fig. 32: Floating wastes obstructing fishing activities along the Amadi – Marine Base Axis

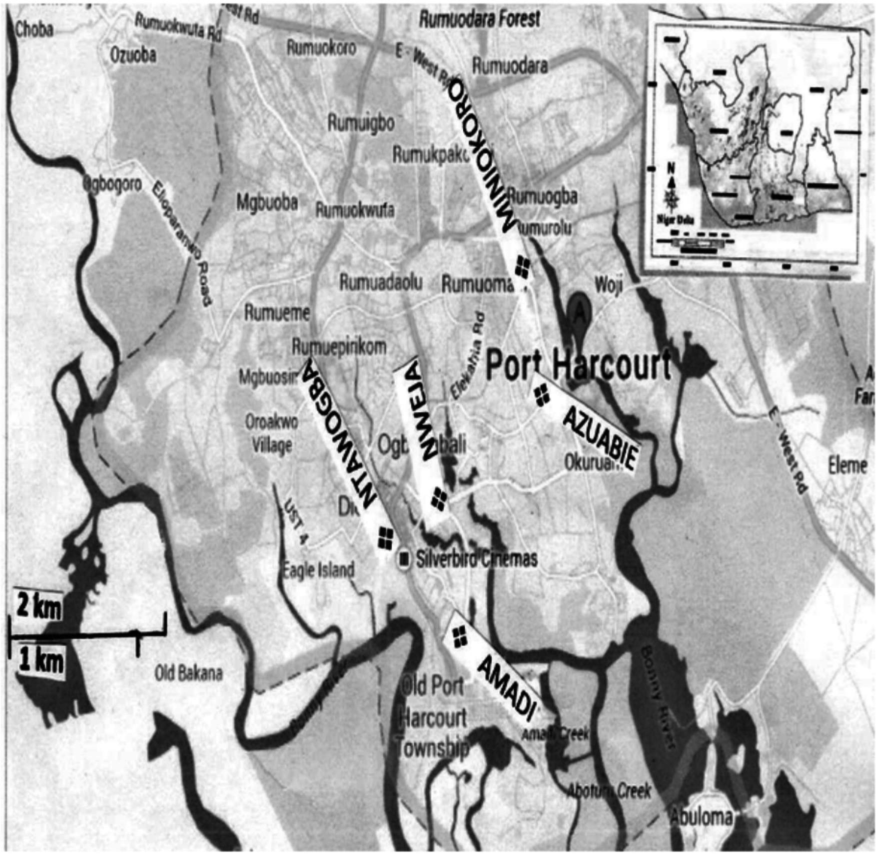

Figure 30:. Map showing the study area

The results show visual effects of the heavy presence of different types of solid wastes in the creeks and rivers (Figs. 31 and 32). The spatial distribution of the types of wastes at the different creeks/sites show minimal variation (Table 18); minor differences could be accounted for by specific activities in The respective sites such as welding, mechanic workshops and abattoir activities as well as petty trading. The most dominant Types of wastes were plastic wastes.

Pielou evenness index (J), Shannon Wiener diversity index (H') and Simpson's dominance index (l) are calculated as follows.

$H' = - \sum Pi \times (\log(Pi)),$

$J = H' / \log Si$

$d = (S-1) \log N$

$\lambda = \sum (Pi)^2$

Where N = Abundance, S = number of species, Pi = the proportion of abundance (n) species from total abundance (N).

Multivariate analysis

Univariate techniques keep the species separate but their identity is not important, so two sites with totally different species present could theoretically produce identical diversity indices, if the patterns of abundance in the two communities were similar. Important information on the actual species comprising the community is retained by multivariate statistical techniques. The aim of multivariate analysis is to determine how closely related the sites are in their species composition in order to detect any divergence from control community structure. Three methods are in common use. Cluster analysis uses similarities between samples and groups of samples to build a dendrogram (Fig. 1). Samples with similar structures (distribution of individuals between species) are linked in pairs and plotted on a scale which reflects the similarity between the members of a pair. The pairs are then linked in second-order pairs and so on. The subsequent levels of pairing reflect the similarity between groups less and less accurately.

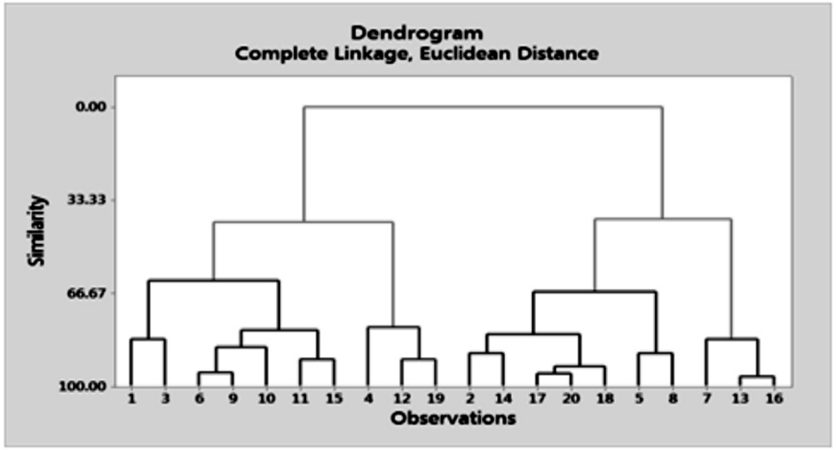

Figure 1: Dendrogram (Source: MINITAB)

Multidimensional scaling (MDS) starts from the calculation of similarities between samples but unlike a dendrogram does not proceed beyond the first level of comparison between them. In order to represent the relationship between all samples, it plots them so that the rank order of the similarities between pairs of samples matches the rank order distance between that pair of samples in the plot. The plot may be produced on two or threedimensions, but as the rank distances are used, the axes have no units (Fig. 2). These 'maps' provide valuable and easily interpreted information on environmental change. ***Principal component analysis*** (PCA) also produces two- or three-dimensional plots. The axes of the plot are defined in such a way that the Principal Component 1 represents as much as possible the variation in the data set. Principal Component 2 is then computed to explain as much as possible the residual variation in the data (that is, variation not explained in Principal Component 1). There are problems in the use of PCA on data points containing many zero values, which is typical of biological data, but it is very powerful when applied to environmental data.

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hazard for consumers. It should be noted that the use of tyre for roasting animal skim has been banned by the Rivers State government since 2012. A study of the amelioration over time is recommended.

Plastic Pollution in the Marine Environment

Mr. Vice-Chancellor, Sir, plastic pollution is a serious global concern and formed the theme of the World Environment Day 2018: 'Beat Plastic Pollution'. In his message for World Environment Day 5 June 2018, the UN Secretary-General, António Guterres, stated amongst others as follows: 'Our world is swamped by harmful plastic waste. Every year, more than 8 million tons end up in the oceans. Microplastics in the seas now outnumber stars in our galaxy from remote islands to the Artic, nowhere is untouched. If present trends continue, by 2050, our oceans will have more plastic than fish'.

It has been estimated that approximately 1 million sea birds die per annum from ingesting plastic, 100,000 mammals die each year from ingesting plastic bags. Over 50% of sea turtles found dead are known to have ingested plastic marine debris or entanglement.

The menace of solid wastes in some creeks and river systems around Port Harcourt: The way forward (Moslen *et al.*, 2015)

Mr Vice -Chancellor, Sir, we assessed the problem of aquatic pollution by solid wastes in rivers and creeks around Port Harcourt metropolis. The study areacovered the Ntawogba, Nweja, Amadi and Azuabie creeks (Fig. 30). Field visits were undertaken (at both flood tide and ebb tides) for physical observations, evaluation and assessments in order to determine the following: class/types of wastes found in the creeks, the dominant waste class, the various discharge points and the extent (stretch) of pollution in the study area.

soot particles of tyre burning which enter the Azuabie creek during periods of elevated surface run-offs (rainy season). The heterogeneity in the BSAF of PAHs has been attributed to variations in the content of soot particles which enter the aquatic system during periods of elevated surface run-offs and which tend to accumulate preferentially with other fine materials in the high inter tidal zone (Capuzzo, 1987). However, all samples in this study were however collected subtidal. PAHs have been reported to bioaccumulate differentially in benthic invertebrates (Maruya et al., 1997), varying over almost three orders of magnitude. Maruya et al., (1997) also reported that biota-sediment accumulation factor (BSAF) of PAHs varied with season and along an intertidal gradient in a costal marsh in San Francisco Bay.

PAHs can enter the human body by many different ways. People near hazardous sites can breathe air containing PAHs. Drinking water and swallowing food is another route. Though absorption is slow; they can enter the body if the skin comes in contact with soil that contains a high level of PAH (ATSDR, 1995). The rate of entry of PAH into the body also depends on the presence of other compounds that one is exposed to at the same time. PAHs enter all the tissues of the body that contain fat and can be changed into various substances which could be harmful. Mice fed high levels of benzo (a) pyrene during pregnancy had difficulty reproducing and so did their offspring (ATSDR, 1995). A meal of C. pallidus from the Azuabie could introduce high levels of PAH (especially during the wet season), however, the human body eliminates PAHs through urine and faeces (ATSDR, 1995).

In conclusion, the highest values of PAH was found in sediments and the tissues of Calllinectes pallidus from Station A which receives run-off of tyre burning effluent. Significantly higher values in the rainy season also confirm the run-off as the major source of PAH in the estuarine creek. The major classes of PAHs found in the sediments and crab were naphthalene, benzo(a)pyrene, benzo(a)anthracene and phenanthrene, which are potential carcinogens, thus crabs and indeed other fish products from the estuary may constitute a potential health

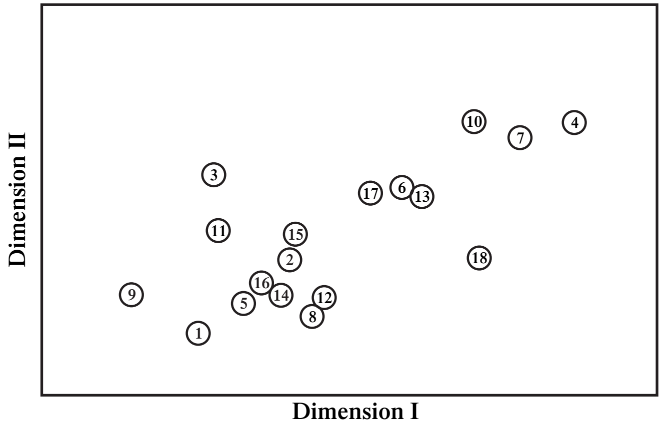

Figure 2: Multidimensional scaling (MDS) Ordination (Source: Anon, 2019)

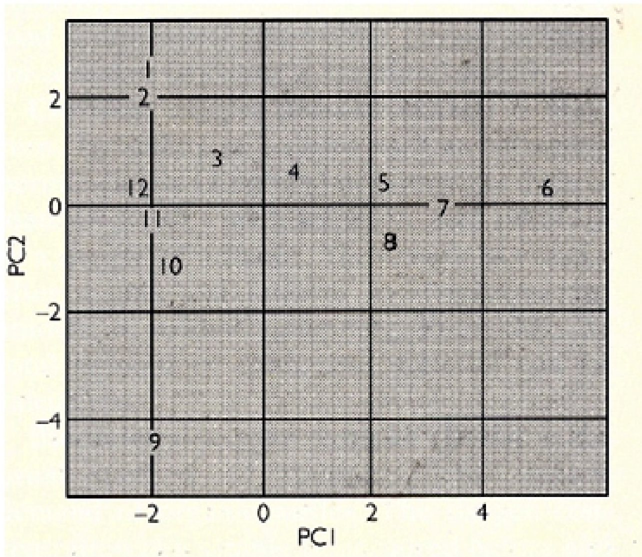

Figure 3: Principal Component Analysis (PCA) of environmental variables at twelve stations across a sewage sludge dump site (Source: Clark, 1998))

3.0 STUDIES ON HEAVY METALS

The term "heavy metal" (used synonymously with "trace metal") refers to most metals and metalloids with the exception of the alkali, alkaline earths, lanthanides and actinides (Förstner& Wittman, 1979). Unlike most other contaminants, they are natural constituents of sea water derived from geochemical and volcanic processes. Rivers are a major contributor of heavy metals to the sea, the nature of input depending on the occurrence of metal and ore bearing deposits in the drainage area (Watling & Emmerson, 1981; Clark, 1992). The sources of anthropogenic input of heavy metals into the aquatic environment include industrial processes (Buckley et al., 1995; Chen & Wu, 1995; Shear et al., 1996), sewage sludge (Blomqvist et al., 1992; Birch & Davey, 1995), power stations (Philips & Unni, 1991) and mining (Davies, 1987; Porvari, 1995). The mining of heavy metals by man is increasing the mobilization of most elements over that achieved by natural geological weathering. Metals such as zinc and copper are being mined and mobilized at rates over ten times those expected from simple geological processes of weathering (Phillips, 1980). Even when mining has stopped, drainage water from spoil heaps is a continuous source of contamination (Bryan & Gibbs, 1983; Southgate et al. 1983; Hunt & Howard, 1994).

A lot of industries discharge one trace metal or the other into water or soil (Nriagu & Pacyna, 1988). Examples of industrial processes which utilize selected heavy metals are given in Table 1. Rivers and freshwater run-off constitute a major route of entry of metals into estuaries and the sea (Bryan, 1976). The atmosphere is also an important route of entry of heavy metals into estuaries and the sea (Vale & Harrison, 1994).

Table 17: Spatial and seasonal differences in the classes of PAH in sediment and tissues (carapace and flesh) of *Callinectes pallidus* of Azuabie Creek

PAH	Station A			Station B			Station C		
	Sed	Cara	Flesh	Sed	Cara	Flesh	Sed	Cara	Flesh
				Wet Season					
Phenanthrene	0.24	0.075	0.245	0.04	0.05	0.105	0.05	0	0.025
Benzo(a)anthracene	1.04	0.125	0.435	0.22	0.08	0.31	0.1	0	0.055
Benzo(a)pyrene	0.72	0.04	0.295	0.225	0.025	0.105	0.02	0	0.005
Naphthalene	0.185	0.025	0.145	0.035	0.03	0.08	0.01	0	0.015
Fluoranthrene	0.02	0	0.055	0	0	0.015	0	0	0
Fluorene	0.015	0	0	0	0	0	0	0	0
Total	2.22	0.28	1.175	0.52	0.185	0.605	0.18	0	0.1
				Dry Season					
Phenanthrene	0.08	0.01	0.08	0.0011	0.0045	0.082	0.006	0.001	0.001
Benzo(a)anthracene	0	0.001	0.014	0	0.002	0.0101	0	0	0
Benzo(a)pyrene	0.0022	0.0003	0.0022	0.00005	0.0015	0.0022	0.003	0	0.001
Naphthalene	0.00055	0.00007	0.00055	0.0002	0	0.00052	0	0	0
Fluoranthrene	0.00285	0		0	0	0	0	0	0
Fluorene	0.014	0		0	0	0	0	0	0
Anthracene	0.00714			0.0001			0		
Total	0.048	0.012	0.03	0.0015	0.008	0.026	0.009	0.001	0.002

Polynuclear aromatic hydrocarbon concentrations were significantly higher during the rainy season in all compartments (sediment; flesh and carapace of Callinectes sapidus). The higher wet season values show that run-off from the ash of tyres used for smoking animals slaughtered at the abattoir was the main source of PAH. More so, PAHs in this study were highest at station A which receives the run-off from tyre ash. The consistency in the reduction for all matrices suggests a flux within the estuary tending towards attenuation during the dry season. Sediments were expected to act as sink that could have led to accumulation over time; however, frequent dredging in the area may have precluded the build-up in sediment. PAHs are formed by incomplete combustion of carbon containing fuels likes diesel, fat, tobacco and tyres. The predominant PAHs found in this study were Benzo (a) pyrene, Benzo (a) anthracene, naphthalene and Phenanthrene. They are known for their carcinogenic, mutagenic and teratogenic properties. Variations in concentration of PAHs can be attributed to variations in the content of

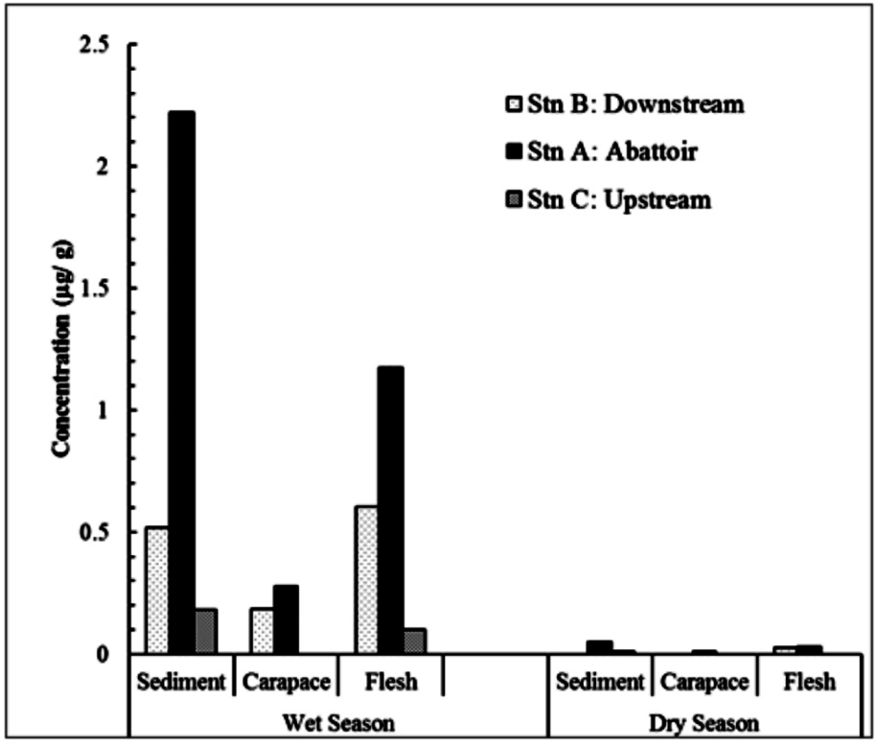

Figure: 29: Spatial and seasonal differences in the concentrations of PAH in sediment and tissues (carapace and flesh) of *Callinectes pallidus*of Azuabie Creek.

Table 1: Some industrial uses of selected heavy metals

Metal	INDUSTRIAL USE
Lead	Storage batteries, metal product, pigments, auto and boat fuel, ammunition.
zinc	Galvanizing iron and steel products and alloys
Copper	Electrical, automotive, construction, plumbing, antifouling paints
Cadmium	Electroplating, pigments in plastic industry, ceramics, paint coating, photography.
Mercury	Insecticides, fungicides, herbicides, bactericides, pharmaceuticals, manufacture of chlorine, electronics
Arsenic	Plant desiccants, poultry and food additives, pharmaceutical and detergents
Nickel	Numerous uses as an alloy in combination with Fe and C (nickel-steel, plantenite)
Silver	Electroplating, food and beverage processing
Chromium	Metal plating, industrial dyes, ink.
Selenium	Smelting of copper
Tin	Antifouling paints

Source: Compiled from Forstner and Wittman, 1979; Moore and Romamoorthy, 1984.

