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Ecological Risk Assessment (ERA) as a Tool to Pollution Control of the Tanning Industry

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Abstract Ecological Risk Assessment (ERA) is a tool vital to evaluate hazards and risks and eventually provide information that could assist in averting and remedying the threats. ERA for the first time has been directed to the tanning industry focusing both at the processing line and occupational hazard to the workers. This review paper attempts to address these aspects by exploring novel techniques used recently through relevant research. For example *Daphnia magna* (primary consumer) and *Escherichia coli* HB101 pUCD607 (Primary decomposers) were used to evaluate the community structure. In addition supportive techniques were also used such as deterministic and probabilistic models. Results using ERA were very successful which yielded a tangible pathway to manage both the pollution generation during processing and waste management at the 'end of the pipe'. It is also imperative to note that the study recognised the importance of integrating other techniques to further complement the reviewed approaches.

Keywords Ecological Risk Assessment, Models, Primary Consumers, Secondary Consumers, Occupational Hazards, Waste Management

1. Introduction

It is now common knowledge through studies particularly involving occupational health that indicate that direct contact with some industrial chemicals can cause disability, illness (toxigenic/carcinogenic) and death in humans [1]. In certain circumstances some minor exposures are known to cause the build-up sizeable toxic levels within living organisms. Some earlier studies by the reporting author have shown that solvents from degreasing and finishing are a source of exposure through vapors. Indeed simple aspects such day to day activities involving human health are vulnerable to toxic hazards. This has been observed by poor unskilled and unprotected handling of pesticides, tanning chemicals and treated hides, skins and leather. This was demonstrated through work done earlier where occupational hazards of the tanning industry were evaluated in details[2]. Other environmental hazards include visual impacts, excessive noise and air emissions closely associated with the leather sector.

Evaluation of the ecological profile or better known as the Ecological risk assessment and for this purpose, of the tanning industry entails consideration of and understanding the categories of hazardous waste, its identification, exposure assessment, ecological effects and risk characterisation[3]. To carry out this exercise and be able to identify the toxic nature of the resultant tannery effluent and particulate matter from the atmosphere, specific bioassays (to evaluate responses to stressors) and chemical analysis (to provide information on the concentration and identification of the stressor) procedures were applied to ascertain the contributing factors.

1.1. Ecological Risk Assessment (ERA)

Unless if anthropogenic in nature, chemical pollutants rarely attain acutely lethal concentrations in nature; thus the majority of their effects are expected to be sub-lethal. Estimation of the likelihood of effects from exposures to sub-lethal concentrations of contaminants in effluent plumes downstream of point sources poses a challenge when conducting ecological risk assessments (ERAs)[4]. In pursuance to this phenomenon the impact of the tanning industry will be evaluated through ecological risk assessment, which is a process that evaluates the probability that adverse ecological effects will occur as the result of exposure to one or more stressors. Studies conducted earlier have indicated that the objective of an ecological risk assessment is to determine and document actual or potential effects of contaminants. This approach is particularly directed to ecological receptors and habitats including fundamental basis for evaluating remedial alternatives. Ecological risk may be expressed as a probabilistic (Ecological Quantitative Risk Assessment (EQRA)) estimate of adverse effects (as in human health risk assessment), or may be expressed in a more qualitative manne[2,5,6].

Quantitative risk assessment (QRA) has been a technique

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of choice used to estimate the probability of an adverse event[22]. The position of QRA is strengthened with an integration of Monte Carlo simulation. This approach has been found to offer precise explanation to the uncertainty and variability associated with the risk[23]. When this theorem was directed to the tanning industry it was purely to evolve the principles of ecological risk assessment. Thus to clearly articulate the definition of the ecosystem it can be portrayed as a grouping of organisms (microorganisms, plants, animal) interacting together, with and through their physical and chemical environment, to form a functional entity[24,25].

Focusing on the true meaning therefore, the terminology related to risk assessment is not yet fixed. However after an initial statement of purpose[5,23,26], the process involves four primary stages described below in relation to the current paper:

1. Hazard identification – literally in this phase it has been explained generally and by various authors also in different manner. However the most direct one cited by the current author[3] identifies the toxic chemical or substance of concern and moves a further stage to include whether the hazard actually is harmful. The problem-formulation process will involve the evaluation of the stressor (earlier defined by the author as a substance that has the inherent ability to impose adverse effects upon a biological system) characteristics, determines also if the ecosystem is at risk, and possible inherent ecological effects.