A distinction is usually made between essential and non-essential heavy metals on the basis of known biological functions. Essential elements include zinc (Zn), copper (Cu), iron (Fe), molybdenum (Mo), manganese (Mn), chromium (Cr), cobalt (Co), vanadium (V), selenium (Se), nickel (Ni) and tin (Sn). These elements are vital components of enzymes and respiratory pigments (White & Rainbow, 1985). For example, haemoglobin contains Fe; Haemocyanin contains Cu; carbonic anhydrase, carboxypeptidase A and B and several dehydrogenases contain Zn; Pyruvate carboxylase contains Mn; vitamin B12 enzymes contain Co; xanthine oxidase contains Fe and Mo; and cytochrome oxidase contains Fe and Cu. Other metals such as mercury (Hg), cadmium (Cd) and silver (Ag) have no known biological function (Bryan, 1984). Whether essential or not, heavy metals exert an adverse effect on organisms when present in the environment in elevated concentrations. The balance between requirement and toxicity of metals is delicate and depends on a variety of abiotic and biotic factors (White & Rainbow, 1985).

3.1 Heavy metals in sediment and biomonitors in the Isle of Man (Daka et al. 2003; Daka, 2005)

The Isle of Man has a long history of mining (Garrod et al., 1972) leading to localized heavy metal pollution from abandoned mines. The distribution of mineral veins and mines (see Figure 4) suggests that zinc, lead, copper and iron are present in small amounts throughout the Manx slate series but the two main groups of mines were at Laxey (zinc) and Foxdale (lead). The freshwater input to the estuaries at Laxey and Peel comes from rivers draining the main former mining areas of Laxey and Foxdale respectively. These provide a convenient system for a variety of studies in which closely adjacent contaminated and uncontaminated catchments and estuaries can be compared. This study was a precursor to a detailed examination of tolerance to metal exposure in Littorina saxatilis from contaminated and uncontaminated areas. It was necessary first to characterize the various sites, which also enabled comparisons with previous studies (Southgate et al., 1983) to show if contamination has reduced with time since the closure of the mines (last worked in the 1930s). Both sediments and bioindicators or biomonitors (Mytilus edulis and Fucus serratus, Littorina saxatilis and Enteromorpha intesinalis) were analysed (Luoma, 1983; Bryan et al., 1985; Bryan and Langston, 1992; Phillips and Rainbow, 1993) as they provide distinct measures of time-integrated levels of contamination and bioavailability. The study emphasised estuaries and included a broad coverage of the whole island (cf. Gibb et al., 1996). Five sites were characterized for heavy metals: four estuaries (Castletown, Laxey, Peel and Ramsey) and a coastal

The results showed that the concentrations of PAH were higher in sediment than crab tissues, with values in the flesh being higher than the levels in carapace (Fig. 28). The overall mean concentrations were: sediment (0.973 ± 0.631 mg/g wet season, 0.020 ± 0.014 mg/g dry season), flesh (0.627 ± 0.311 mg/g wet season, 0.019 ± 0.008 mg/g dry season), carapace (0.155 ± 0.082 mg/g wet season, 0.007 ± 0.003 mg/g dry season). There was significant difference in the PAH values between the seasons ($p = 0.01$), but no significant difference was observable between sediment and the crab tissues, neither was there any significant interaction between environmental matrix and season.

PAH levels in sediment were higher at station A, followed by station B with the least being station C in both rainy and dry seasons (Fig. 28). Mean concentrations ranged from 0.18 at Station C to 2.22 at Station A (wet season) and 0.002 to 0.048 (dry season). Values were significantly higher during the rainy season ($p < 0.01$). There were significant differences between sampling stations ($p < 0.001$) and pair-wise comparisons showed significant differences between means in the order: Station A > Station B > Station C (Table 17). Similarly, the highest values of PAH in crab tissues (flesh and carapace) followed the order Station A > Station B > Station C (Fig. 29) with much higher values during the wet season (the only exception was the putatively higher dry season values carapace as wet season was <0.001 mg/g). The mean values ranged overall from <0.001 mg/g (below detectable limit) to 0.280 mg/g in carapace and 0.001 mg/g to 1.175 mg/g in flesh. ANOVA showed significant differences between stations for both carapace ($p < 0.01$) and flesh ($p < 0.001$). Tukey test multiple comparisons for mean PAH in carapace showed significance where Station A = Station B > Station C, while the pattern for flesh was Station A > Station B > Station C.

The PAH classes found in the samples include Phenanthrene, Benzo(a)anthracene, Benzo(a)pyrene, Naphthalene, Fluoranthrene, Fluorene, Anthracene (Table 17). All classes were found in sediment and crab tissues but anthracene was detected only the in sediment during the dry season.

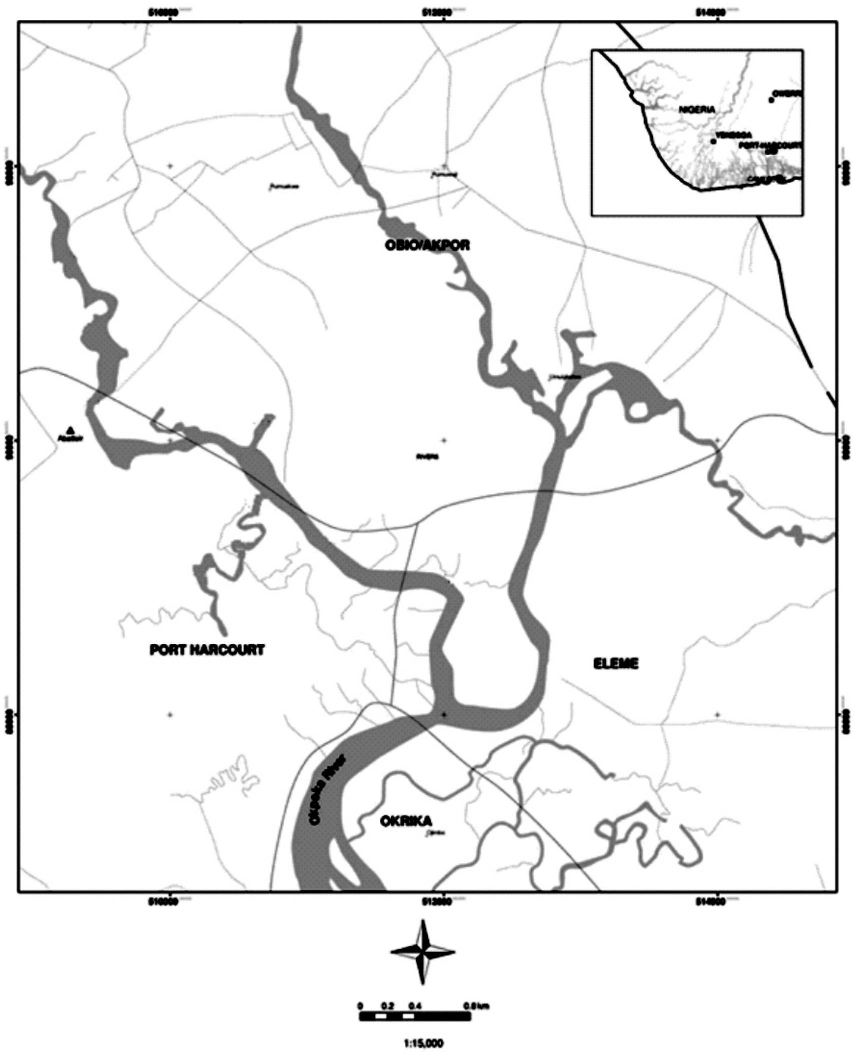

Figure 28: Azuabie Creek showing locations of sampling stations.
Inset – The Niger Delta showing location of the creek.

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site at the Castletown Bay end of Langness near Derbyhaven (Fig. 4). Laxey and Peel Estuaries drain historical mining regions in the Isle of Man (Southgate et al., 1983) and the other three were considered relatively uncontaminated control sites.

Heavy metals were acid extracted from the sediment (using a mixture of 4:1 nitric:hydrochloric acids, analaR grade, BDH) and three replicates of estuarine sediment reference material (European Communities Bureau of Reference - BCR ref. material 227), and blanks were included. Analysis was performed on a Pye Unicam SP9 atomic absorption spectrophotometer in the air-acetylene flame mode, calibrated with standards of known concentrations. The extracts, reference material and blanks were analysed for Zn, Pb, Cu, Cd and Fe. The tissues of seaweed, mussels and winkles were oven-dried to constant weight at 105oC before grinding and the use of 0.5 (0.001) g of ground tissue for digestion in analaR grade nitric acid according to Harper et al. (1989). Blanks and reference materials of Ulva lactuca (European Communities Bureau of Reference - BCR ref. material 279) and Mytilus edulis (European Communities Bureau of Reference - BCR ref. material 278) were included in the batches of seaweed and mollusc digests. Samples, reference materials and blanks were analysed for Zn, Pb, Cu and Cd. Metal concentrations were blank-corrected and the concentrations measured in the various reference materials were all within 10% of certified values.

It was observed that heavy metal levels in sediment and biomonitors from Laxey and Peel estuaries were higher than those from other sites (Table 2). This shows that elevated concentrations of heavy metals still existedin estuaries associated with previously heavily mined areas of the Isle of Man. This set the premise for further studies with Littorina saxatilis.

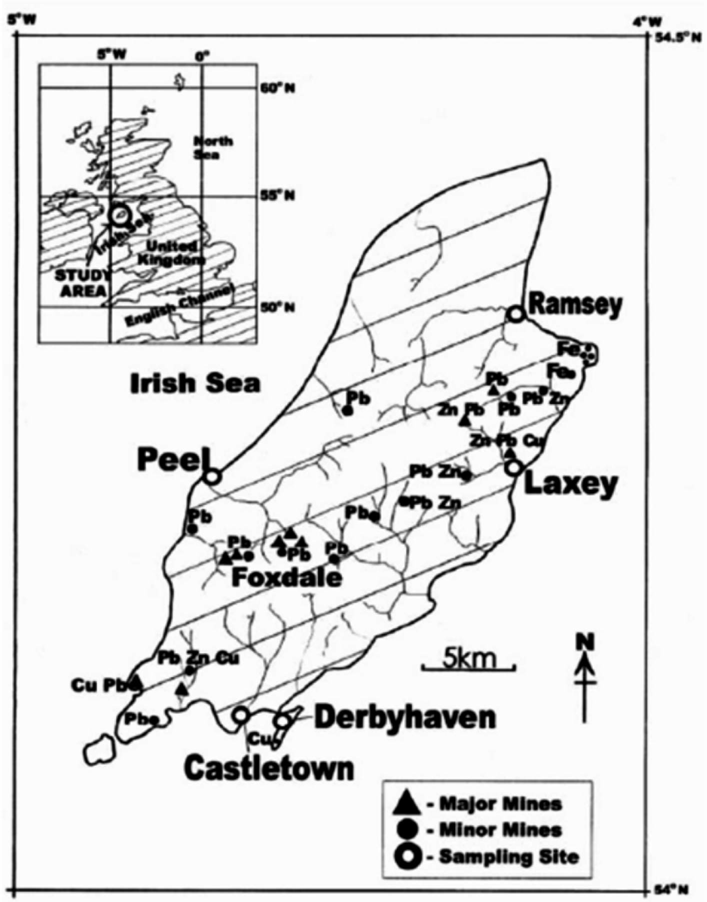

Figure 4: Locations of sampling sites (open circles) around the Isle of Man and past mining. Filled triangles and circles represent major and minor producing mines respectively with an indication of the order of importance of the ores produced (Cu, copper; Fe, iron; Pb, lead; Zn, zinc).

Inset: The British Isles showing the geographical location of the Isle of Man.

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Three stations were established (Fig. 28) as follows:

- ❖ Station A: Abattoir - Opposite abattoir representing point source of surface run-off from the tyre burning activity from the roasting of animal skins.
- ❖ Station B: Downstream - Ca. 1 km downstream of the abattoir
- ❖ Station C: Upstream - Ca. 1 km upstream of the abattoir

Samples of sediment and the swimming crab (Callinectes pallidus) were collected from each station during the wet season July, 2007; and dry season November, 2007. Sediment samples were air-dried, disaggregated and sieved. The crabs were dissected to separate the flesh (edible portion) from the carapace before the tissues were dried to constant weight in an oven and ground. 10 g of dry sediment or ground tissue samples were mixed with 60 ml of xylene in a Sohxlet apparatus. 4 ml of cyclohexane was further added to the mixture for extraction. The extracts were treated with Silica gel and Centrifuged before determination of PAH with Unicam PROGC gas chromatography. PAH was measured ng/µL and converted to mg/g.Two-way Analysis of Variance (ANOVA) was used to test for significant differences at between environmental matrices (sediment, tissues of Callinectes flesh/carapace). One-way ANOVA (and Tukey tests for mean separation where ANOVA gave significant differences) were performed to determine spatial differences for each environmental matrix as two-way ANOVA showed no significant interaction between season and location for sediment/tissue. Data were log (x+1) transformed before input into the ANOAVA model. Statistical analyses were performed using MINITAB software.

Polycyclic aromatic hydrocarbons in sediment and tissues of the crab *Callinectes pallidus* from the Azuabie creek of the upper Bonny estuary in the Niger Delta (Daka and Ugbomeh, 2013)

Polycyclic aromatic hydrocarbons (PAHs) are compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents (Fetzer, 2000). PAHs occur in oil, coal and tar deposits and are produced as a by-product of fuel burning. They are of concern as a pollutant because some of them are carcinogenic, mutagenic and teratogenic (causing malformation of an embryo). According to Luch (2005), the PAHs known for their carcinogenic, mutagenic and teratogenic properties are benz(a) anthracene and chrysene, benzo(b) fluoranthene, benzo (j) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, benzo(ghi) perylene, coronene, dibenz(a,h) anthracene (C2OH12), indenol (1,2,3-Cd) pyrene (C22H12) and ovalene. Their toxicity is structurally dependent, with isomers varying from being non-toxic to extremely toxic.

Burning tyres can have serious environmental impact as they produce vast amount of harmful emissions that will pollute the atmosphere and water courses through run-offs. Burning tyres can have a serious environmental impact and tyre fires are quite common in Nigeria. The use of tyres for roasting meat in abattoirs is also a common practice. This burning results in palls of black smoke that is visible from quite a distance. They produce vast quantities of harmful emissions that will pollute the atmosphere and water courses by input of potentially harmful compounds, including PAHs through run-offs.

Uptake of hydrocarbons, particularly PAHs compound by aquatic biota is very rapid and may accumulate to high tissue concentrations (Eisler, 1987, Varanasi et al., 1989). In this research, we reported the concentrations of PAHs in sediment and tissues of the edible crab Callinectes pallidus from Azuabie creek which receives run-off of effluents from tyre burning activities.

Table 2: Mean concentrations ± SE (n=5) of zinc, lead, copper and cadmium in sediment, *Mytilus edulis, Fucus serratus andLittorinasaxatilis* (n=10 except lead, n=5) from sites around the Isle of Man in June 1995. All values are in µg g^{-1} dry weight (sediment <500µm) tissue. *M. edulis and F. serratus* samples were collected from the mouths of the estuaries. Sediment values are for locations close to the area of collection of L. *saxatilis* for tolerance *studies;* N.B. different values (Daka*et al.*, 2003) were obtained at other points along the estuaries but the rank order was the same.

Metal	Castletown	Derbyhaven	Laxey	Peel	Ramsey
			Sediment		
Zinc	--	np	879 ±27	554 ±12	99 ±20
Lead	52 ±2	np	181 ±13	264 ±8	81 ±17
Copper	19 ±1	np	83 ±14	37 ±1	17 ±0
Cadmium	3 ±0	np	2 ±0	3 ±0	1 ±0
			Mytilus edulis		
Zinc	124 ±13*	np	257 ±25	339 ±71	99 ±10
Lead	Nd*	np	79 ±4	309 ±54	16 ±2
Copper	10 ±1.6*	np	13 ±2	9 ±1	10 ±1
Cadmium	Nd*	np	3 ±0	3 ±0	2 ±0
			Fucus serratus		
Zinc	80 ±7	76 ±7	2333 ±219	628 ±118	120 ±10
Lead	6 ±0	6 ±0	20 ±2	38 ±9	6 ±0
Copper	3 ±0	3 ±0	8 ±1	4 ±0	4 ±0
Cadmium	2 ±0	2 ±0	4 ±0	2 ±0	2 ±0
			Littorinasaxatilis		
Zinc	111.3 ±4.3	96.0 ±3.2	470.7 ±14.9	142.6 ±6.4	141.2 ±2.9
Lead	11.5 ±1.1	2.3 ±0.4	16.6 ±0.3	16.6 ±1.0	7.6 ±0.8
Copper	91.5 ±11.2	30.6 ±2.1	79.7 ±6.3	71.4 ±2.2	126.9 ±7.4
Cadmium	2.8 ±0.2	1.8 ±0.0	3.8 ±0.1	2.1 ±0.1	1.7 ±0.1

np, not present in sufficient quantities for analysis; * a very few mussels were found at the start of the study in Castletown and values for zinc and copper are given from preliminary work in April 1994; nd, reliable data were not collected for lead and copper during this pilot survey.

3.2 Studies on the gastropod mollusc *Littorinasaxatilis* in the Isle of Man

Tolerance to heavy metals (Daka and Hawkins, 2004)

Mr Vice-Chancellor, Sir, acute toxicity tests with aquatic organisms play a major part in the setting of regulatory standards for the emission of substances into the marine environment (Hunt & Anderson, 1993; Widdows, 1993). Factors affecting heavy metal toxicity include those influencing metal uptake and those affecting the ability of the organism to handle and detoxify accumulated trace metals (Rainbow et al., 1990). Regulatory limits for metals based upon toxicity data extrapolated from test species may be affected by such tolerance in a manner similar to pesticide resistance and renders the adoption of uniform standards for all situations difficult (Benjamin & Klaine, 1995).

The highest concentrations of zinc and cadmium were found in the animals from Laxey, but only zinc values were significantly higher across-the-board in the samples from Laxey in comparison with all other sites (ANOVA, Tukey tests, $p<0.01$). The concentration of lead in the animals from Peel and Laxey were also higher than those of the three other sites. The animals from Laxey represent a source of samples for contamination treatments (especially with respect to zinc) while individuals from other sites provide comparison with various degrees of contamination including essentially uncontaminated controls sites (see Table 2).It was therefore hypothesized that the metal may be present in concentrations capable of inducing tolerance to zinc in animals from Laxey Estuary in comparison with those from Peel, Castletown, and Ramsey Estuaries and from the open coast near Derbyhaven. Tolerance to zinc was tested by means of long duration acute toxicity tests with lead, copper and cadmium being similarly assessed to examine if co-tolerance to these metals exists.

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Table 16: Range, Mean (and Standard deviation) of cadmium and lead concentrations (mg/kg) concentrations (mg/kg) in fish species from the Azuabie creek, upper Bonny Estuary. F values and significance levels for single factor ANOVA for differences in metal concentrations between species.