2. Exposure assessment – this is stated as a second phase of approach to ERA and thus the same author in his earlier work, states that at this stage thrust is to determine the environmental concentration range of a particular stressor and estimating its rate of intake in target organisms. After establishing of the same the measurement will combine quantifiable indices that could be used describe the frequency and magnitude of contact. For future projections and development of tangible interventional goals mathematical models will be formulated to ascertain the resultant exposure to a stressor and to determine the outcome of a variety of scenarios.

3. Ecological effect is the next crucial stage which has to integrate toxicity assessments. To elucidate the factors affecting this particular aspects warrant the need to identify and quantify the adverse effects elicited by a stressor. Subsequently this will than make it easy to determine the cause-and-effect relationship detected in various ecologically threatened conditions. Resultant data include acute toxicity data which forms the basis of primary input needed during the simulation stage of the developed model.

4. Risk characterization – as a final input to the model this phase includes comparison of the exposure and stressor-response profiles to determine probabilistic effects taking into cognizance the contaminant and the predisposed population in the set scenario.

1.2. Bioassays

Bioassays involve usage of biotics (living organism) in controlled environment, responses towards xenobiotics, pollutants or contaminants in the environment (e.g. Phytotoxicity, bioluminescence response etc.)[3,27]. Bioassays have larger variability than most chemical analysis due to biological variation. The major advantage of bioassays is that the total toxicity of wastewater can be assessed by taking into account bioavailability and synergistic or antagonistic effects. Also, transforming information on concentration to information on biological response is useful for risk assessment. Chemical analysis provides information on the concentration of a substance in a sample and may help to identify that substance[28]. However, this does not give direct information relating to the bioavailability and impact of environmental pollutants.

1.3. Biomass Activity

Monitoring and evaluation of biomass activity (e.g. intracellular enzyme activity) has been established[17] at the river sediment level, the basis of this study was the provision of vital information on stressor-response and ecological effects. More advanced has well been articulated and demonstrated that knowledge related to the reduction of sediment capacity to act as a fully functioning mineralization medium for natural pollutant substrates (Figure 1) is critical in overall river health assessment[29].

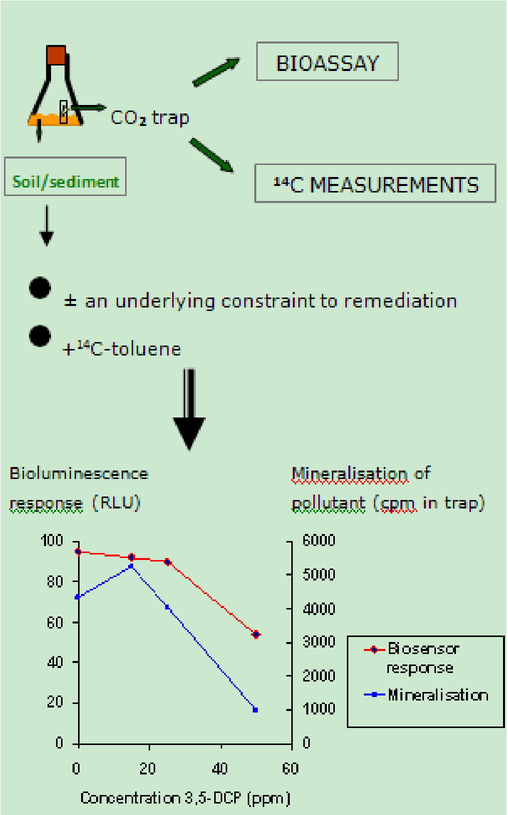

Figure 1. Correlation to Mineralisation of natural pollutant substrate and biosensor response[29].

1.4. Weight of Evidence in Ecological Risk Assessment

When carrying out weight of evidence in any ERA programmes it becomes quite necessary to utilise well defined pathways for an all inclusive risk assessment. One of such technique is the use of multiple criteria or multiple lines of evidence (also referred to as weight of evidence). This is reported in this paper and essentially used earlier in determining the ecological systems[7,8] and even recommended in evaluating risk to the environment[9-13]. Drawing from earlier presentation the following criterions such as Strength of association; Consistency of association; Specificity of association; Time order or temporality; Biological gradient; Experimental evidence and Biological plausibility, were chosen for application during preparation of this paper. This is because they have already been established in this area[14], and are readily applicable to environmental samples sourced from the Kenyan tanning industry. A linkage was developed using the three levels and seven tiers reported[15] (Table 1), involved in a casual identification, including identification of effects, development of correlative relationships and confirmation that specific chemicals are responsible for the observed effects.

1.5. ERA–Query Points

Two questions were developed to develop the Ecological Risk Assessment (ERA): (1) has the water quality of the river been affected by the discharged tannery effluent? and (2) has the river sediment health been affected by the deposition of the contaminants?