Fish Species	Cadmium			Lead		
	Range (n=2)	Mean	SD	Range (n=2)	Mean	SD
Liza falcipinnis	0.045-0.055	0.050	0.007	0.083-0.125	0.104[b]	0.030
Sardinella madenensis	0.025-0.027	0.026	0.001	0.103-0.124	0.114[b]	0.015
Tilapia mariae	0.054-0.056	0.055	0.001	0.165-0.206	0.186[b]	0.029
Pomadasys jubelini	0.010-0.047	0.029	0.026	0.124-1.144	0.134[b]	0.014
Gobiusniger	0.045-0.052	0.049	0.005	0.227-0.268	0.248[a]	0.029
Cynoglossussp	0.010-0.012	0.011	0.001	0.144-0.206	0.175[b]	0.044
Chrysichtysesnigodigitatus	0.043-0.079	0.061	0.025	0.289-0.330	0.310[a]	0.029
FAO/WHO, 2011		**0.3**			**0.3**	
ANOVA	$F_{6,7} = 3.36$, $p=0.069$			$F_{6,7} = 13.36$, $p=0.002$		

The safe limits for heavy metals in seafood vary from region to region (Ashraf, 2006). The concentrations of cadmium and lead found in the fish from the upper Bonny estuary were lower than the FAO/WHO (2011) limits of 0.3 mg/kg respectively, which appear to indicate that they are suitable for human consumption. However, the concentrations of lead in *Chrysichthys nigrodigitatus* was higher than 0.3 mg/kg which suggests potential hazard to human health. Ekweozor et al. (2003) reported that oysters from the lower Bonny estuary had cadmium concentrations in their tissues that did not suggest any hazards to human health but cautioned on the need for continuous monitoring.

Cadmium and lead levels in some fish species from Azuabie Creek in the Bonny Estuary, Nigeria (Daka *et al.*, 2008)

In this study, we examined the concentrations of heavy metals (cadmium and lead) in some food fishes from *Azuabie.. Seven fish species (Liza falcipinnis, Sardinella madenensis, Tilapia mariae, Pomadasys jubelini, Gobius niger, Cynoglossus sp, Chrysichthys nigrodigitatus)* were assayed for their tissue cadmium and lead burdens.

The concentrations of cadmium ranged from 0.010 to 0.079 mg/kg, with means of 0.011 (+ 0.001) mg/kg in *Cynoglossus* sp. to 0.055 (+ 0.001) mg/kg in *Chrysichthys nigrodigitatus* (Table 16).There were no significant differences in cadmium concentrations between species ($F_{6,7}$ = 3.32, p=0.071). The lowest value of lead was found in Liza *falcipinnis* (0.104 + 0.030 mg/kg) while the highest value was found in *Chrysichthys nigrodigitatus* (0.310 + 0.029 mg/kg); lead burdens were significantly different between species ($F_{6,7}$ =p<0.01). Tukey tests show that *C.nigrodigitatus* and G. niger had significantly higher concentrations of lead that other fish species analyzed. The mean concentration of lead in the fishes was significantly higher than that of cadmium (t_6 = 5.53, p<0.01). This implies that of all the species examined, the likelihood of obtaining high lead dosage from eating fish from the study area is more apparent than that of cadmium. Lead is known to cause serious concern to health on land, but the contamination of the sea and marine products does not appear to be a matter for serious concern (Clark, 1997).

Littorina saxatilis were collected and acclimatized for 7 days to laboratory conditions (constant temperature room of 10 1oC, salinity ~34 psu) in tanks containing aerated seawater. They were subsequently transferred to test chambers (Parrish, 1985), where the test animals were suspended in labelled nylon mesh bags. Test chambers consisted of 2-l conical flasks aerated via a hollow glass tube through the stopper. After acclimatization, the animals were placed in test solutions for up to 44d. Test concentrations were prepared by diluting a freshly prepared stock solution (1000 mg l 1 in distilled water) of the respective metal salts with filtered seawater equilibrated to the test temperature. Metal salts used were zinc sulphate ($ZnSO_4.7H_2O$), copper sulphate ($CuSO_4.5H_2O$), cadmium sulphate ($3CdSO_4.8H_2O$), and lead nitrate $Pb(NO_3)_2$. The test concentrations selected were strong enough to elicit acute effects (cf. Mance, 1987): 5.0, 10.0 and 20.0 mg l-1 added zinc and added lead; 0.5, 1.0 and 2.0 mg l-1 added copper and added cadmium. Five replicate treatments of each concentration and controls (no metal added) were used. Replication was achieved by a randomised complete block design, with each block (test flask) containing bagged individuals (ten per bag) from each of the five sites. All tanks, flasks and bags were acid-washed before use. Test solutions were replaced every other day and individuals were examined for mortality every four days in clean seawater. An individual was considered dead if it failed to withdraw when touched. The test animals were not fed before or during the experiment, but since no control mortality was observed (except 4% in just one case) starvation caused no significant mortality.

The results of this study show that prior exposure to zinc in the field resulted in enhanced tolerance to lethal concentrations of zinc in Littorina saxatilis; animals from Laxey which had the highest zinc levels were significantly more tolerant on exposure to 10 mgl-1 zinc than animals from Castletown, Derbyhaven, Ramsey and Peel which showed similar levels of mortality (Fig. 5, Tables3 and 4). There were also indications of tolerance to zinc at 5mgl-1 but not at 20mgl-1. The responses to 20mgl-1 zinc by animals from most sites were similar, indicating that the mechanism(s) by which tolerance was achieved at the lower concentration were unable to cope with the excess metal. On the basis of results of laboratory experiments, Roesijadi and Fellingham (1987) constructed a conceptual model which relates changes in metal tolerance to the magnitude of metal exposure. The model qualitatively separated the response of individual organisms to metal exposure into four states: (I) responses to natural background conditions and low but elevated, exposures: no discernible difference between control and exposed organisms; (II) exposure results in bioaccumulation; protective systems are mobilised; protection against toxicity conferred; (III) maximal participation of protective systems; upper limit of compensatory response; (IV) severe exposure: acutely toxic, mobilisation of detoxification systems not sufficient to protect essential metabolic pathways. The intraspecific responses to zinc obtained for Littorina in this study broadly conform to this model. The elevated zinc level in Laxey means that the animals from that estuary have protective systems mobilised at the time of sampling (stage II). The concentration at which tolerance was demonstrated (10 mgl-1 Zn) conformed to stage III, but at the higher test concentration, stage IV is reached whereby the protective systems are overwhelmed by the severity of exposure.

Littorina saxatilis from Laxey were also more tolerant to lead at 5mgl-1 lead than animals from all other sites (Fig. 5, Tables 3 and 4). However, while tolerance to 10mgl-1 zinc was significantly positively correlated with tissue burdens of zinc, lead tolerance at 5mgl-1 was not significantly correlated with tissue lead levels. There was, nevertheless, a significant correlation between tissue zinc concentrations and the LT50

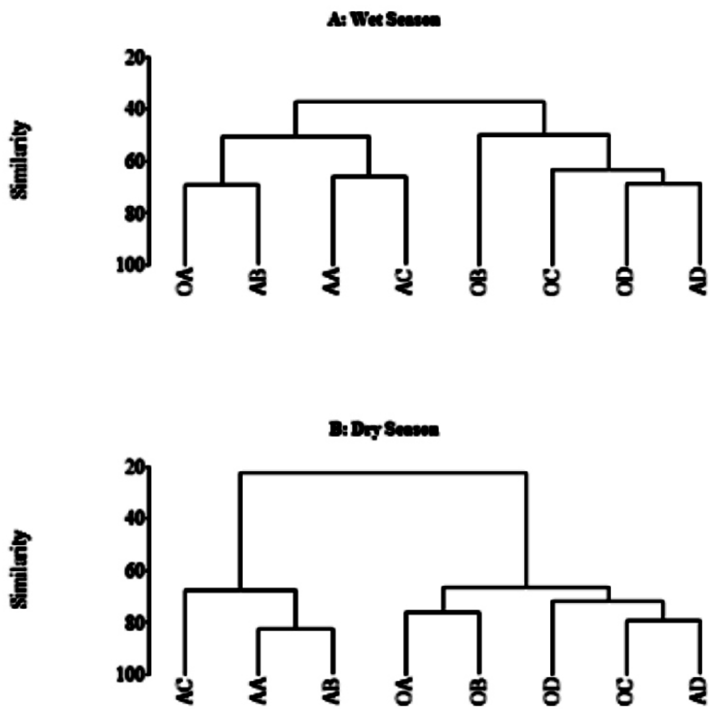


Figure 27: Dendrograms of infaunal benthos in Obufe (OA to OD) and Azuabie (AA to AD) creeks in the upper Bonny Estuary

Clear pattern of distribution in relation to the two creeks was not however, discernible in the wet season. However, in the dry season, two clusters or groups were identified both in the dendrogram and the MDS ordination. Group I (AA, AB and AC) and group II (OA, OB, OC, OD, and AD). The stations in group I are the polluted sites and this pattern corroborates the patterns found for the univariate indices.

Multidimensional Scaling (MDS) ordination (Fig. 26) and dendrograms from Cluster Analysis (Fig. 27) show groups of benthic communities present at all stations in Azuabie and Obufe creeks. Both multivariate techniques gave a clearer pattern in the dry season than wet season. The results of the MDS also show the stress factor which gives an indication of the reliability of the diagram. Low values of stress coefficients (0.01 - 0.05) indicate excellent correspondence and reliability(UNEP, 1995); thus the values for the dry season ordination gave greater reliability than that of the wet season (Fig. 26). The results of cluster analyses are consistent with the corresponding MDS ordinations for each period.

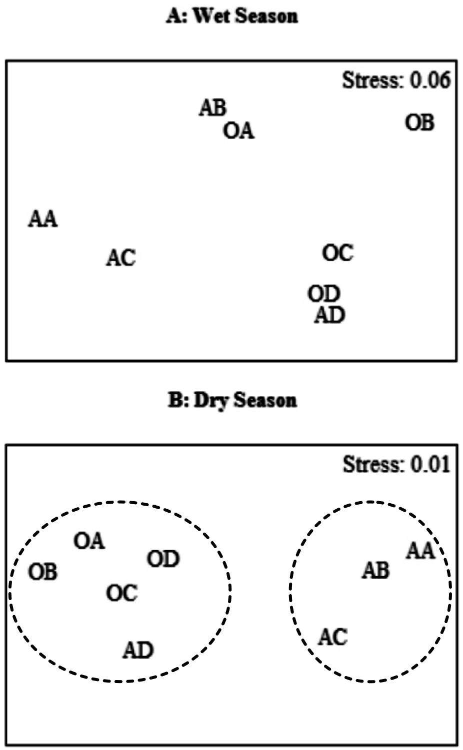


Figure 26: 2-D Multidimensional Scaling (MDS) ordinations of infaunal benthos in Obufe (OA to OD) and Azuabie (AA to AD) creeks in the upper Bonny Estuary

values for 5mgl-1 lead (n=5, r=0.929, p<0.01). This suggests that there was co-tolerance between zinc and lead in the Laxey population, with the presence of zinc tolerance predisposing the animals to lead tolerance. The individuals from Laxey also had the highest median lethal times to copper exposures (0.5, 1.0 and 2.0 mgl-1 Cu) but were only significantly more tolerant than those from Ramsey at all concentrations. The populations from Laxey, Derbyhaven, Castletown and Peel showed similar levels of tolerance to copper at one concentration or the other (see Tables 3 and 4). There were no significant differences in tolerance to cadmium at 0.5 and 1.0 mgl-1, and at 2.0mgl-1 cadmium the LT50 values for individuals from Derbyhaven,

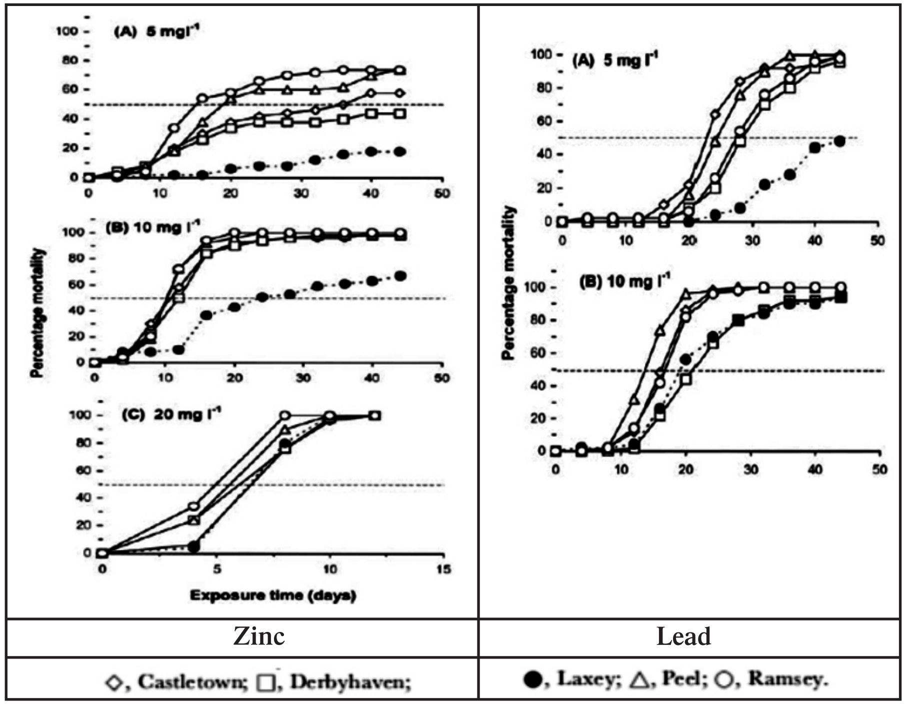


Figure 5: Mortality of *Littorinasaxatilis* from sites in the Isle of Man exposed to Zinc and Lead

Laxey and Ramsey were similar. The indications, therefore, were that no co-tolerance to copper or cadmium existed with tolerance to zinc in L. saxatilis from Laxey Estuary.

Table3: Median Lethal Times LT50 (days) of *Littorinasaxatilis* from various sites in the Isle of Man exposed to different concentrations of zinc, lead, copper an cadmium *(N=5, mean (x) ± SE).*

Metal	Concentration $(mg\ l^{-1})$	Castletown	Derbyhaven	Laxey	Peel	Ramsey
Zinc	10	[illegible]	11.1 ±1.1	23.2 ±2.7	10.7 ±0.5	10.4 ±1.0
	20	6.5 ±0.3	6.0 ±0.3	6.5 ±0.3	5.4 ±0.5	4.6 ±0.5
Lead	5	22.5 ±1.0	27.9 ±1.2	39.9 ±2.4	24.3 ±0.8	27.9 ±1.4
	10	16.4 ±0.7	21.7 ±1.7	19.8 ±1.2	13.6 ±0.8	16.8 ±0.9
Copper	0.5	23.0 ±1.5	19.4 ±1.0	24.9 ±1.4	18.4 ±1.0	15.0 ±0.8
	1	14.7 ±0.8	12.8 ±0.8	15.8 ±1.0	14.4 ±0.9	11.6 ±0.4
	2	11.8 ±0.6	12.3 ±0.5	12.5 ±0.8	9.4 ±0.9	7.3 ±0.5
Cadmium	1	21.0 ±1.2	23.5 ±1.1	21.3 ±0.9	20.5 ±1.4	21.1 ±1.4
	2	11.3 ±0.6	13.1 ±1.1	14.4 ±1.3	10.2 ±0.3	14.3 ±1.8

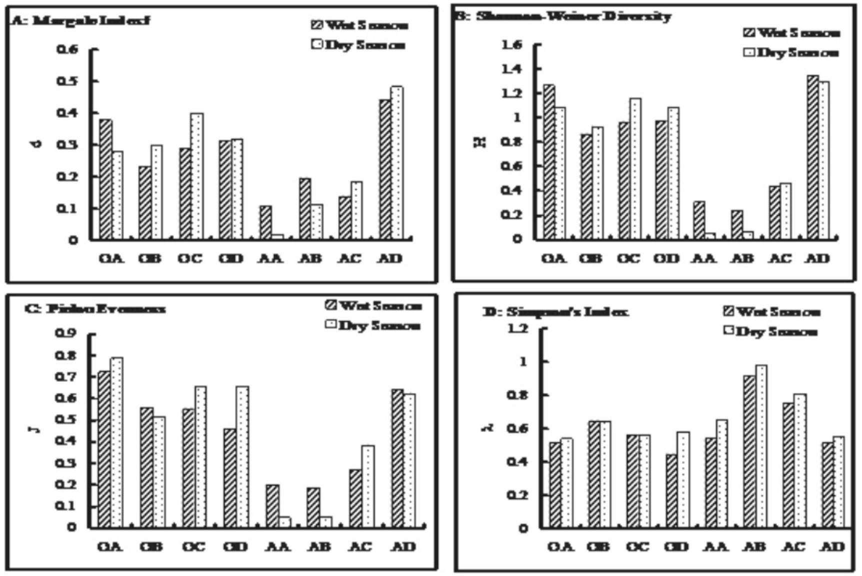


Figure 25: Univariate benthic community indices of Obufe (OA to OD) and Azuabie (AA to AD) creeks in the upper Bonny Estuary

Species diversity is a function of species richness and evenness of distribution of individuals among the species(Clark, 1997). Species richness, evenness, diversity were low at stations AB, AC and AA which are the polluted sites in Azuabie creek. However, dominance was higher at these stations. This pattern closely reflect the picture depicted by the abundance of Streblospio sp. discussed above. The high Simpson index in the three Azuabie locations is therefore, as a result of the dominant abundance of Streblospio at these sites. Belan (2003) has also reported that low value of biomass, ecological indices and maximal abundance characterize high pollution areas including organic carbon. Where evenness, richness and diversity tend to be low, dominance tends to be high; indicating an inverse relationship and this was also observed in this study.

will become relatively more numerous and will dominate the community, while many less tolerant species will become increasingly rare or disappear. Species that are sensitive to pollution may be used as indicators. Indicator species are therefore, species whose presence indicate or suggest the possibility of pollution in the environment. Studies have shown that some polychaetes are good indicators of pollution in the environment. According to Rygg (1985), those species which are opportunistic, and increase in their dominance under pollution, can be regarded as positive pollution indicators. Species, which occur frequently in less polluted areas, but eventually disappear when their habitat becomes polluted, may be used as negative indicators of pollution. Some polychaetes proposed as indicator species in the Niger Delta estuaries due to their numerical abundance in polluted areas include Nereis sp., Nephtys sp., Notomastus sp., and Capitella capitata(Ebere, 2002). In this study however, these species were not dominant at polluted sites, rather the numerical abundance of the spionid Streblospio sp. was consistently high at the polluted sites (AC, AB and AA) of Azuabie creek; therefore Streblospio sp. could be used as positive indicator species in low salinity areas of the Niger Delta.

Species richness (Margalef index - d), Shannon-Weiner Diversity Index (H') and evenness (J) were lower in the three Azuabie creek locations (AA, AB and AC) whereas Simpsons index was higher at these stations (Fig. 25 A D). ANOVA gave significant differences between locations for all the indices, with Tukey tests showing in most cases that AA, AB and AC were significantly different from other locations.

Table 4. Analysis of Variance (randomised-block design) on LT_{50} values (log$x$+1 transformed) for *Littorinasaxatilis* from sites in the Isle of Man exposed to different concentrations of zinc, lead, copper and cadmium.
Sites that are not significantly different at p<0.05 are underlined.

Metal	Concentration mg l^{-1}	df	MS	F	*P*	Tukey Test Inferences
Zinc	10	4	0.093	13.99	<0.001	L C D P R
	20	4	0.016	4.87	<0.01	L C D PR
Lead	5	4	0.042	45.50	<0.001	L R D PC
	10	4	0.027	8.04	<0.001	D L R CP
Copper	0.5	4	0.033	12.53	<0.001	L C D P R
	1.0	4	0.012	8.42	<0.001	L C PD R
	2.0	4	0.041	12.31	<0.001	L D CP R
Cadmium	1.0	4	0.003	2.92	>0.05	D L R C P
	2.0	4	0.016	7.40	<0.001	L R DC P

Sites: L=Laxey, C=Castletown, D=Derbyhaven, P=Peel, R=Ramsey

Mechanism of tolerance (Daka and Hawkins, 2004)

Mr Vice-chancellor, Sir, having established tolerance to zinc and lead in the winkles from Laxey, we went further to determine population differences in the accumulation of zinc and lead in order to elucidate the mechanisms of tolerance. Two types of experimental designs were used. The accumulation of zinc was determined at fixed concentrations of zinc with time, while the other involved accumulation of lead with increased concentration in a fixed time. Collection and acclimatization procedures were as described above, but for zinc accumulation studies, acclimatization to the test chambers involved three replicates of thirty individuals for each site. Before exposure to metals, four individuals were removed from each bag for the assessment of initial metal concentration. The rest were transferred into three replicates of the nominal exposure concentrations of 2.5 mgl-1 and 5 mgl-1 zinc. Four individuals representing a pooled sample for metal analysis were collected every two days (with the exposure solutions replaced) and this was continued until the 8th day.For lead accumulation, sets of ten individuals per bag were exposed in triplicate to the appropriate metal concentrations after acclimatization to the test chambers. The nominal concentrations were 0.1, 0.5, 1.0 and 2.0 mgl-1 lead. The solutions were changed every two days and the experiments were terminated after six days when test animals were also collected for metal analysis.At the end of each exposure to metals, the animals were placed in boiling water for a few seconds to facilitate removal of the soft tissue from the shell and stored frozen until analysed for the respective metals. After extraction from the shell, the animals were oven-dried to constant weight at 105oC. The dry tissues were digested in nitric acid according to Harper et al. (1989) and analysed by atomic absorption

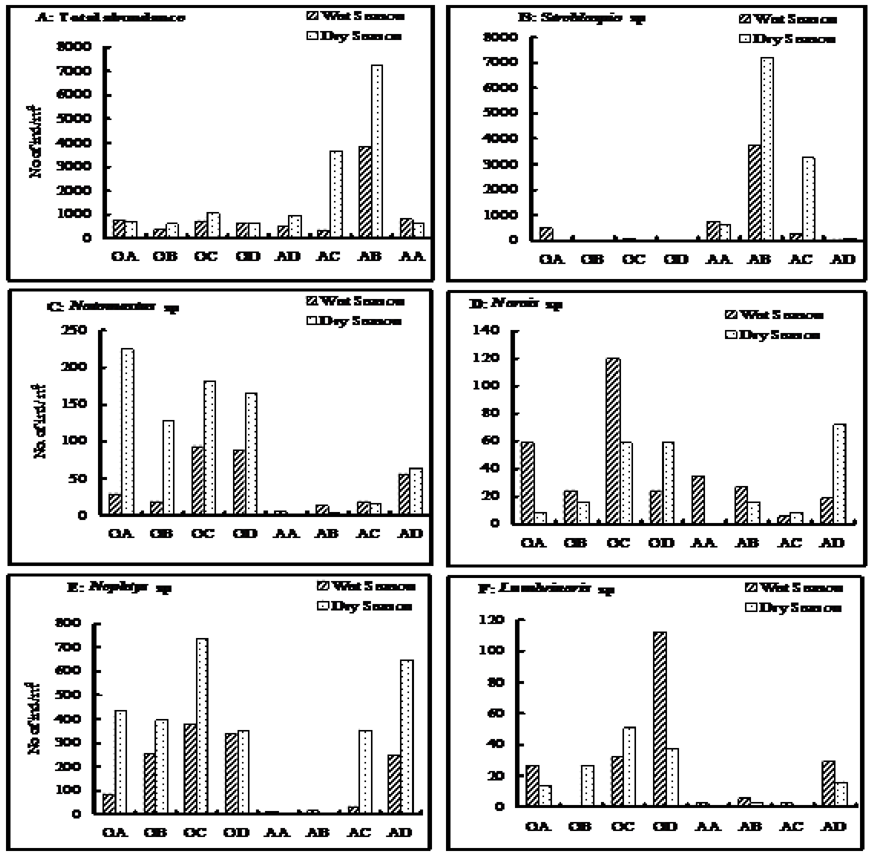


Figure 24: Mean total abundance, and mean densities of some key polychaete genera in Obufe (OA to OD) and Azuabie (AA to AD) creeks in the upper Bonny Estuary

Spatial differences in the composition of benthic communities along estuarine gradients could also be related to changes in salinity, depth, sediment grain size and organic content Day et al (1989). Stations AC, AB and AA have been reported to have higher proportion of the silt-clay fraction as well as higher percentages of organic carbon in sediment (Daka et al., 2007). It is well documented that pollution often leads to structural changes in benthic communities (Belan, 2003); Pearson and Rosenberg, 1978); Clark, 1997). A few tolerant or opportunistic species

Table 15: Checklist of infaunal benthos found in Obufe Creek (OA to OD) and Azuabie Creek (AA to AD) in the upper Bonny Estuary

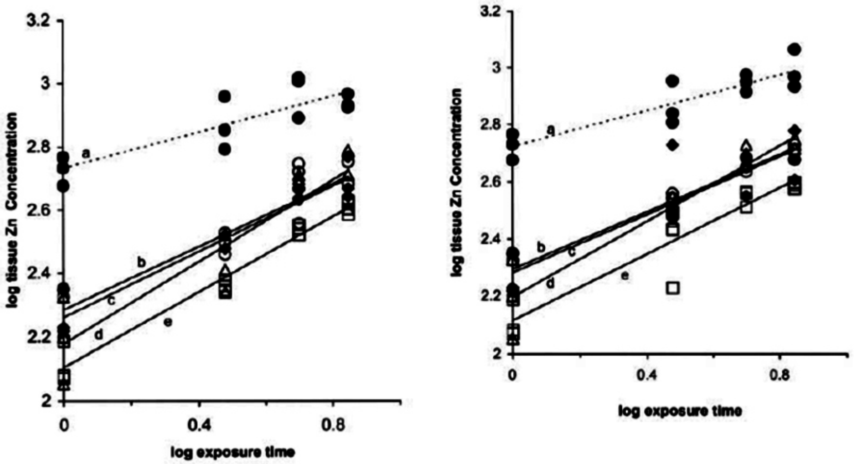
Taxa	**OA**	**OB**	**OC**	**OD**	**AD**	**AC**	**AB**	**AA**
POLYCHAETA								
Polydora sp	+	+	-	-	-	-	-	-
Streblospio	+	+	+	+	+	+	+	+
Marphysa sp	+	-	+	+	+	+	+	+
Eunice sp	+	-	-	+	+	-	+	-
Pilargis sp	+	+	-	+	+	-	+	+
Notomastus sp	+	+	+	+	+	+	+	+
Nereis sp	+	+	+	+	+	+	+	+
Nephtys sp	+	+	+	+	+	+	+	+
Glycera sp	-	+	+	+	+	+	-	-
*Lumbrineris*sp	+	+	+	+	+	+	+	+
*Scoloplos*sp	-	-	-	-	-	-	+	+
*Nothria*sp	-	+	-	-	-	-	-	-
MOLLUSCA								
Bivalves	+	+	+	+	+	+	+	+
CRUSTACEA								
Penaeus sp	-	-	-	+	+	+	+	-
*Callinectes*sp	+	-	-	+	+	+	+	-
FISH								
Anguila sp	-	+	-	+	-	+	+	-
INSECTA								
larvae	-	+	-	+	+	+	-	-

+ = Present; - = Absent

spectrophotometry. Regressions of tissue metal concentrations were plotted against time (zinc) or nominal exposure concentrations (lead) and the slopes of the regressions were compared by Analysis of Covariance (ANCOVA) using MINITAB for Windows. Log (x+1) transformations were made of the plotted values (and corresponding ANCOVA) where these improved the regressions.

The accumulation of zinc in L. saxatilis from five sites at are given as log-log regressions of tissue metals against time in Fig. 6. At both concentrations (2.5 mgl-1 and 5 mgl-1 added zinc), individual regression lines were significant for all sites ($p<0.001$). The regression coefficients (slopes) indicate that the animals from Laxey had a much lower rate of zinc accumulation than individuals from all other sites. Analysis of Covariance (ANCOVA) confirmed that there were significant differences in regression coefficients between sites for both zinc exposure concentrations (2.5 mgl-1, $F_{4,50}=7.25$, $p<0.001$; 5.0 mgl-1, $F_{4,50}=7.24$, $p<0.001$).

The regressions of lead accumulation with increasing lead concentration for individual sites were all highly significant (Fig. 7, $P<0.001$) with significant differences between regression coefficients (ANCOVA, $F_{4,65}=12.15$, $p<0.001$). Littorinasaxatilis from Laxey had the highest slopes (i.e. the highest rate of lead accumulation), and animals from other sites were in the order Peel>Castletown>Ramsey>Derbyhaven.



a=Laxey: $y=2.73 + 0.285x$. b=Ramsey: $y=2.29 + 0.496x$. c=Castletown: $y=2.26 + 0.519x$. d=Peel: $y=2.18 + 0.644x$. e = Derbyhaven: $y=2.11 + 0.593x$

a=Laxey: $y=2.72 + 0.316x$. b=Ramsey: $y=2.29 + 0.502x$. c=Castletown: $y=2.28 + 0.508x$. d=Peel: $y=2.20 + 0.662x$. e=Derbyhaven: $y=2.11 + 0.582x$

◇, Castletown; □, Derbyhaven; ●, Laxey; △, Peel; ○, Ramsey.

Figure 6. Regressions of zinc accumulation with time in *Littorinasaxatilis* from five sites in the Isle of Man exposed to 2.5 and 5.0 mgl^{-1} Zn.

Assessing the impact of urban/ industrial activities on benthic communities of two creeks of the upper Bonny Estuary, Niger Delta using univariate and multivariate techniques (Daka et al. 2009).

A total of about 17 genera were recorded in this study (Table 15) indicating a generally low abundance of fauna. Polychaetes were most abundant with a total of 12 genera accounting for 99.05 % of the abundance; other groups of fauna identified, which were virtually low in abundance included bivalves (0.15 %), crustaceans (0.54 %), fish (0.21 %) and insects (0.06 %). This is consistent with previously reported pattern of benthic community structure in the Bonny estuary(Snowden and Ekweozor, 1990; Ikomah et al.,2005). Higher mean total infauna were recorded at stations AB and AC in the Azuabie creek than other stations (Fig. 24A), showing significant differences. Streblospio sp. was the most abundant polychaete in Azuabie creek (Fig. 24B) showing significant differences between locations ($p< 0.001$). Tukey tests showed that stations AB, AC, and AA in the Azuabie Creek had significantly higher abundances of Streblospio sp. than stations OA, OB, OC, OD (Obufe Creek) and AD. On the other hand, the mean density of Notomastus sp. (Fig. 24C), Nereis sp. (Fig. 24D), Nephtys sp. (Fig. 24E) and Lumbrineris sp. (Fig. 24F) were generally higher in Obufe creek stations; with apparent departures to the general pattern by Nephtys and Nereis. There were significant differences ($p< 0.001$) in mean density of Notomastus sp. between locations (Tukey inferences: AB = AC = AA but significantly different from stations OA, OB, OC, OD and AD). ANOVA also showed significant differences between locations in mean abundances of Lumbrineris (Tukey, $p<0.05$: AC = AB = AA OC = OD) and Nephtys (Tukey, $p<0.05$: AC = AB = AA OA, OB, OC, OD; AD = AC AA). However, the densities of Nereis did not show any significant differences between locations. All the polychaete genera achieved higher abundances in the dry season, except for Lumbrineris and Nephtys which showed some inconsistencies (Fig. 24).

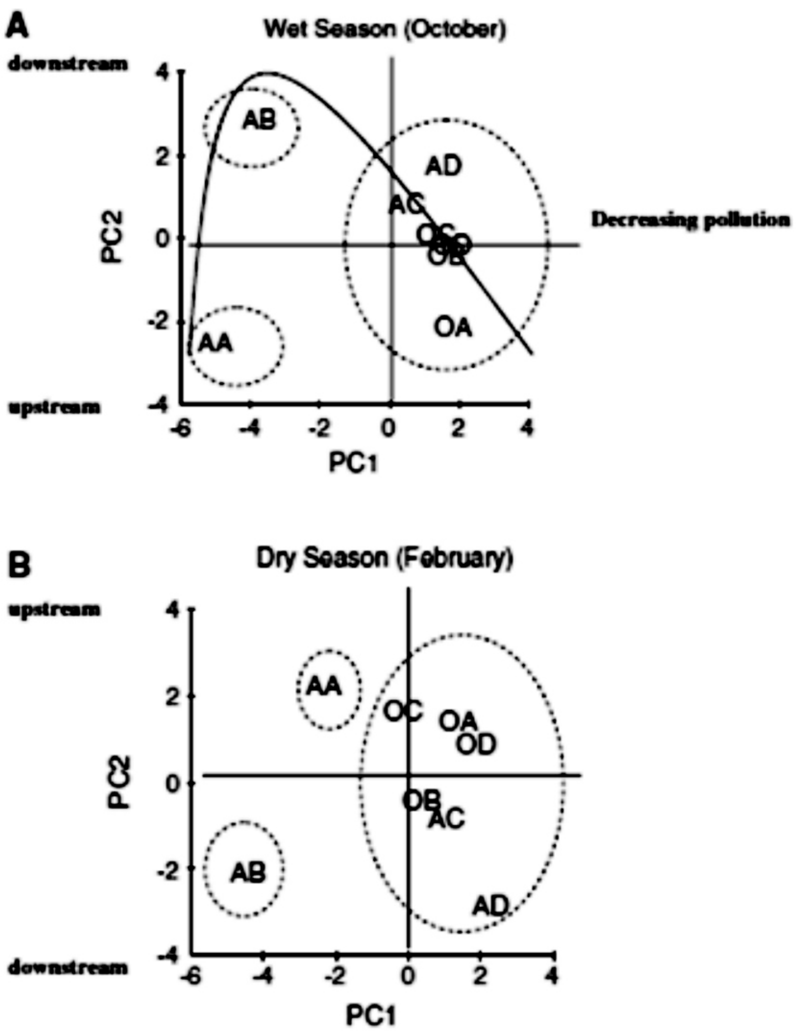


Figure 23: Discrimination of sites by Principal Component Analysis (PCA) using sediment data.

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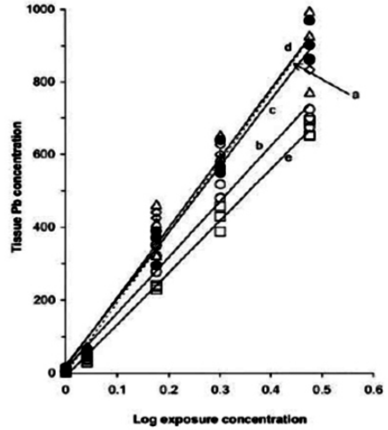


a=Laxey: y=3.10 + 1917x. b=Ramsey: y=13.2 + 1521x. c=Castletown: y=21.8 + 1817x. d=Peel: y=17.5 + 1901x. e=Derbyhaven: y=8.34 + 1416x

◇, Castletown; □, Derbyhaven; ●, Laxey; △, Peel; ○, Ramsey.

Figure 7. Regressions of tissue lead burdens (μgg^{-1} dry weight) with increasing exposure concentration (mgl^{-1}Pb) in *Littorinasaxatilis* from five sites in the Isle of Man.

Zinc tolerance in the Laxey population was coincident with low zinc accumulation and significant negative correlations were found (2.5 mgl-1 Zn, n=5, r= -0.898, p<0.05; 5 mgl-1 Zn, n=5, r= -0.860, p<0.05). There appears to be no relationship between lead accumulation and lead tolerance (n=5, r=0.192, p>0.05).

The metal accumulation studies have shown that the tolerances to zinc and lead observed for L. saxatilis in our study were associated with different mechanisms. Zinc tolerance was correlated with reduced accumulation probably resulting from reduced uptake. Lead tolerance, on the other hand, was correlated with higher lead accumulation in the animals from Laxey. The metal accumulation studies also confirm the indications that there was co-tolerance to lead arising from the zinc tolerance. At 5 mgl-1 lead, apart from the fact that the individuals from Laxey showed enhanced tolerance than those from all other sites, there were also significant differences in tolerance between littorinids from Castletown and Derbyhaven in comparison with Ramsey. Correlations between LT50 and lead accumulation values (excluding values for Laxey) showed that the putative tolerance of the Castletown and Derbyhaven populations of L. saxatilis could be attributed to lower accumulation. However, in the case of the Laxey population, enhanced tolerance was coincidental with higher lead accumulation, suggesting that lead was sequestered on an excess metal binding capacity (Bryan, 1976) in the tolerant winkles.

Copper and Cadmium accumulation; Interactive effects on metal accumulation (Daka and Hawkins, 2006; Daka 2009)

Further studies on the accumulation patterns of copper (an essential metal) and cadmium (a non-essential metal) were performed in the gastropod mollusc L. saxatilis to determine how tolerance to zinc and lead could affect the accumulation of these metals (Daka, 2009). Different profiles of accumulation were found between the essential metal copper and the non-essential metal cadmium in L. saxatilis. Cadmium accumulation was monotonic over the entire range of concentrations to which the winkles were exposed, giving a significant linear relationship whereby nearly all of the variation of the regression was accounted for by the coefficient of determination (0.994 0.999) (Fig. 8).On the other hand, linearity of the regression of copper accumulation was observed up to 0.5 mgl-1 Cu, above which it was lost and a quadratic fit gave a better coefficient of determination (Figure 9, Table 5). No significant differences were found in the slopes (using linear regressions) for Cu accumulation, whereas there

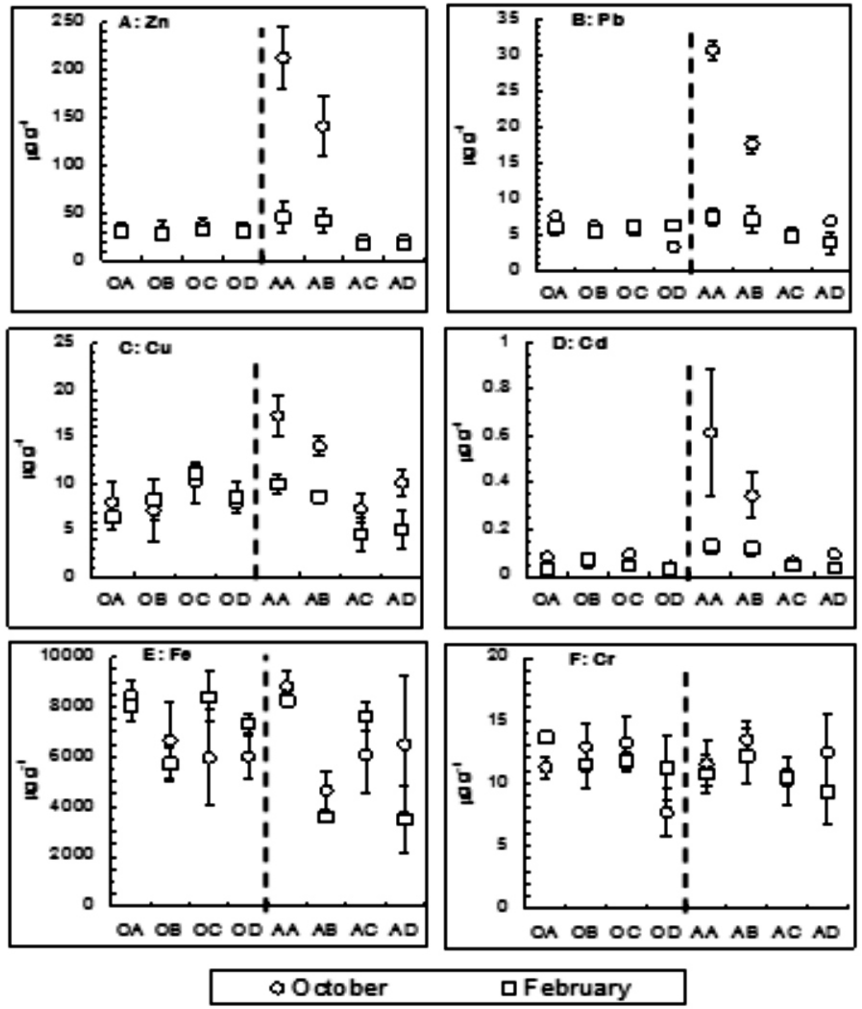


Figure 22: Concentrations of heavy metals (mean $\pm$ SD, n=3) in sediments from the study area.