2. Discussion

2.1. Approach to Ecological Risk Assessment (ERA)

This paper envisages to discuss the ecological risk caused by the leather sector particularly its tannery industry. It is envisaged that this will be achieved by responding to the risk questions or query points raised here-above. In lieu therefore there is a dire need to establish attainable but well defined criterions as follows:

i) Identify stressors/hazards.

ii) Apply biological technique (e.g. Bioassay) and chemical assays (to determine heavy metals, COD, BOD, Total Phenols etc) – this for the purpose of determining the stressors and resultant effects to the environment.

iii) Determine through probabilistic models that the stressors (toxic chemicals from the tanning industry) cause quantified impact to the ecosystems.

iv) Ascertain the resultant impact of the risk mitigation put in place to curtail the ecological contamination risk.

Ecological evaluations require optimal techniques to determine potential impacts and risks. Therefore this study focused on risk assessments applying bioassays as a novel technique were a series of different scenarios integrating time as a factor to exposure of the bio-entity in identified system to the hazard, toxicity levels were conducted at known sampling points and bioluminescence evaluation determined on application of a genetically modified biosensor. The mentioned parameters was integrated and run using the deterministic model. Inclusively, chemical, identified modulation programme and protocols defined by the environmental agency in the US including capturing aspects related to acute toxicity in effluents[9-12] were adopted to ascertain ecological risk. Collection of experimental samples was obtained from both river sources and tannery lagoons. This approach of ascertaining ERA's also include the study of multiple stressors to provide an in-depth evaluation[3,16].

The investigation entailed the effluent treatment phase which started from raw effluent through treated effluent like general sedimentation and final effluent where for this case was carried out using anaerobic lagoons, explored upstream and downstream of the riverine by carrying out sampling which eventually provided the basis of risk assessment. To strengthen the statistical position of the study it was important to ensure that it was random and repeated eight times over a period of sixteen weeks. Parameters recorded included observations on visual (water colour, vertebrates, plants etc) and observable odorous peculiarities. Moreover to strengthen our scientific investigation biological and chemical investigations were performed to identify the class or causative aspects of the pollutants or contaminants involved.

Table 1. Identification Levels of Causal Determination by Identifying the Key Questions and Providing Appropriate Evidence[15].

Level	Tier	Approach	Key Question	Evidence
1	I	Point source confirmation Ecoepidemiological correlation	Do similar discharges cause the effect at other sites?	Comparability of responses at sites receiving similar Effluents
	II	Site-specific correlation	Is the effluent at particular site causing the changes?	Temporal and spatial compatibility with hypothesis of Causation
	III	Response pattern identification	Is the response pattern characteristic of a response type?	Comparability of response pattern with confounding stresses
2	IV	Process correlation systematic evaluation of process wastes	Where in the production process is the effect originating?	Experimental approaches that identify individual process wastes that are the source(s) of causative agents
3	V	Causal demonstration Chemical characteristic identification	Can we characterize the responsible chemicals by i) behaviour and response characteristics and ii) exposure characteristics?	Exposure conditions and initial effluent manipulations
	VI	Chemical class identification	Can we isolate or eliminate chemical classes that may be responsible?	Bio-assay directed fractionation
	VII	Chemical identification	What specific compounds are responsible for the effects?	Detailed fractionation, chemical and toxicological verification that candidate chemicals cause the effect

2.2. Approach to Data Analysis

To articulate the various scenarios carried out, the risk assessment model was run applying the deterministic model as indicated in Table 2.

Table 2. The different scenarios under which the risk assessment was run using a deterministic model adopted[3].

Scenario No	Scenario	Base Scenario value
1	Amount of contaminants in the effluents before treatment (C_{re}); i. COD ii. BOD iii. Cl iv.Sulphide v.SS vi.Total Cr vii.Grease/oil	 2437.84 1255 1725 62 562 23 332
2	Amount of contaminants in the effluent after sedimentation C_{sed}) i. COD ii. BOD iii. Cl iv. Sulphide v. SS vi. Total Cr vii. Grease/oil	 1579.30 5738 1875 57 448 1.71 273
3	Amount of contaminants in the final effluent C_{fin}); i. COD ii. BOD iii. Cl iv. Sulphide v. SS vi. Total Cr vii. Grease/oil	 1355.93 438 1926 89 330 0.9 94
4	Effect of introducing efficiency (percentage) during effluent treatment: i.) raw effluent ii.) sedimentation iii.) final effluent	 10 30 20

It is worthy to note that the input data for the model were obtained from the scientific literature, ongoing studies into tannery effluents in Kenya and expert opinion (Table 3). Importance analysis which incorporates quantitative ranking measures for components adequately conducted by performing deterministic model to determine stressors characteristics and correlate the impact with resultant contamination to the identified ecosystems.