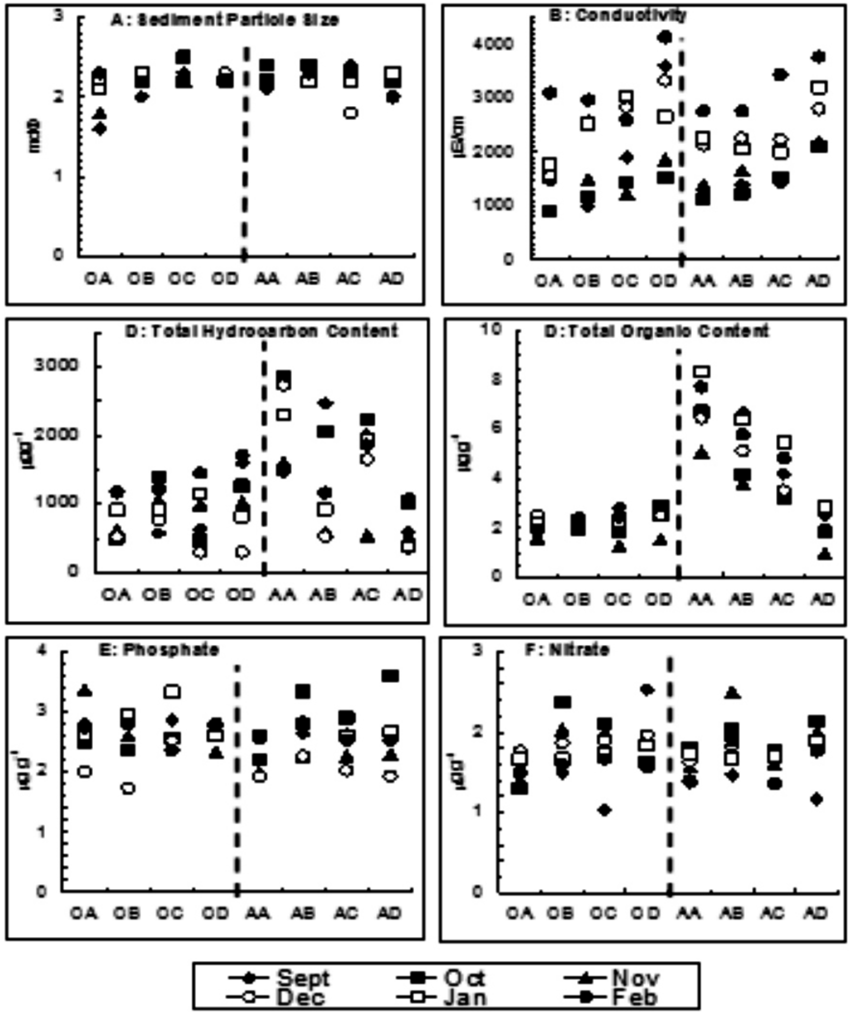
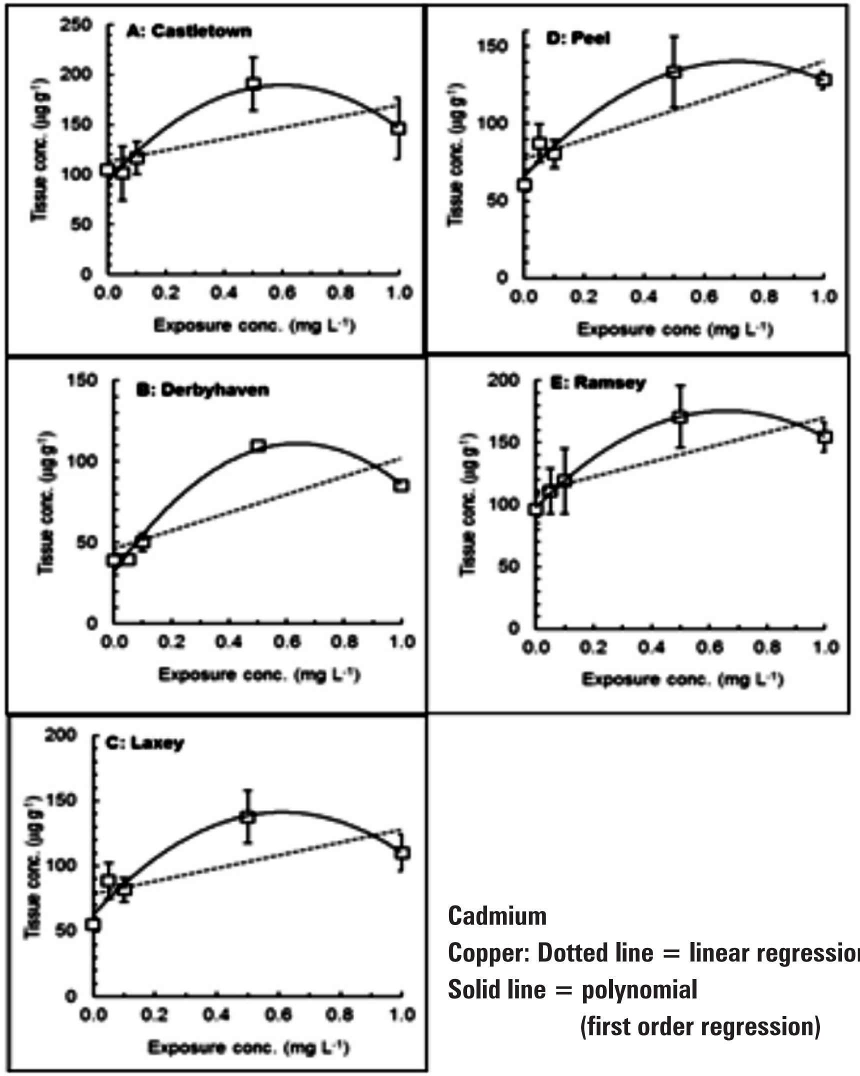


Figure 21: Some physico-chemical variables of sediments (mean values, n=18) in the study area.

were significant differences in regression coefficients for Cd accumulation. The differences did not appear to be related to initial Cd levels in the tissues of the animals.



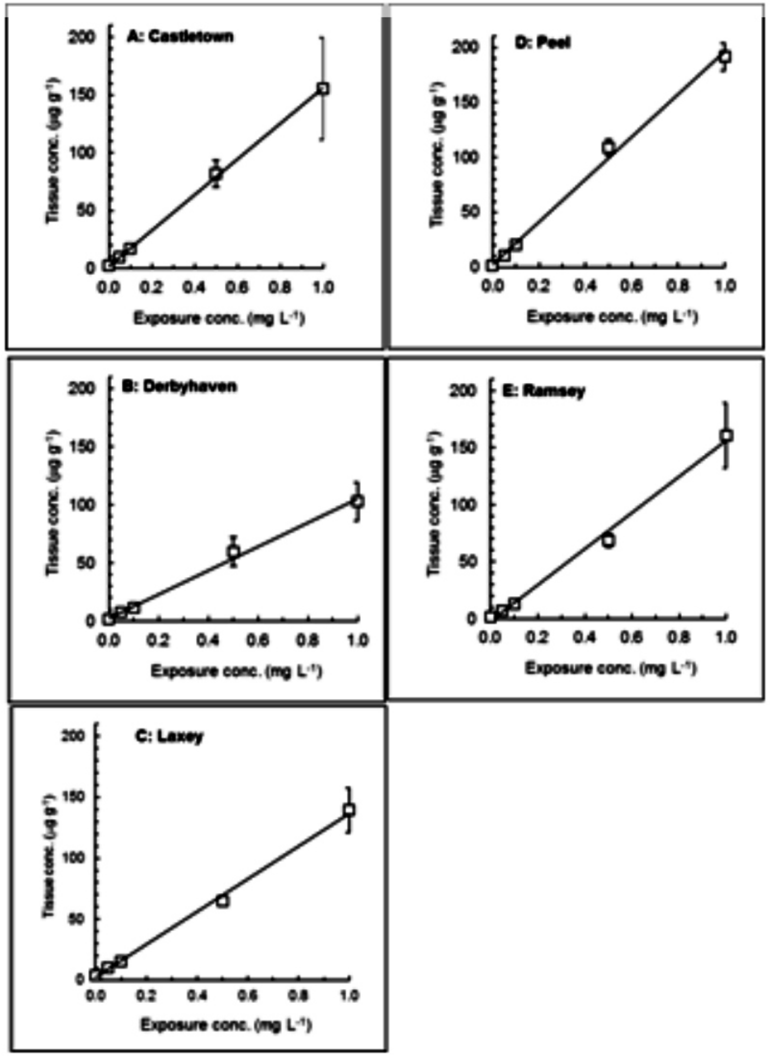
Cadmium

Copper: Dotted line = linear regression;

Solid line = polynomial

(first order regression)

Figure 8: Regressions of tissue copper burdens (µg g^{-1} dry weight) with increasing exposure concentration (mg L^{-1} added Cu) in *Littorina saxatilis* from sites around the Isle of Man



Cadmium

Castletown: y = 154.02x + 2.3989; r² = 0.999; Derbyhaven: y = 102.89x + 2.5868; r² = 0.995; Laxey: y = 134.46x + 2.4959; r² = 0.998; Peel:y = 193.01x + 2.8639; r² = 0.996; Ramsey: y = 158.67x - 2.2849; r² = 0.994

Figure 9: Regressions of tissue cadmium burdens (mg g-1 dry weight) with increasing exposure concentration (mg/L added Cd) in Littorina saxatilis from sites around the Isle of Man

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Table 13. F values from ANOVA to test for significant differences for some sediment variables.

Source of variation	df	**Cond.** F	**TOC** F	**THC** F	**NO_3** F	**PO_4** F
Creek	1	0.03	83.12***	7.92**	0.97	1.36
Location	3	24.61***	24.34***	3.75***	9.25***	0.67
Period	5	35.89***	5.71***	3.50**	9.37***	7.43***
Location x Creek	3	0.2	32.5***	9.46***	1.23	1.55
Location x Period	15	1.68	0.5	1.23	2.09*	1.06
Creek x Period	5	0.65	1.04	1.47	3.12*	2.23

* = p<0.05, ** = p<0.01, *** = p<0.001

Table 14. Enrichment Factors (*x* and SD - mean and 1 standard deviation, n=3) of zinc, lead, copper and cadmium in sediments from the study area. Values in bold are enriched.

Site	Zinc				Lead				Copper				Cadmium			
	Oct		Feb		Oct		Feb		Oct		Feb		Oct		Feb	
	x	SD	*x*	SD	*x*	SD	*x*	SD	*x*	SD	*x*	SD	*x*	SD	*x*	SD
OA	0.7	0.2	0.6	0.01	0.9	0.0	0.8	0.2	1.4	0.5	1.1	0.1	0.3	0.1	0.1	0.0
OB	0.7	0.1	0.8	0.03	1.0	0.3	1.0	0.0	1.5	0.4	**2.0**	0.3	0.2	0.0	0.4	0.0
OC	1.0	0.1	0.6	0.04	1.0	0.4	0.7	0.1	**2.7**	1.4	**1.9**	0.1	0.5	0.2	0.2	0.1
OD	0.9	0.3	0.7	0.1	0.6	0.2	0.9	0.1	**1.9**	0.6	**1.7**	0.3	0.2	0.1	0.1	0.0
AA	**3.9**	0.9	0.9	0.3	**3.5**	0.4	0.9	0.2	**2.8**	0.6	**1.7**	0.1	**2.1**	1.1	0.5	0.1
AB	**5.1**	1.8	**1.9**	0.6	**3.9**	0.9	**2.0**	0.6	**4.4**	1.0	**3.4**	0.4	**2.3**	1.0	1.0	0.3
AC	0.6	0.1	0.3	0.1	0.9	0.3	0.6	0.0	**1.7**	0.1	0.9	0.4	0.3	0.0	0.2	0.0
AD	0.6	0.4	0.8	0.2	1.2	0.5	1.2	0.1	**2.5**	1.3	**2.0**	0.3	0.5	0.2	0.3	0.0

positive correlations between the metals and TOC ($p<0.05$), showing that incorporation of metals by flocculation with organics influenced the concentration in sediment. It is, however, possible that the frequent dredging in the creeks results in the removal and export of contaminated sediment particles such that a build-up of metal levels is ameliorated. This may also explain the variable status of enrichment between periods.

The result of PCA ordinations (Fig.23) using sediment quality characteristics indicate three groupings. This was much clearer in February samples than it was for October. Stations AA and AB (the most heavily impacted areas in Azuabie creek) each stood out separately, while the four stations in Obufe creek (OA, OB, OC and OD) were grouped together with AC and AD (the less contaminated sites in Azuabie creek). The graphs (especially Fig. 23A) show that the main factor (1st axis) is a decreasing pollution from upstream to downstream. It opposed AA to OA. The second organizing factor (2nd axis) is the trivial upstream-downstream gradient, opposing AA and OA to AD and OD. This is more marked for the Azuabie creek. The two factors (pollution and downstream gradient) are correlated; this explains the guttman effect observed on the two graphs. This indicates that Stations AA and AB are hot-spots of contamination because of their proximity to sources of anthropogenic impacts. In conclusion, this study showed that the Azuabie creek had higher levels of contamination with organic matter and heavy metals than the Adjacent Obufe creek, with gradients of contamination showing higher values at the upstream reaches. Pollution was the most organizing factor which hides partially the trivial upstream-downstream gradient. However, the level of contamination with hydrocarbons was lower than the values obtainable from areas chronically contaminated with petroleum hydrocarbons in the Bonny Estuary

Table 5: Regression equations using linear and polynomial (first order) models for the accumulation of copper in *L. saxatilis*.

Site	*Linear model*		*polynomial (first order) model*	
	Equation	r^2	*Equation*	r^2
Castletown	$y = 56.358x + 113.14$	0.411	$y = -266.59x^2 + 319.79x + 93.519$	0.958
Derbyhaven	$y = 55.998x + 46.302$	0.569	$y = -193.73x^2 + 247.43x + 32.044$	0.975
Laxey	$y = 49.491x + 78.434$	0.454	$y = -208.02x^2 + 255.05x + 63.125$	0.931
Peel	$y = 63.598x + 76.86$	0.725	$y = -146.75x^2 + 208.61x + 66.061$	0.955
Ramsey	$y = 58.974x + 110.86$	0.644	$y = -179.2x^2 + 236.06x + 97.668$	0.998

Perhaps an interplay of physiological and behavioural mechanisms (mainly retraction and shell closure) is involved. Intracellular activities, the complex interactions of which may determine the distribution and concentrations of metals in Littorina littorea have been identified (Mason, 1983), and these could be applicable to L. saxatilis. One type involved very specific cells, such as pore cells and connective tissue calcium cells, which occur diffusely in the connective tissue and which accumulate specific metals (i.e. Cu and Mg, respectively) along precise metabolic pathways protected from the influence of other interfering metals. These cells are involved in the metabolism of the copper-containing respiratory protein haemocyanin. Webb(1990) showed that Cu may be bound to a different type of ligand (from Zn, Mn and Fe) in L. saxatilis since excretion of these metals occurred but no Cu excretion was observed under his experimental conditions, suggesting that behavioural responses might be important in explaining the Cu accumulation patterns observed. Non-essential metals may be accumulated without excretion or with some excretion (Rainbow, 2002). The accumulation pattern observed in this study confirmed that no regulation of Cd was apparent in its uptake from solution by L saxatilis. It is, however, not possible to state whether accumulation is accomplished with or without excretion as no radioactive tracers were used in the experiments. Basophil cells of the digestive gland and the nephrocytes of the kidney, occur at specific sites and apparently produce non-specific ligands capable of binding a wide variety of metals(Mason and Simkiss, 1983). Much of the Cd accumulated by aquatic invertebrates is bound to metallothionein in the cytosol of the organ predominantly used for accumulated Cd storage (Langston, 1998; Rainbow, 2002). It is therefore likely that Cd accumulation occurred without much excretion.

In conclusion, the accumulation Cu and Cd in L. saxatilis showed different patterns of accumulation, basically reflecting the essential or non-essential nature of the metals. The Cu accumulation pattern also highlights the importance of behavioural mechanisms in the accumulation of the metal above the threshold of regulation, while Cd was accumulated without regulation. Tolerance to Zn and Pb did not reflect in the inter-population profiles of Cu and Cd accumulation.

Mr Vice-Chancellor Sir, since heavy metals do not occur singly in nature, we went further to examine how the concurrent presence of lead, copper or cadmium with zinc could affect zinc accumulation in Littorina saxatilis (Daka and Hawkins, 2006). In this experiment, the animals were exposed in triplicate (10 individuals per replicate) treatments to 2 mg/L Zn alone or a mixture of 2 mg/L Zn and 0.01, 0.1, 1 mg/L added Cu, Cd, or Pb. The exposure was terminated after 6 days after which the metal concentrations in the tissues of the winkles were measured.

it suggests that the trace metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002; Feng et al., 2004). However, if a value of EF is greater than 1.5 (i.e., EF > 1.5), it suggests that a significant portion of trace metal is delivered from non-crustal materials, or non-natural weathering processes; the trace metals are provided by other sources (Feng et al., 2004). The EF values for Zn, Pb, Cu and Cd are presented in Table 14. Zn, Pb and Cd were found to have EF values above 1.5 at Stations AA and AB during the wet season sampling period (October) but in February only Pb fell above the threshold value. EF values for Cu were higher than 1.5 at all stations in the Azuabie creek in addition to two stations in Obufe creek. Analysis of Variance showed significant differences in EF at the levels of creek, locations and seasons as well as interactions between creek and location. Tukey tests show that AA and AB had significantly higher ($p<0.01$) EF values for zinc, lead and cadmium than all the other sites. Copper for which EF values showed enrichment in most sites or verged on it, significant differences were found only between AB and the other sites.

The overall order in the concentrations of metals in sediments followed the order: Fe>Zn>Pb>Cu>Cr>Cd. Although the spatial profiles depicted elevated concentrations of some metals in Azuabie creek, particularly at Stations AA and AB (which also had the highest EF values), the highest mean values obtained were lower than values recorded in heavily polluted mining areas (Daka et al., 2003) or industrialized areas (Bryan and Langston, 1992). Industrial activities capable of contributing to elevated concentrations of heavy metals include plastic industry, auto and boat fuel, construction, galvanizing iron and steel products, electroplating (Förstner and Wittmann, 1979, Moore and Romamoorthy, 1984). A number of industries in the Trans-Amadi industrial layout fall into the above categories, thus leading to elevated concentrations of Zn, Pb, Cu and Cd in the Azuabie creek. The high concentrations of these metals at Stations AA and AB are attributable to their proximity to the sources of contamination. Also, there were higher levels of TOC at these stations with significant phosphate values ranged from 1.73 (+0.09) mgg-1 at Station OB in December to 3.6 (+ 0.25) mg g-1 at Station AD in October.

The concentrations of Zn, Pb, Cu and Cd were higher during the wet season (October) than the dry season (February) but Fe and Cr did not show such seasonal trends (Figure 22). Also, the concentrations measured in October gave the highest mean values of Zn (214.4 mgg-1 - Figure 22A), Pb (30 mgg-1 - Figure 22B), Cu (17.26 mgg-1 - Figure 22C) and Cd (0.62 mgg-1 - Figure 22D) at Station AA in Azuabie creek; followed by Station AB, which had higher levels than other stations in Azuabie creek as well as locations in Obufe creek. Enrichment Factor (EF) was used as an index evaluate anthropogenic influences of heavy metals in sediments; which is the observed metal to iron ratio in the sample of interest divided by the background metal/iron ratio. Normalization of trace metal concentrations in sediments using Fe, or Al is effective in reducing textural control of trace metal concentrations; this is evident for Fe, an element that is not substantially enriched by anthropogenic contamination due to high natural concentrations (Niencheski et al., 1994). The EF is expressed mathematically (adapted from Feng et al., 2004, who used Al in place of Fe) by:

$$EF = [(Me_{Sample})/(Fe_{Sample})]/[(Me_{Background})/(Fe_{Background})]$$

where (Me/Fe)Sample is the metal to Fe ratio in the samples of interest; (Me/Fe)Background is the natural background value of metal to Fe ratio.

Background values were obtained from Nweke (2000) for locations in the upper Bonny Estuary that are not exposed to industrial pollution. Average background concentrations (n=12) of metals used were 13.0 mgg-1 Zn, 2.08 mgg-1 Pb, 1.47 mgg-1 Cu, 0.07 mgg-1 Cd, 2080 mgg-1 Fe (no value was available for Cr). Enrichment factor (EF) is a useful indicator reflecting the status of environmental contamination (Aloupi and Angelidis, 2001; Fenget al., ., 2004). If an EF value is less than 1.5,

The effects of increasing concentrations of Cu, Cd and Pb (0.01, 0.1, and 1 mg/L added metal) on Zn accumulation (at constant Zn concentration, 2 mg/L) indicated that, of the three metals, Cu had the most profound effect on Zn accumulation (Figs. 10 to 12). An increase in Zn accumulation (above values observed in Zn only solutions) was observed in mixtures with the lower concentrations of Cu, with values at 0.1 mg/LCu being higher than values for 0.01 mg/L (Fig. 10). At 1 mg/L Cu, Zn accumulation dropped to values much lower than values in other combinations as well as for the Zn only treatment. This pattern of Zn accumulation was consistent for animals from all sites. Analysis of Variance showed that there were significant differences in net uptake of zinc between the different Zn/Cu combinations in individuals from all sites ($p<0.001$). Bonferoni tests against Zn only showed significant differences in accumulation for Zn + 1 mg/L Cu but not for Zn + 0.01 mg/L Cu or Zn + 0.1 mg/L Cu. No significant interaction occurred between concentration and site, showing that the differences observed were consistent for all sites, although the initial zinc levels were different in the individuals from different sites.

Lead did not appear to have much effect on Zn accumulation and slight differences were obtained between sites (Fig. 11). There was a general tendency for Zn accumulation to be higher in Pb+Zn combined solutions than for accumulation from Zn only solutions. No appreciable increase in Zn accumulation occurred with an increase in the concentration of Pb, and in animals from Derbyhaven and Ramsey no effect was apparent. No significant differences in accumulation were found ($p>0.05$,).

Zinc accumulation in Cd+Zn solutions were also generally enhanced above values in solutions of Zn only (Fig. 12); accumulation in the animals from Peel being the only exception. However, ANOVA showed these differences were not significant ($p>0.05$)

Comparisons of Cu, Pb and Cd accumulation alone with accumulation in combinations with 2 mg/L Zn were made for 0.1 mg/L and 1 mg/L of the respective metals. The percentage increase or reduction of accumulation of each metal was calculated as:

$$\delta\Delta_c\,(\%) = (\Delta_{c1} - \Delta_{c2} / \Delta_{c1}) \times 100$$

where Δ_{c1} = accumulation from metal only solution (µg/g)

Δ_{c2} = accumulation from metal/Zn solution (µg/g)

The values for the accumulation of Cu, Pb and Cd at concentrations of 0.1 and 1.0 mg/Lof each metal (Fig. 13) showed that Zn had minimal effect on Cu accumulation although animals showed an erratic and inconsistent pattern between sites (Fig 13A). On the contrary, lead accumulation (Fig 13B) and Cd accumulation (Fig 13C) were both reduced in the presence of 2 mg/LZn in comparison with the accumulation of the respective metals alone in solution but no inter-site differences were apparent

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($p<0.05$) as AA = AB = AC > OA = OB = OC = OD = AD. The appreciably high organic carbon in the upstream stations of Azuabie creek is attributed to the presence of an abattoir and the large quantities of organic wastes discharged into the near-shore sediments at these stations. Waste spills from abattoir operations could introduce excess nutrients into surface waters (Meadows, 1995) which may have been reflected in the high TOC levels in Azuabie creek.

The lowest mean THC value (305.4 + 25.2 mgg-1) was recorded at stations OC and OD in December while the highest mean value (2865.0 + 240.3 mgg-1) was obtained at station AA in October (Figure 21D). THC was clearly higher in Azuabie creek (except at Station AD) in September and October but less so in January and February with some inconsistency in November. Significant differences in THC occurred between creeks, locations and also time (Table 13). Creeks and location also showed significant interactions, but no significant interactions between locations and time, creeks and time. Tukey tests indicate THC levels at station AA to be significantly higher than stations OA, OB, OC, OD and AD while station AC was higher than OC, and AB higher than AD. The THC values observed in this study fall within the range reported by Ekweozor et al. (2004) from various parts along the Bonny estuary and generally lower than 3,584 19,981 mgg-1 recorded by Ebere (2002). The high values recoded by Ebere could be due to the influence of refinery effluent and loading of petroleum products at the Okrika jetty that were part of his sampling sites. The elevated THC levels at stations AA, AB, and AC are attributable to industrial waste discharge by some industries present in the area and the materials washed off from large volume burnt tyre used for roasting at the abattoir.

There were minimal spatial variations in the mean concentrations of nitrate (Figure 21E) and phosphate (Figure 21F) and no significant variations between creeks were found for either variable (Table 13). The mean concentration of nitrate in sediment ranged from (1.03 + 0.07) mgg-1 to 2.53 (+ 0.35) mgg-1, both recorded in September while

Sediment samples were collected randomly in triplicates per station with an Ekman grab from September, 2003 to February, 2004, covering both rainy season and dry season. Threeway ANOVA were applied to sediment data (for heavy metals, the concentrations obtained were normalized against the concentration of iron; enrichment factors [EFs] were calculated and the values used for ANOVA) to test for significant differences at the levels of creek, location (within creek) and time. Where significant interactions were found between creek and location, twoway ANOVA were performed which also enabled pair-wise comparison between stations (and time) using Tukey tests. Data were log (x+1) transformed (except EF values) before statistical analysis. Principal Component Analysis - PCA (correlation-based because of differences in units of variables) was performed to visualize multivariate ordinations in sediment data.

The sediments were generally sandy to muddy sand. Median particle size analysis also showed sand fractions as the median particle size (Figure 20A). The mean sediment conductivity ranged from 900 (+58) mScm-1 at station OA in October to 4133 (+348) mScm-1 at station OD in February (Figure 20B). There was no significant difference in conductivity between creeks but significant differences were found between locations as well as period (Table 13); interaction between creek and location was not significant. The significant differences between locations as well as periods are indicative of the natural gradients and influence of freshwater inputs during the rainy season.

Total organic carbon (TOC) ranged from an average of 0.97 (+ 0.03) % to 8.37 (+ 0.33) %. The mean TOC values were consistently higher in Azuabie creek than Obufe creek (Figure 20C) in all sampling months, showing significant differences between creeks, locations as well as time (Table 13). Creek and location had significant interactions while, locations and time did not show significant interactions. In each month, the highest TOC value in Azuabie creek was recorded at location AA with an upstream gradient such that the values at Station AD were similar to those in Obufe creek. Tukey tests indicated significance

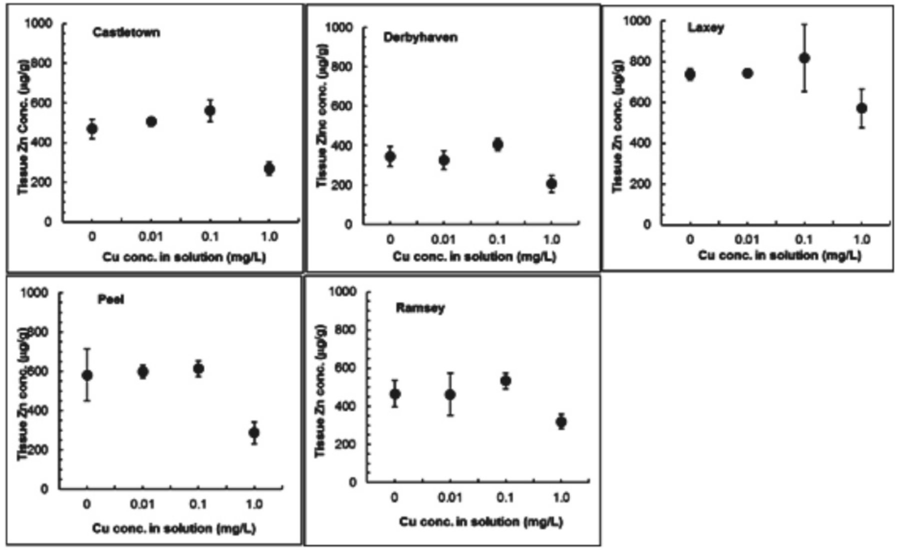

Figure 10: Concentrations of Zn in *Littorinasaxatilis* from five sites exposed to 2 mg/L added Zn and different concentrations of added Cu

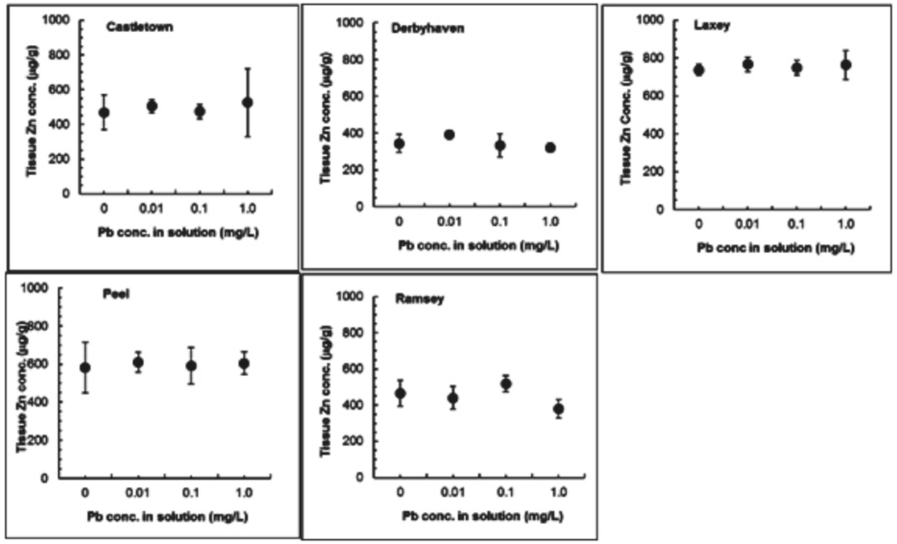

Figure 11: Concentrations of Zn in *Littorinasaxatilis* from five sites exposed to 2 mg/L added Zn and different concentrations of added Pb

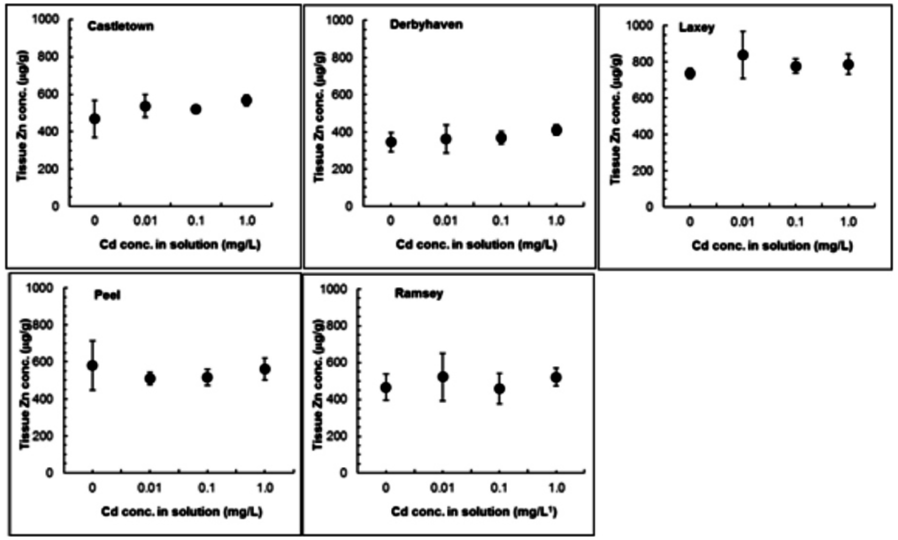

Figure 12: Concentrations of Zn in *Littorinasaxatilis* from five sites exposed to 2 mg/L added Zn and different concentrations of added Cd.

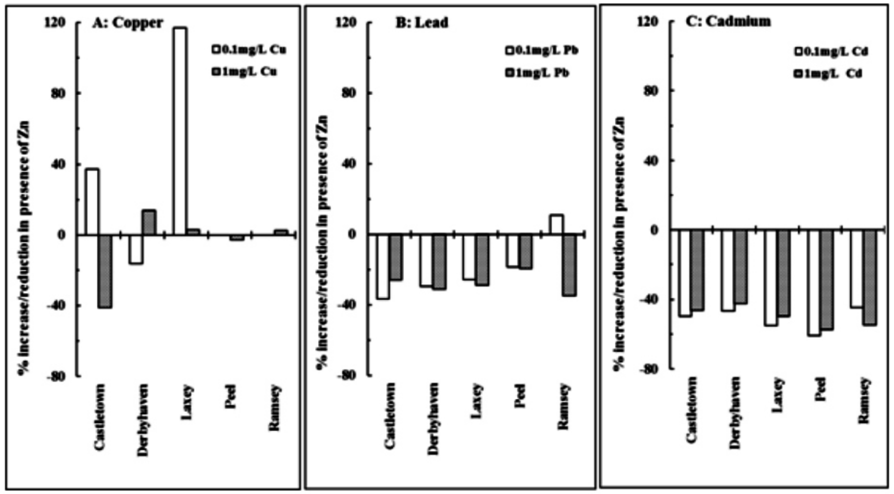

Figure 13: Effects of 2 mg/L Zn on the accumulation of Cu, Pb and Cd in *Littorinasaxatilis* at 0.1 mg/L and 1 mg/L of the respective metals. Values plotted are percentage differences - $\delta\Delta_c$

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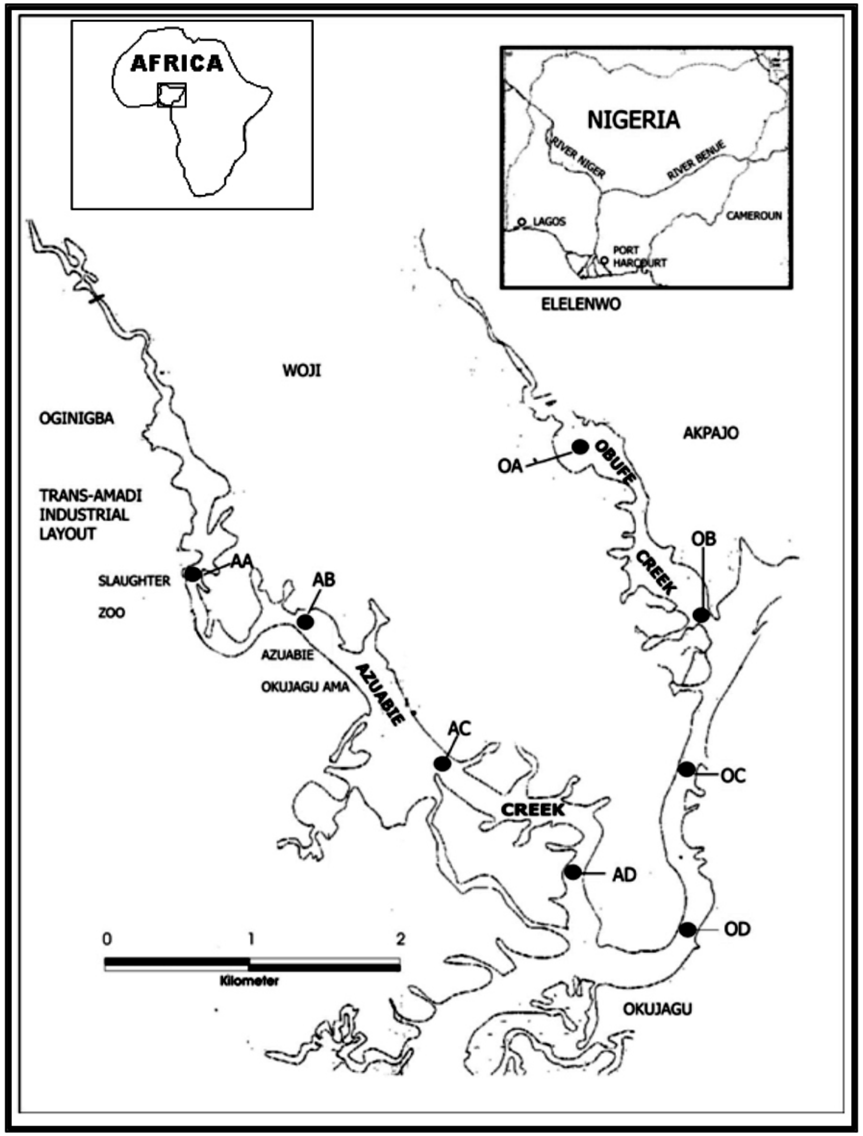

Figure 20: Location of study site and sampling stations

sprawling waterfront settlement, and a major abattoir. The main activity in the Obufe creek is dredging of sand (for sale and occasionally to make the creeks navigable), which also takes place in the Azuabie Creek. We examined some sediment characteristics of these creeks; to evaluate how industrial and other human activities have influenced the sediment quality of Azuabie creek with reference to the adjacent Obufe creek, and by small-scale spatial variation along the creeks.

A total of eight sites were chosen (four from each creek located as approximate spatial equivalents of one another with respect to upstream-downstream gradient, and taking into consideration possible sources of contamination (Fig.20). These were coded (upstream to downstream) AA to AD in Azuabie Creek and OA to OD in Obufe Creek.