2.3. Preview of Risk Assessment and Identification

2.3.1. Hazard Identification and Problem Formulation

Within the leather sector it was very important in hazard identification and problem formulation certain crucial aspects need to be considered. Table 4 depicts the processing stage, water pollutants and air pollutants and average trend in effluent produced over time as indicated in Figure 2.

i.) 1st stage of leather processing - soaking activities

An important stage and the most preliminary of the processes in the tanning industry is the soaking process. The processing of skins and hides at this stage targets cleaning, rehydration of the material, conditioning and facilitate attainment of appropriate moisture content. Once achieved than subsequent processes related to liming, deliming and pickling as important stages of beam house operations. Because of many of the raw material being wet salted apparently results in production of salts. Other debri or contaminants are also associated with free ammonia, mal-odours, soil related dirt, blood, dung and other related physico materials related to the bio chemicals and synthetics (e.g. wetting agents, surfactants, emulsifiers etc) which, are released during the tanning process.

Table 3. Model variables[3].

Variable	Description	Model formulae / Units
T_{re}	Toxicity measurements of raw Effluent	%
T_s	Toxicity measurement of effluent after sedimentation	%
T_{fe}	Toxicity measurements at final effluent	%
RE_v	Raw effluent values	mg L^{-1}
RE_{COD}	COD level in raw effluent	mg L^{-1}
RE_{BOD}	BOD level in raw effluents	mg L^{-1}
RE_S	Sulphide levels in raw effluents	mg L^{-1}
RE_{Cr}	Total Cr levels in raw effluent	mg L^{-1}
RE_{Ph}	Total phenols in raw effluents	mg L^{-1}
S_v	Effluent contaminant values after general sedimentation	mg L^{-1}
S_{efc}	Effluent treatment efficiency after general sedimentation	$S_{efc} = (RE_v - S_v) \times 100/RE_v$
S_{COD}	COD level in effluent after Sedimentation	mg L^{-1}
S_{BOD}	BOD level in effluent after Sedimentation	mg L^{-1}
S_S	Sulphide levels in effluent after sedimentation	mg L^{-1}
S_{Cr}	Total Cr levels in effluent after sedimentation	mg L^{-1}
S_{Ph}	Total phenols in effluent after sedimentation	mg L^{-1}
FE_v	Final effluent values after anaerobic lagoons	mg L^{-1}
FE_{efc}	Final effluent treatment efficiency after anaerobic lagoons	$FE_{efc} = (S_v - FE_v) \times 100/S_v$
FE_{COD}	COD level in the final effluent after anaerobic Lagoons	mg L^{-1}
FE_{BOD}	BOD level in the final effluent after anaerobic lagoons	mg L^{-1}
FE_S	Sulphide levels in the final effluent after anaerobic lagoons	mg L^{-1}
FE_{COD}	Total Cr levels in the final effluent after anaerobic lagoons	mg L^{-1}
FE_{Ph}	Total phenols in the final effluent after anaerobic lagoons	mg L^{-1}
P_{MCL}	Maximum contaminant levels (target) for identified pollutants	mg L^{-1}

ii.) Beam-house activities

This stage involves the preparation of the hide/skin (known as pelts) for stages prior to the tanning process. During this stage particular chemicals and enzymes are used associated with high volume of water are both consumed and spewed as effluents with a very high pollution load. Essentially the effluent is loaded with quite high dissolved substances, COD, suspended solids, chlorides, sulphides, organic nitrogen and high pH[3]. Indeed it has been reported that, conventional liming-reliming processes lead to 35-45 kg of BOD, 100-125 kg of COD and 140-160 kg of total solids (TS) for every ton of raw skins/hides processed[18]. Comparatively BOD and COD loads contribute 50-70% of the total load from a tannery wastewater while TS load accounts for 15-20% (solid waste containing lime sludge, fleshing and hair[19]. Thus it is quite apparent to note that beam-house activities contribute immensely to the total pollutant load of the tannery effluent. As an ecotoxicological concern it was important to review the role of sulphides which have been associated with the production of the toxic and foul smelling hydrogen sulphide gas. These investigations indicated that ammonical nitrogen (ammonium) resulted to high oxygen demand (which leads to anoxic conditions where loss of oxygen is quite toxic to biotic entities in aquatic systems), this conditions both lead to stimulation of eutrophication. What is emerging to-date is that conventional or traditional cleaning-up treatments do not reduce chlorides and sulphates levels after completion of the pickling solutions to meet the limits required by regulations; for example if chloride content in the region of 9 g L^{-1} way above most legal requirements could represent a considerable problem for biological plants[20].