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In interactions between Cd and Zn, Zn accumulation appears to be higher in solutions of Zn+Cd than from Zn alone, except for accumulation in animals from Peel (Figs 11 and 12). As with Pb, Zn had an antagonistic effect on Cd accumulation (Fig.13). The reduction of accumulation was greater for Cd than it was for Pb possibly because of the higher chemical similarity between Zn and Cd. As a result of their chemical affinities, Cd and Zn may share similar uptake pathways into organisms (Rainbow, 1997). It has been similarly observed that in many molluscan species, exposure to the non-essential metal Cd had no effect on Zn accumulation; whereas exposure to essential metal Zn had an antagonistic effect on Cd accumulation (Amiard-Triquet and Amiard, 1998). Littorinids are generally considered to be good indicators of contamination with dissolved Cd (Stenner and Nickless, 1974; Manga and Hughes, 1981; Bryan et al., 1983). The effect of Cu on Cd accumulation is however, unknown and is worthy of further investigation.

The interactive effects of metal accumulation may be influenced by tolerance of a population, within a species, to the metals concerned (Brown, 1978; Amiard-Triquet and Amiard, 1998). Littorina saxatilis from one of the sites used in this study, the Laxey Estuary, is tolerant to Zn and Pb in comparison with individuals from the other sites (Daka and Hawkins, 2004), with the tolerance resulting to a different accumulation profile for each metal. This did not appear to affect the interactive effects of metals (in the concentrations used for this experiment) as ANOVA did not show any interaction effects between concentration and site for any metal combination. It is concluded that at high concentrations of Cu, Cu was antagonistic to Zn accumulation in Littorina saxatilis due to physiological and behavioural responses. Pb and Cd did not significantly affect the accumulation of Zn but Zn had an antagonistic effect on both metals.

Stress on Stressresponse (Daka 2006)

Mr Vice Chancellor Sir, pollution-induced stress indices at various levels of organization, from sub-cellular to organismal level, have been investigated as a means of identifying and monitoring environmental contamination. Since changes elicited by toxic materials must occur at the biochemical, cellular and tissue levels of organization before effects would be observed at the organismal level, such measures have been suggested as potential short-term, functional indices which can be used to predict the effects of chronic exposures at higher levels of organization (Giesy, 1989). An organismal level response, the "scope for growth" (SFG) response, is thought to combine both quick response and ecological relevance (Bayne,1979). The SFG assay evaluates the effects of stress at the level of individual energy budgets and reflects the balance between energy acquisition (feeding and digestion) and energy expenditure (metabolism and excretion). Thus, it provides an instantaneous measure of the energy status of an animal (Maltby, 1990; Widdows, 1995).Viarengo (1995) proposed the use of stress on stress (SOS) response (in mussels) as an index of general stress at the organismal level, which can be applied as a monitoring tool for the assessment of contaminated coastal areas. As presented earlier, the populationof Littorina saxatilis from the metal contaminated Laxey estuary in the Isle of Man has been shown to be tolerant to zinc and lead owing to mine-related contamination by heavy metals (Daka and Hawkins, 2004). The stress on stress response has been extended to evaluate physiological trade-off to metal tolerance by studying the differences in salinity and desiccation tolerance of L. saxatilis from metal contaminated and uncontaminated sites in the Isle of Man.

4.0 Population and Community level changes from Anthropogenic and Industrial Activities in the Niger Delta

Mr Vice Chancellor, Sir, the Niger Delta is one of the richest and largest deltaic formations in the world with a high abundance and diversity of natural flora and fauna (Powell, 1995). Over the last three decades, increasing urbanization and industrialization have drawn attention to the environment in the Niger Delta. The Bonny estuary is a mangrove swamp with similar species to those found in the rest of the estuarine portion of the Niger Delta. It is a busy transport route for vessels and the presence of a number of industries such as petroleum refineries, petrochemical industries, tyre industries, bottling companies and other oil and gas companies which are sited along the banks or close to the banks of the estuary exposes it to several activities, some of which are capable of inducing environmental stress. We have carried out a number of studies in the Bonny Estuary which include fouling organisms (Daka and Abby-Kalio, 1997, Daka et al., 2002a, Daka et al., 2002b) and the impact of industrialization and other anthropogenic activities in the Bonny Estuary (Ekweozor et al. 2004; Ikomah et al. 2005; Daka et al., 2017; Dakaet al., 2009; Davids et al.2002, Daka and Moslen, 2013). In this section, I will focus on studies in the Azuabie Creek and Environs).

Sediment quality status of two creeks in the upper Bonny Estuary, Niger Delta, in relation to urban/ industrial activities (Daka et al. 2007)

The Azuabie and Obufe creeks are two adjacent creeks (running about parallel to one another) in the upper Bonny estuary; at the eastern flank of Port Harcourt a rapidly urbanizing city with heavy oil and other industrial presence (e.g. tyre manufacturing, breweries, canning, plastic industries, metal fabrications etc.). The Azuabie creek runs towards an industrial layout and is exposed to inputs from industrial operations, near-shore direct-discharge lavatories, waste from a production of non-specific ligands. Non-specific ligands capable of binding a wide variety of metals are produced by basophil cells of the digestive gland and the nephrocytes of the kidney which occur at specific sites (Mason and Simkiss, 1983).

As a result of their chemical affinities, Cd and Zn may share similar uptake pathways into organisms (Rainbow, 1997). Zn was mostly antagonistic to Cd accumulation (highly variable data for 0.5 mg/L + Cd combinations gave putative synergism). However, in contrast to Cu, Zn did not depress Cd accumulation in proportion to the concentration of Zn in solution. On the other hand, the concomitant dosage of Cd and Zn did not show clear effects on the accumulation of Zn in any of the combinations. It has been similarly observed that in many molluscan species, exposure to the non-essential metal Cd had no effect on Zn accumulation; whereas exposure to essential metal Zn had an antagonistic effect on Cd accumulation (Amiard-Triquet and Amiard, 1998; Daka and Hawkins, 2006). However, Ahsanullah et al. (1981) reported for the decapod crustacean Callianassa australiensis, that exposure to a mixture of Zn and Cd, increased the bioaccumulation of both elements.

We conclude that Tympanotunus fuscatus may be used as a suitable biomonitor of Cd in Niger Delta estuaries, but not for Zn and Cu. Also, the presence of the essential metals Cu and Zn may have repercussions in the interpretation of Cd data in T. fuscatus and should be taken into consideration in biomonitoring programmes involving this species.

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After acclimatization, the animals were introduced to the appropriate treatment of hypo/hyper saline solutions. Salinities tested were 0, 17 and 60 practical salinity unit (psu); and 100% sea water (34 psu) was used as control. Zero psu was obtained from double distilled water, 17 psu was prepared as a 1:1 dilution of sea water in double distilled water and 60 psu was prepared by the addition of a commercial aquarium salt (Instant Ocean, Aquarium Systems, France) in sea water. The tests were run in five replicates for each salinity. Replication was achieved by a randomized complete block design, with each block (test chamber) containing bagged individuals (ten individuals per bag) from each of the five sites. Aeration was maintained throughout the experiment with filtered air and the animals were not fed before or during the experiment. Mortality was examined every four days. At 0 and 60 psu the experiments were terminated on total mortality, obtained on the 12th day but the 17 psu treatment and controls were monitored for a further 12 days. Tolerance to desiccation was tested by aerial exposure of five replicates of 10 bagged individuals (per replicate) at 24 oC (variations of up to 3 oC were recorded). Replicates were placed in a completely random order in a controlled-temperature room and the experiment was run for 44 days. Mortalities were examined every four days by placing animals in sea water for 30 minutes. Live animals usually emerged from the shell or showed opercular response to gentle mechanical stimulation.

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No control mortalities were observed throughout the study period and the mortalities at 50% seawater (17 psu) were also very low with the highest average mortality of only 14% at the termination of the experiments after 24 days exposure. The order of tolerance was also similar in both 0 psu and 60 psu with an indication that L. saxatilis from Laxey were the most tolerant and those from Ramsey the least. The order of tolerance of animals from the other site was Derbyhaven, Castletown, Peel. The median lethal times (LT50s) were generally higher at 0 psu than 60 psu. However, analysis of variance (ANOVA) did not show any significant difference in mean LT50s between sites at any salinity exposure (Table 6).

Table 6: Median lethal times – LT_{50} (days) of *Littorinasaxatillis*from five sites in the Isle of Man exposed to extreme salinity (0 psu and 60psu) and desiccation stress. Values are mean S.D., n=5. No LT_{50} values for control (34 psu – no mortality) and 17 psu (low mortalities).

	LT_{50} (mean ± S.D., n=5)		
Site	**0 psu**	**60 psu**	**Desiccation**
Castletown	6.9 ± 0.4	7.8 ± 1.0	35.7^{1}± 3.5
Derbyhaven	7.1 ± 0.6	7.9 ± 0.9	$25.2^{1,2}$± 9.9
Laxey	7.5 ± 1.3	8.4 ± 0.9	10.4^{3}± 4.3
Peel	6.8 ± 0.4	7.7 ± 0.9	$14.4^{2,3}$ ± 7.1
Ramsey	6.6 ± 0.6	7.0 ± 0.7	10.1^{3}± 3.3
ANOVA	$F_{4.16}$ =2.978,P>0.05	$F_{4.16}$=1.749, P>0.05	$F_{4.20}$ =13.49, P<0.01

Superscripts with different numbers along a column show significant difference (Tukey tests, p<0.05)

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It is also likely especially with respect to Cu which had a negative tissue to exposure concentration relationship that changes in membrane characteristics were induced to reduce the influx of the metal at the higher concentrations.

Non-essential metals may be accumulated without excretion or with some excretion (Rainbow, 2002). Much of the Cd accumulated by aquatic invertebrates is bound to metallothionein in the cytosol of the organ predominantly used for accumulated Cd storage (Langston and Zhou, 1987; Rainbow, 2002). The similarities of the BFs across the range of concentrations (see Table 12) also suggest that Cd accumulation in the periwinkles was without much excretion, but this requires confirmation with radiotracer studies. Similar results were obtained for Littorina saxailis from the Isle of Man (Daka and Hawkins, 2006).

The interactions obtained in the accumulation of Cd in mixed solutions suggested synergistic effects at the lowest Cu concentration (0.05 mg/L Cu) in combination with all Cd concentrations. However, at higher concentrations, Cu produced antagonistic effects on Cd accumulation. Daka and Hawkins (2006) have similarly reported that the accumulation of Zn by L. saxatilis from Zn and Cu combined solutions, indicated concentration-dependent interactions, switching from synergism at low concentrations of Cu to antagonism at high concentration of Cu. They suggested on mechanisms primarily targeted at reducing the influx of Cu rather than competition for ligands, resulted in a reduced accumulation of Zn. Looking at the accumulation pattern for Cu alone (Fig 14C) and that for the Cd + Cu mixtures Fig 15)), there is a trend indicative of a similar effect in T. fuscatus, whereby the regulation of Cu also led to antagonistic effects on Cd. The synergistic effects observed in combinations with the lowest Cu concentration (0.05 mg/L) might be as a result of the increased

The different accumulation patterns between Zn and Cu on the one hand and Cd on the other may be related to the fact that Zn and Cu are essential for metabolic activities. For example, carbonic anhydrase, carboxy-peptidase A and B and several dehydrogenases contain zinc, while haemocyanin contain copper. Conversely, Cd is considered a non-essential metal because it has no known biological function (Bryan, 1984). Accumulation patterns for essential metals include regulation of body metal concentration, accumulation without excretion, and accumulation with some excretion either from the metabolically active pool or from the detoxified store (Depledge and Rainbow, 1990; Rainbow, 2002). In the littoral crustacean Palaemon elegans, the body concentration of Zn does not show any change over an increasing range of dissolved Zn exposures until a threshold external dissolved availability is reached. Although new Zn is entering the body in significant amounts at all exposures but an equivalent amount of Zn is excreted to match the rate of Zn uptake. When the rate of Zn uptake from the solution exceeds the rate of excretion, the body concentration of Zn then rises above the regulated values. There also appears to be regulation of Cu in the same species over a wide range of Cu availabilities until regulation breaks down. Then an increase in body Cu concentration follows any further increase in dissolved Cu exposure concentration, with a pattern reflective of accumulation with some excretion. Some gastropod molluscs are known to be capable of regulating the levels of certain metals especially those essential for metabolic activities such as Cu, Zn, Mn and Fe (Bryan et al., 1983; Webb, 1990). The progressive reduction of the BF with increasing exposure concentrations (Table 12) show that both Cu and Zn are regulated in T. fuscatus. The accumulation patterns suggest that the uptake of these metals take place with excretion, with the rate of excretion adjusted to match the uptake to keep the tissue concentrations within the levels required for metabolism.

There was clear inter-site differences in the tolerance of L. saxatilis subjected to desiccation stress (aerial exposure at 24 oC). Animals from Laxey which suffered the least mortalities at extreme salinities were amongst the most susceptible to aerial exposure, whereas Castletown samples showed the highest tolerance. Mean LT50 values for the various sites are presented Table 6 and these were shown by ANOVA to be significantly different ($p<0.001$). Multiple comparisons by Tukey tests indicate that animals from both Castletown and Derbyhaven were significantly more tolerant to desiccation than those from Laxey and Ramsey. Individuals from Castletown also had significantly higher LT50 values than those from Peel ($p<0.005$); but no significant difference was found between the Derbyhaven and Castletown populations. Littorina saxatilis from all sites were less susceptible to desiccation stress than exposures to 0 psu and 60 psu

There were negative correlations between LT50 values for desiccation: 10 mg/L Zn and 5 mg/L Pb (Table 7) the concentrations at which clear tolerance was demonstrated for these metals by animals from Laxey Estuary (cf. Daka and Hawkins, 2004). All correlations between 0 psu and 60 psu and all metal-concentration combinations were positive, but most were not significant (Table 7). As indicated above, no significant differences were found in tolerance to extreme salinity stress in L. saxatilis from sites in the Isle of Man. However, significant differences were obtained on exposure to desiccation stress, with animals from Laxey which showed enhanced tolerance to Zn and Pb being amongst the most susceptible to desiccation. This implies that the detection of any physiological trade-off or "cost" of metal tolerance would depend on the stressor applied. The desiccation experiment detected an apparent "cost" of tolerance to metals as the LT50 values for desiccation were negatively correlated with LT50 values for exposure to 10 mg/L Zn and 5 mg/L Pb (the concentrations at which unequivocal tolerance was demonstrated for these metals by the animals from Laxey, Daka and Hawkins, 2004). Also, animals from the relatively uncontaminated sites, Castletown and Derbyhaven, were significantly more tolerant to desiccation than those from Laxey. The pattern of intraspecific tolerance to extreme salinity exposure did not detect any physiological trade-off in animals from Laxey. In fact, animals from Laxey nominally showed the least susceptibilities at both salinity concentrations. However, these responses would have to be examined in the light of uncontrollable spatial heterogeneity of conditions at the sites from which the animals were collected.

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Cd+Zn did not produce any significant differences in the accumulation of Zn for any of the metal combinations (Fig.19).

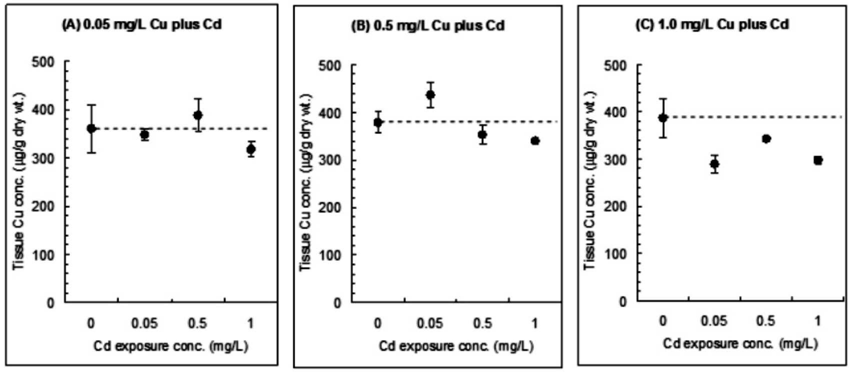

Figure 18: Concentrations of copper in *Tympanotonusfuscatus* exposed to copper (0.05 mg/L, 0.5 mg/L, 1.0 mg/L) and different concentrations of cadmium. Tissue Cu concentrations are in µg/g dry weight; values are mean ± SD, n = 3.

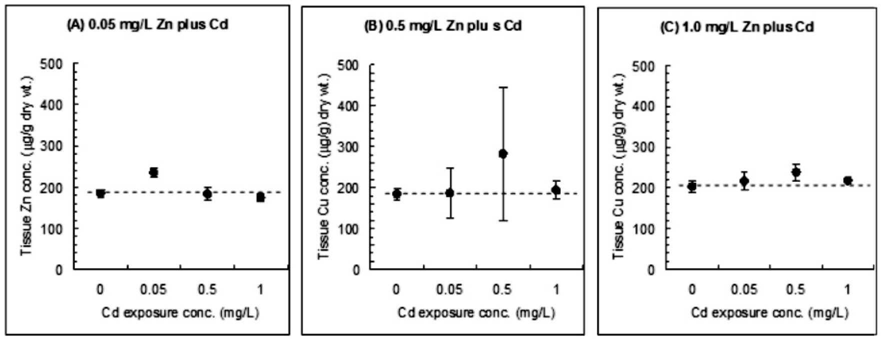

Figure 19: Concentrations of zinc in *Tympanotonusfuscatus* exposed to zinc (0.05 mg/L, 0.5 mg/L, 1.0 mg/L) and different concentrations of cadmium. Tissue Zn concentrations are in µg/g dry weight; values are mean ± SD, n = 3.

Figure 17 shows that the rate of Cd accumulation is affected by the addition of Cu or Zn. The addition of 0.05 mg/L Cu gave a regression coefficient higher than that of Cd alone in solution, while the addition of 0.5 mg/L Cu and 1.0 mg/L Cu gave lower regression coefficients; 1.0 mg/L Cu produced a higher depression of the slope than 0.5 m/L Cu (Fig.17). The addition of 0.05 mg/L Zn produced a higher depression of the regression slope of Cd accumulation than 1.0 mg/L Zn.