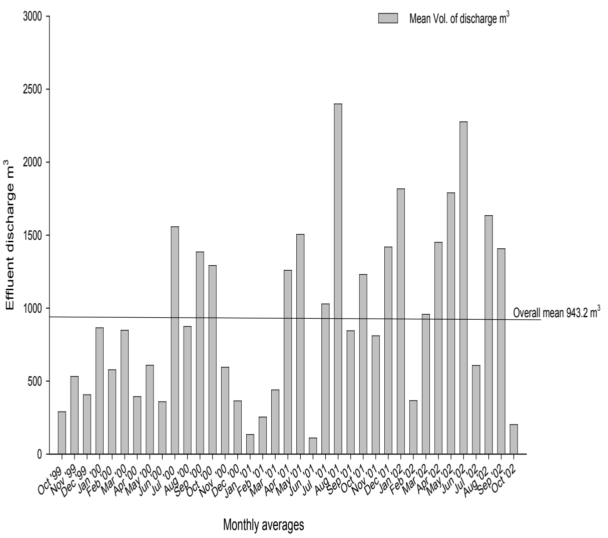

Figure 2. Tannery effluent mean monthly discharge 1999 – 2002 at a Kenyan site adopted[3].

iii.) Evolvement of Tan Yard Activities

Modern tanning processing utilise large volumes or quantities of water. It is important to note that the pelts quality based on the appropriate processing techniques. For example the tannery effluent in Kenya was found to be characterised with sizeable quantities of COD, surfactants, chlorides, sulphates, ammonium-N and chromium (mostly Cr^{3+}). Studies have indicated that a third of the output from the chrome yard is discharged to the effluents particularly in African countries where recycling is minimal. For instance chrome applied in tanning goes into useful leather with the rest (if not re-used) discharged into the effluent where this cause's the concern. In addition to the intra-substrate fibres in the pelts and leather form the major solid waste source where the effluent has high chromium concentration. In addition the liquors also contain organic and inorganic materials e.g. proteinuos material, neutral salts including sodium sulphate and chloride.

Table 4. Identified water and air pollutants depicted under the background of leather processing stages[17].

Leather processing stage	Water pollutants	Air pollutants
Soaking/Liming	BOD, COD, SS, DS, Sulphides	H_2S
Deliming & Bating	BOD, COD, SS	NH_3
Degreasing	BOD, COD, DS	
Re-tanning / Bleaching / Dyeing	Acids, Salts, Chrome, Chlorinated phenols	Volatilized, chlorinated phenolics

iv.) Post tanning activities

Post tanning activities compose mechanical operations (e.g. sammying, splitting, shaving and trimming), wet work, drying and finishing. These operations could yield a combination of solid wastes, squeezed-out water and unfixed tanning chemicals with the finishing process producing mostly air emission of solvents[21].

v.) Effect of Chromium

As has been discussed earlier about Chromium as an environmental concern it is also important to view it on a larger scope. Thus when occupational hazards are considered the toxicity and mutagenicity of hexavalent chromium is also important. When the valency behaviour chromium is considered the oxyanion, Cr6+ was found to be highly mobile in soil and water environments. On the other side trivalent chromium, is a cationic species and considered very immobile. This is associated with its low solubility, high adsorption and complexation. In effect therefore is the fact that due to its toxic characteristic and mobility, hexavalent chromium as a pollutant in the environment has often been considered pernicious than Cr3+. It has been established that when introduced into various ecosystems, the chromium speciation is easily altered in the environment or even persist (i.e unchanged for a long time) depending upon environmental conditions[30].

vi.) Effect of pH

The Kenyan tanning industry effluent was characterised to have a pH at discharge point observed to vary between 7.72 (Raw effluent) to 7.66 (Final effluent). What is important to note is that most of the biological processes are known to function at optimal levels nearly at pH (6.0–7.5). Due to the fact that hydroxylions, influence the carbonates level in aquatic media, it's imperative to determine pH of various media when evaluating technique. Another example For example the presences of carbonates and bicarbonates exert a buffering effect in water systems and could maintain the pH to tolerable range of (~6-8) following acid rain events for a long time (in years)[31].