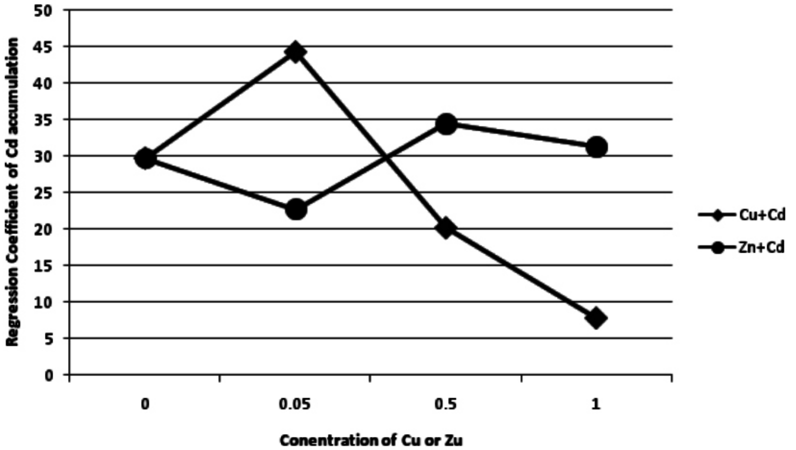

Figure 17: Accumulation of Cd in in *Tympanotonusfuscatus* exposed to individual metal solutions and from solutions containing binary mixtures (Cd+Cu or and Cd+Zn)

There was a tendency for Cu accumulation to be reduced in Cd+Cu mixed solutions; significant reductions in Cu accumulation were observed in combinations of 0.05 mg/L Cu with 0.5 mg/L Cd compared to 0.05 mg/L Cu alone (Fig.18A), and all combinations of 1.0 mg/L Cu with 0.05, 0.5 and 1.0 mg/L Cd compared to accumulation from 1.0 mg/L Cu only (Fig 18C). The exposure of the winkles to

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Table 7: Correlations (r) between LT_{50} values of *Littorinasaxatillis* exposed to general stressors (salinity and aerial exposures) and LT_{50} for exposure to different heavy metals. Asterisks indicate significant correlations (n=5)

Metals	Conc. (mg l^{-1})	Desiccation	0 psu	60 psu
Zinc	10	-0.403	0.881*	0.738
Zinc	20	0.528	0.772	0.909*
Lead	5	-0.587	0.797	0.552
Lead	10	0.091	0.614	0.441
Lead	20	0.308	0.838	0.795
Copper	0.5	0.321	0.822	0.916*
Copper	1	0.125	0.701	0.848
Copper	2	0.485	0.820	0.915*
Cadmium	1	0.283	0.302	0.219
Cadmium	2	-0.459	0.331	0.002

Levels of significance * $p<0.05$

In conclusion, it appears that metal tolerance may be exerting an effect on the ability of the population of L. saxatilis from Laxey to withstand basic intertidal stress, especially desiccation. This is probably a physiological trade-off in function but ecological differences between sites may partly account for the differences observed.

Reproductive effects of heavy metals (Daka and Hawkins, 2002)

It has been suggested that Littorina saxatilis could be a useful organism for monitoring the reproductive effects of contaminants because embryos are found in the brood pouches all year round(Dixon and Pollard, 1985). Embryonic development is internal and takes place in the brood pouch of the female so local pollution events would affect all stages of embryonic development. Hence, the number and size of juveniles may be affected. All stages of development from uncleaved eggs to pre-emergent fully formed juveniles can be found in the brood pouch of female L. saxatilis at the same time. However, in addition to normal stages of development, the brood pouch may contain a proportion of abnormally developed embryos. Sublethal concentrations capable of inducing tolerance to metals may exact reproductive effects. Also, tolerance may have energetic costs, which might indirectly affect reproductive output (Posthuma etal., 1993). The occurrence of such effects in L. saxatilis from sites around the Isle of Man with different levels of heavy metal contamination was studied. Inter-site differences in the proportions of abnormal embryos were examined to assess usefulness of reproductive indices in monitoring the effects of sub-lethal concentrations of contaminants.

For determination of fecundity and size of juveniles at birth about fifty animals of reproductive size (>6mm shell height) from each site were placed in white plastic containers after acclimatisation to 16 oC for 6 to 7 days in other tanks. The individuals transferred were thoroughly cleaned to avoid transfer of juveniles on the shells. The warm temperature was a means of inducing the free young to emerge from the brood pouch of the parents, which is entirely a function of the juvenile activity (Berry, 1961). Juveniles that emerged were removed from the containers every 24 hours for five days and preserved in 70 % ethanol prior to measurement. The measurements (accurate to + 0.001 mm) were made on a stereomicroscope (Wild Heerbrugg, Finlay Microvision Ltd.) equipped with a video camera. Images were captured and calibrated to a set magnification using NIH Image Analysis software (1.58 VDM) on a Macintosh Computer.Embryo abnormalities were determined in samples collected

Cadmium accumulation in solutions of 0.05 mg/L Cd in combinations with 0.05, 0.5 and 1.0 mg/L Zn showed a progressive reduction with increase in Zn (Fig.16A) and there were significant reductions between all Zn+0.05 mg/L Cd combinations compared to values in Cd alone ($p<0.01$). Reduced accumulations were also found in combinations of 0.5 mg/L Cd with Zn (Fig.16B), but these were not significantly different from Cd alone. Similarly, accumulations from 1.0 mg/L Cd with Zn did not produce any significant differences at any combination, although a tendency for enhanced accumulation was observe in the combinations with 0.5 and 1.0 mg/L Zn (Fig.16C).

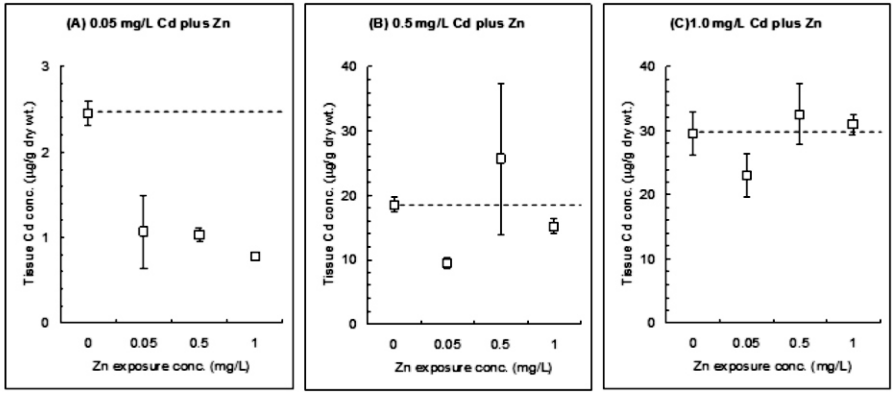

Figure 16: Accumulation of cadmium in *Tympanotonusfuscatus* exposed to cadmium (0.05 mg/L, 0.5 mg/L, 1.0 mg/L) and different concentrations of zinc. Tissue Cd concentrations are in µg/g dry weight; values are mean ± SD, n = 3.

negative relationship between net uptake and concentration which was not significant. This shows that Tympanotonus fuscatus is not a good candidate for the monitoring of these two metals in aqueous media. On the other hand, the accumulation of Cd from single metal exposures gave a positive concentration dependent relationship. This implies that T. fuscatus is good bioindicator of ambient Cd levels in solution.

Cd accumulation from binary mixtures with Cu showed interactions ranging from enhanced accumulation to depressed accumulation, depending on the interacting pairs of metals/concentrations (Fig. 15). A general pattern of response was observed at the three Cd concentrations. However, in interactions with 0.05 mg/L Cd, enhanced net uptake was found with 0.05 mg/L Cu and 0.5 mg/L Cu, the earlier giving more enhancement than the latter (Fig.15A). At 0.5 and 1.0 mg/L Cd, enhanced accumulations were found in combinations with 0.05 mg/L Cu, while reduced accumulations were obtained with 0.5 mg/L Cu and 1.0 mg/L Cu (Fig.15B and 15C). ANOVA and Bonferroni tests show that accumulations in all combinations of Cu with 0.5 mg/L Cd and 1.0 mg/L Cd were significantly different from accumulation from exposure to Cd alone.

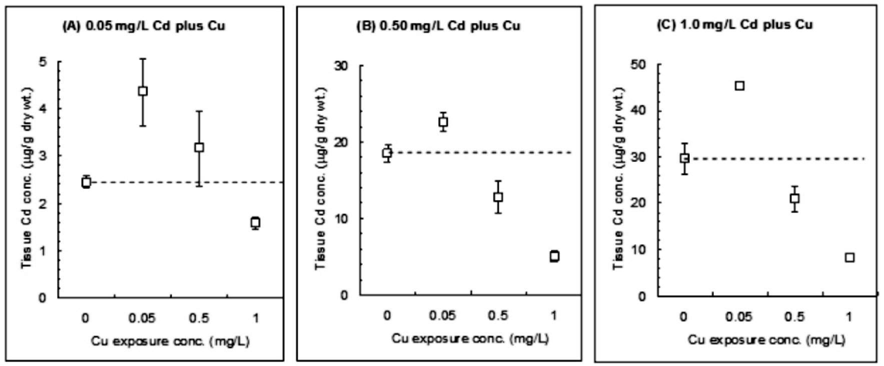

Figure 15: Accumulation of cadmium in *Tympanotonusfuscatus* exposed to cadmium (0.05 mg/L, 0.5 mg/L, 1.0 mg/L) and different concentrations of copper. Tissue Cd concentrations are in µg/g dry weight; values are mean $\pm$ SD, n = 3

during the middle of the reproductive season. After collection, animals were stored at ambient temperature in the laboratory for a few days before dissection. The brood pouch content of females were placed in a Petri dish and viewed under a stereomicroscope for counting and examination of embryo abnormality. Total number of embryos in each pouch was counted and each embryo was examined for abnormality. Abnormalities involving unshelled embryos (mainly characterised by the physical disruption of soft tissues, resulting in the presence of a number of separate, floating, cell masses within the egg capsule; double embryos) and shelled embryos (multiple embryos, mostly twins; abnormal shells, mostly uncoiled shells) were counted separately.

The results show that animals from Laxey, the contaminated site, had the highest mean number of embryos (Table 8). However, the animals from Laxey (with the highest absolute pouch content) had the smallest juveniles while those from Derbyhaven were the largest (Table 9). One-way Analysis of Variance showed a significant difference in the mean length at birth ($F_{4,1412}=123.0$, $p<0.001$). Tukey multiple comparisons indicated that significant differences conformed to the following order: Derbyhaven > Castletown > Ramsey > Peel = Laxey.

Much of the abnormalities in animals from all sites were found in the unshelled embryonic stages (Table 10). Individuals from Derbyhaven had by far the highest proportion of unshelled abnormals; those from Peel had the least with Laxey site showing intermediate values. The mean proportions of shelled abnormalities were similar in all sites. There was very high intra-site variability in the proportion of abnormals. Coefficients of variation ranged between nearly 100% to well over 200%. Contamination by heavy metals may be exerting direct or indirect effects leading to a reduction in the size of embryo at birth in L. saxatilis from Laxey Estuary. No evidence for induction of embryo abnormalities by heavy metals was apparent in this study. The high proportions of abnormal embryos in animals from Derbyhaven which are not known to be exposed to high levels of heavy metal pollution may be due to disease and/or genetic factors. It is concluded that embryo abnormality in L. saxatilis may not be a good indicator of sub-lethal effects of heavy metals in the field.

Table 8. Number of embryos in brood pouches of *Littorinasaxatilis* from five sites in the Isle of Man. Highest mean values in bold.

Site	N	Min.	Max.	Median	Mean	C.V. (%)
Castletown	39	46	798	338	359	45.7
Derbyhaven	63	38	690	278	289	47.3
Laxey	52	80	1117	**366**	**432**	59.5
Peel	46	70	835	320	357	56.0
Ramsey	50	115	580	287	305	34.3

Kruskal-Wallis One-way Analysis of Variance (H) and Dunn Tests ($p<0.05$):
H=9.86, p=0.043
Laxey = Castletown = Peel = Ramsey = Derbyhaven

Table 11: Regression equations, coefficients of determination and summary of regression ANOVA for accumulation of Cd, Cu and Zn by *Tympanotonusfuscatus* exposed to a range of concentrations of each metal

concentrations of each metal

Metal	Equation	R^2	ANOVA		
Cd	$y = 38.88x + 0.07$	0.999	1073	7514	<0.0001
Cu	$y = -116.5x + 357$	0.463	9656	4.5	0.125
Zn	$y = 4.7x + 173$	0.018	15.82	0.056	0.828

Bioaccumulation Factors (BF) were calculated as a proportion of the tissue metal concentrations to experimental exposure concentrations. The highest BF values were obtained for Cu, followed by Zn with Cd having the least (Table 12).

Table 12: Bioaccumulation Factors for *Tympanotonusfuscatus* exposed to various concentrations of heavy metals

Exposure conc. (mg/L)	Bioaccumulation Factor		
	Cu	Zn	Cd
0.01	36828	15636	92
0.05	6144	3814	35
0.10	3465	1676	37
0.50	719	379	40
1.00	213	171	39

However, while BF values reduced remarkably with an increase in the concentrations of Cu and Zn, those of Cd were considerably similar across the range of exposure concentrations. The accumulation profiles of the Zn and from single metal solutions did not indicate any concentration-dependent relationship. In the case of Cu, there was a generally atomic absorption spectrophotometer (Perkin Elmer Analyst 100). Linear regression models were used to determine the relationship between metal accumulation and exposure concentration. Analysis of variance (ANOVA) was applied to accumulation data from binary mixtures of metals. Where ANOVA showed significant difference between treatment combinations, Bonfferoni tests were used to evaluate pair-wise differences between accumulation from metal mixtures and metal alone (as control) for each exposure concentration.

The results show that, in individual metal exposures, the accumulation of Cd from the solution was monotonic with concentration over the range of exposure concentrations (Fig.14A) while those of Zn and Cu did not show linearity in accumulation with concentration (Fig.14B and 14C). The regression of tissue Cd concentrations against Cd exposure concentrations was significant ($p<0.0001$) with high coefficients of determination ($r2 = 0.999$). For Cu and Zn, no significant regressions were obtained and the coefficients of determination for the regressions were low.

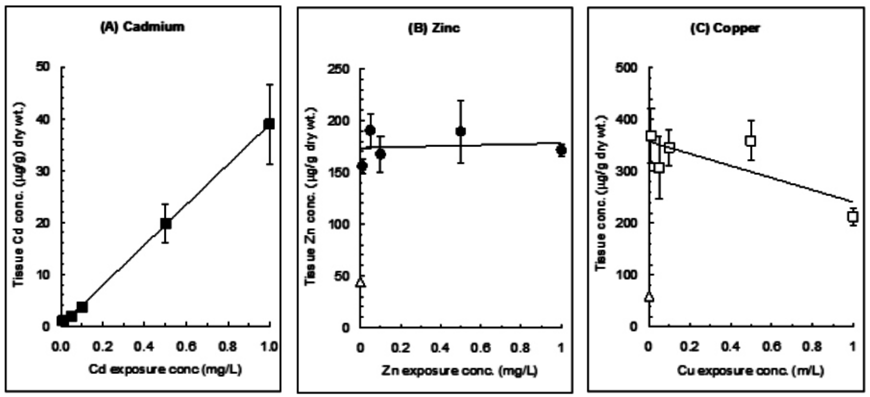

Figure 14: Patterns of accumulation of cadmium, zinc and copper in *Tympanotonusfuscatus* exposed to a range of concentrations of each metal in single metal exposures. Tissue metal concentrations are in µg/g dry weight; values are mean ± SD, n = 3.

Table 9. Size at birth (mm) of juveniles of *Littorinasaxatilis*from five sites in the Isle of Man. Lowest mean size in bold.

Site	N	Minimum	Maximum	Mean	S.D.
Castletown	186	0.405	0.876	0.574	0.071
Derbyhaven	103	0.457	0.776	0.632	0.063
Laxey	419	0.356	0.676	**0.518**	0.048
Peel	417	0.375	0.700	0.525	0.053
Ramsey	292	0.394	0.732	0.547	0.047

Analysis of Variance $F_{4,1412} = 123.0$, $p<0.001$.
Multiple Comparisons(Tukey Tests, $p<0.05$): Derbyhaven Castle town Ramsey Peel = Laxey

Table 10: Proportions of abnormal embryos (unshelled, shelled and total abnormals) in *Littorinasaxatilis* from five sites in the Isle of Man. Results of Kruskal-Wallis One-way Analysis of Variance are shown.

Site	N	Mean	C.V. (%)	Mean	C.V. (%)	Mean	C.V. (%)
Castletown	39	3.3	120	1.3	108	4.6	106
Derbyhaven	63	14.3	108	1.4	232	16.0	104
Laxey	52	4.1	170	1.4	188	5.5	171
Peel	46	2.3	131	1.0	117.8	3.2	99
Ramsey	50	3.0	100	1.0	124.1	3.9	99
Kruskal-Wallis ANOVA		H=33.87, p<0.001		H=4.16, p=0.386		H=25.03, p<0.001	

3.3 Studies on the gastropod mollusc *Tympanotonus fuscatus* in Niger Delta

Accumulation of heavy metals from single and mixed metal solutions by the gastropod mollusc *Tympanotonusfuscatus* linnaeus: Implications for biomonitoring (Daka *et al.*, 2006)

Mr Vice-Chancellor,Sir, having had extensive studies on metal accumulation patterns on a temperate gastropod, we decided to study a gastropod in the Niger Delta, and to assess its suitability as a biomonitor. The gastropod mollusc *Tympanotonus fuscatus* appears to satisfy a number of criteria for an ideal biomonitor. These include the ability to accumulate pollutants without being killed by the levels encountered in the environment; sedentary in order to be representative of the study area; sufficiently long-lived to allow the sampling of more than one year-class, if desired; be of reasonable size, giving adequate tissue for analysis; be easy to handle and identify, and hardy enough to survive in the laboratory to allow defecation before analysis (if desired) and laboratory studies of pollutant uptake; tolerate brackish water to allow transplantation; and the existence of a simple correlation between the pollutant content of the organism and the average pollutant concentration in the surrounding water (Phillips, 1980; Phillips and Rainbow, 1993; Langston and Spence, 1994). The assessment of the criterion concerning correlation of metal concentrations in an organism with that in the surrounding medium requires experimental studies of accumulation from media of known concentrations. We examined the accumulation of cadmium, zinc and copper from single metal exposure solutions to test the relationship between metal concentration dosages and tissue metal levels. The net uptake of metals from binary mixtures was also determined to evaluate the nature of interactions between metals and their implications for biomonitoring using *T. fuscatus*.

The gastropod Tympanotonus fuscatus belongs to the subclass Prosobranchia. They are found in intertidal locations and are widely distributed in coastal and estuarine areas in the Niger Delta. Periwinkles (T.fuscatus) were collected from the mangrove swamp near Eagle Island, Port Harcourt in the upper Bonny Estuary of the Niger Delta. Individuals were washed on site with surface water to remove mud on the shells and transported to the laboratory in plastic containers in quantities that were not overcrowded. Individuals of similar size (32 + 2 mm) were used to control for possible effect of size on the accumulation of metals. Individuals were acclimatized to laboratory conditions for four days using filtered water from the site of collection in 10L nitric acid pre-cleaned plastic containers. The water was replaced every other day to compensate for possible depletion of dissolved oxygen. The samples were then exposed to test solutions of the appropriate metal (Cu, Cd, and Zn) concentrations with concentration range: 0.01, 0.05, 0.1, 0.5, 1.0 mg/l added metal). Appropriate metal concentrations were made up by dilution of freshly prepared stocks of metal salts ($ZnSO4.7H2O$, $CuSO4.5H2O$ and $3CdSO4.8H2O$) with filtered estuarine water obtained from the site of collection of the test animals. The periwinkles were exposed in triplicate treatments (12 individuals per replicate) by submerging them in the metal solutions and controls (no metal added) in test chambers.

` In another experiment, the animals were exposed in triplicate (12 individuals per replicate) treatments to a combination of Cd and Zn or Cd and Cu. These were 0.05, 0.5 and 1.0 mg/L Cd in combination with 0.05, 0.5, and 1.0 mg/L Zn; 0.05, 0.5 and 1.0 mg/L Cu. In addition, individuals were also exposed singly to each metal concentration and control (no metal added).

Samples of ten pooled individuals per replicate were processed and analyzed for the required metals (Cu, Cd, Zn) by flame