Table 5. Characterization of the Kenyan Tannery Effluent Showing Identified Parameters and Levels in Three Main Phases (Raw Effluent, Treated Effluent and Final Effluent) (n=5)[3].

	Raw effluent	Treated effluent(Generalsedimentation)	Final effluent(Anaerobic lagoons)	LSD(5%)
pH	7.72 (0.19)	7.1 (0.1)	7.66 (0.24)	0.58
COD	2437.84 (660.3)	5978.16 (4626.1)	1307.4 (291.4)	8329
BOD	1255 (309.9)	5738.1 (4688.7)	438.5 (194.9)	8366
Cl	1725 (495.5)	483.9 (216.4)	1693.7 (757.4)	1719
Sulphide	62.4 (14.7)	57.2 (15.1)	89.96 (26)	60
Susp. Solids	562 (121.6)	448.2 (153)	330.67 (43.3)	394
Total Cr	23.02 (18.3)	1.71 (0.4)	0.93 (0.2)	33
Oil/grease	332.3 (108.2)	273.9 (101)	94.38 (31)	267

Figures in parenthesis are SEM's (Standard errors of means)

Other important observation indicates that the water solubility of most metals increases as pH decreases. Reduction of the impact of metal is important to underscore the environmental stability[31]. Metal toxicity (imparted by changes in speciation and partitioning effects of the metals)[32-34] and other pH dependent toxicity within the tannery effluents were observed.

2.2. Description of Exposure Assessment

2.2.1. First Line of Action-End-Points and Conceptual Model

To achieve end points and develop a conceptual model it is important to screen risk assessment. It is also important to include and review ecotoxicity literature review, and the complete exposure pathways, development of a conceptual model. In deed this is a an approach also used[35] when conducting exposure studies for threatened bull trout and rainbow trout. However, for the leather industry two main contaminants of the effluent (Chromium and Phenols) were earmarked, known to influence acutely or chronically toxically organism within an aquatic community. This was in the basis that direct exposure of the untreated effluent to the river was found to cause acute or chronic toxicity to the overall aquatic zoo and phyto organisms. The current status of the effluent after treatment was determined and evaluated for contents toxicity. The exposure pathways were therefore evaluated through direct contact with contaminated sediments and water. *Daphnia magna* (primary consumer) and *Escherichia coli* HB101 pUCD607 (Primary decomposers) were used to evaluate the community structure.

As was indicated in earlier paragraphs it is imperative to complement the bioassay test with chemical evaluation technique. As such river sediments were also analysed for heavy metals (Table 6). To determine the diffusion potential the speed and the depth of the river at the discharge point (1.17 m s^{-1} (high water levels –rainy seasons) to 0.513 m s^{-1} (reduced water flow period low rainy seasons)) were observed[3]. This inclusion brought to the fore the importance of river dynamics and dilution factor of the river.

Table 6. Total Phenols, pH, and Metal Concentrations of Tannery Effluent，Treatment Pits (mg L-1), Anaerobic Lagoons (mg L-1) and Riverine Sediments (mg kg-1).

Samp- les	Ph	Cr	Pb	Fe	Cu	Cd	Zn	Ni	Total Phe-nol
Beam-house	12	0.1	0	1.8	0.0	0.0	0.1	0	ND
General sedimentation	8.0	0.0	0	0.2	0.0	0.1	0.1	0	72
Chrome stripping	9.6	23	0.1	1.4	0.0	0.0	0	0.2	ND
Chrome sedimentation	8.3	192	0	7.4	0.1	0.0	0.7	0.5	52.9
Equalisation tank	8.1	0.3	0	0.5	0	0.0	0	0.0	36.8
Lagoon 1	7.8	0.1	0	0.2	0	0.0	0.0	0.0	30
Lagoon 2	7.9	0.1	0	0.1	0.1	0.1	0	0.0	NA
Lagoon 3	8.3	0.1	0	0.0	0	0.0	0	0.0	48.1
Lagoon 4	7.8	0.1	0	0.0	0.0	0.0	0.0	0.0	24.5
Lagoon 5	8.4	0.0	0	0	0	0.0	0.0	0.1	17.0
200m upstream	7.0	2	1	1139	0.5	0.0	2.0	0.8	ND
100m upstream	7.1	1.14	0	772	0.2	0.0	0.8	0.4	ND
0 m discharge point	8.0	1.4	0	423	0.6	0.0	1.6	0.7	30
100m Downstream	7.3	1.3	0	1048	0.4	0.0	1.1	0.6	17.7
200m Downstream	7.3	1.7	1	1362	0.7	0.0	1.2	1.1	11.4
400mDownstream	7.4	1.8	1	1349	0.5	0.0	1.3	1.0	5.5

LOD - The limit of detection (LOD) was determined on the basis of five blank samples at average blank signal plus three and ten times the standard deviation.
NA - Not available
ND – None detected

The study indicated above captured the following data which subsequently than assisted to determine the rate of exposure. For instance total chromium levels were highest at the chrome stripping (22.58 mg L^{-1}) and chrome sedimentation tank (191.47 mg L^{-1}). When the river ecosystem was observed, high levels of chromium in the sediments at 200 m (1.65 mg L^{-1}) and 400 m (1.76 mg L^{-1}) downstream. In tandem the observed trends was observed for all the metals analysed (Table 6). In interpreting this observation a clear observation was demonstrated a settling out of solution of the metals to the sediment as the speed of the river slowed downstream (between 0.68 and 0.40 m s^{-1}) in comparison to the discharge point (between 1.17 and 0.51 m s^{-1}). Organics in the other hand had its own peculiarity where, total phenols had no detection observed. The low levels of organics observed at the discharge point (Table 6), kept eventually diluting downstream.

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a.) Toxicity assessment of the trophic levels

The exposure assessment used the concentration ranges of the effluent (stressor) within all three phases (raw effluent, treated effluent (general sedimentation), final effluent (anaerobic)) (Table 6) to predict the fate and resultant exposure to the stressor using a mathematical (deterministic) model. Toxicity assessment on trophic levels involved actual downstream biotic (LD) values for daphnia (Table 7) and percentage bioluminescence for treatment pits, anaerobic lagoons and riverine sampling points.

Table 7. Lethal Dose (LD) Values of *Daphnia magna* on Treatment Pits, Riverine and Anaerobic Lagoons of a Kenyan Tannery Site.

Samples	LD values *D magna*
Treatment pits	
Beam-house	LD 50
General sedimentation	LD 50
Chrome stripping	LD 100
Chrome sedimentation	LD 100
Equalization tank	LD 90
Anaerobic Lagoons	
Lagoon1	LD 90
Lagoon2	LD 85
Lagoon3	LD 85
Lagoon4	LD 80
Lagoon5	LD 80
Riverine	
400 m upstream	NE
200 m upstream	NE
100 m upstream	NE
50 m upstream	NE
Discharge at 0 m	LD 85
50 m downstream	LD 80
100 m downstream	LD 80
200 m downstream	LD 80
400 m downstream	LD 60
600 m downstream	LD 60
800 m downstream	LD 50

b.) Invertebrate trophic level (Daphnia magna)

Higher LD values were observed at the treatment pits (Chrome stripping, sedimentation and equalisation pits) (Table 7). The anaerobic pits showed a reduction on LD values indicating a reduction in toxicity as the effluent flows from lagoon 1 (LD 90) to lagoon 5 (LD 80). Similarly, the trend was observed in the riverine sampling points, with lower LD values noted downstream. The dilution effect of the river (reduction of LD value observed progressively) downstream and the source of toxicity at the discharge point was demonstrated. There was no effect observed upstream for *D. magna* upstream (50m, 100m, 200m and 400m upstream), indicating that the source of toxicity was from the tannery effluent at the discharge point (LD 85) (Table 7).

Bioluminescence was generally low in all the treatment pits with extreme values observed within the Beam-house, general sedimentation and chrome-stripping tank. During chrome sedimentation, a slight reduction in toxicity is observed (with increased luminescence values) indicating effluent treatment effect at that stage.

c.) Primary decomposers trophic level (*Escherichia coli* HB101 pUCD607)

2.3. Outline of Ecological Risk Characterization

This phase comprised the comparison between exposure and stressor-response profiles to estimate the probability of effects, using the distribution or magnitude of the stressor in the areas sampled. When reviewing this work a link identified the 'cause and effects' (as shown in Table 1). This is further elaborated and established using correlative relationship and specific chemicals to determine the observed stressor effects[15] (Table 1).

Thus author in reference made an interesting observation where he conclude that 'the decrease in percentage bioluminescence (64%), dehydrogenise activity (0.0058 μgTFg^{-1} sediment 6 h^{-1}) and daphnia count (LD 85) values at the discharge point, and immediately thereafter downstream indicated the impact of the stressor to the riverine ecosystems'. However, to comment on the same further it was observed that no effect was observed upstream, demonstrating the possible source of contamination emanated from the tannery discharge point. In retrospect, similarly, chemical analysis showed that an increase of the stressor at the discharge point when compared to areas upstream and extreme sampling points downstream (Table 6 and 7).

2.4. Potential Ecological Risk Mitigation Suggested

Leather processing generally involves a combination of single and multi-step processes that employ as well as expel several biological, organic and inorganic materials[36]. As a follow-up in the review of this paper, base values (Table 2) were determined and model variables identified (Table 3) after the tannery effluents were analysed (Table 5). This was necessitated by the requirement to reveal in-plant methods of reducing the quantity and quality of the wastewater. By the beginning of the investigation, it was anticipated that there would be a reduction of the pollution load from the tannery. The result associated would therefore mean that there will be an improvement on water, energy and chemical consumption[21]. Hence, appropriate mitigation strategies are strongly envisaged for purposes of addressing complexes which were performed through an importance analysis using a deterministic model. The different scenarios (Table 2) are now included as probable mitigation strategies (Table 9). The reduction of contaminants and or increase in treatment efficiencies was also manipulated to meet target requirements in the effluent composition (Table 8).

2.4.1. Description of Mitigation Strategies

Certain mitigation has been developed to fit into the ERA redirected towards the leather industry. To achieve this a deterministic model was found to be able to amend so as to take into account a single input parameter change or alternately a change in one of the assumptions upon which the model is based. Essentially this was important when appraising the hypothetical risk mitigation strategies indicated in Table 9. These strategies can be implemented in the model and the change in the output (i.e. to meet set out domestic use in related maximum contaminant levels guideline for identified tannery effluent pollutants discussed in part I of an earlier paper) can be calculated to determine whether it is feasible or not. The following strategies were considered as detailed in a study by[17];

Table 8. Key Questions and Evidence for Causal Determination to a Riverine Ecosystem at a Site in Kenya (Adopted[3]).

Tier	Key questions	Evidence
I	Do similar discharges cause the effect at other sites?	Yes - Studies of a tannery (Bulleys) in another town (Thika) showed similar effects (with current site).
II	Is the effluent at particular site causing the changes?	Yes - refer to upstream, discharge point and downstream results (Table 7).
III	Is the response pattern characteristic of a response type?	Yes - as areas of low toxicity (upstream) behave different to exposed areas downstream
IV	Where in the production process is the effect originating?	Mostly the beam-house and tan yard and reported in related studies elsewhere[20,37].
V	Can we characterize the responsible chemicals by;- i.) behaviour and response characteristics and ii.) exposure characteristics?	Yes, through use of bioassays (different trophic levels), biomass activity (river sediment) and chemical analysis from effluent production to ecosystem receptors (Table 4, 5, 7).
VI	Can we isolate or eliminate chemical classes that may be responsible?	Yes through use of clean technology and remediative options on tannery effluents treatments (e.g. charcoal, sparging, filtration and pH adjustment)
VII	What specific compounds are responsible for the effects?	Chemical analysis results (Table 6)

Strategy 1: Reducing contaminant levels in the raw effluents (mg L^{-1}). The author implied that the base result took into cognisance that reduction of the contaminant was targeted to the raw effluent phase. At this stage one isn't required to carry out the function at that stage. The concluding remark at this level was that the reduction on effluent contaminant load, reuse of recovered liquor and recycling of spent liquors during processing was recommended to attain the requirement of this mitigation strategy.

Strategy 2: Reducing contaminant levels at the treatment pits (chrome stripping, sedimentation and equalisation tank) (%), After dealing with the first strategy where we concentrated with the raw material, we now review the second strategy where the focal point was on formulating interventions at the treatment pits holding all procedures intact.

Strategy 3: Reducing contaminant levels (%) in the final anaerobic lagoons. At this stage a quick review demonstrates that an easy to adopt and cost effective technology integrating physical-chemical treatment eliminated 95% of suspended solids and 70% of BOD[20,21]. Moreover, after the secondary treatment the tertiary phase which included filtration, stripping, Redox processes further assisted the decrease in the contaminant load in the effluent from the tannery[21,38,39]. In contrast we still needed another strategy to assist in improving the efficacy of decreasing the total produced effluent in the production process. The author enumerated that absence of using cleaner technology was resultant to the inadequacy of efficiently reducing optimally the contaminant load.

Strategy 4: Combination of strategies 1, 2 and 3. At this stage the temptation was to 'hybrid' all the previous strategies a more elaborate improvement was established especially to improve on effectiveness and efficiencies at both treatment pits and anaerobic lagoons as illustrated in Table 9.

Therefore it will be realised that the decrease in pollution and contaminants load and or intensification in providing more effectiveness and efficiencies if treatment are adjusted within the model to attain set targets (Table 9).

2.4.2. Adopted Mitigation Calculation

The applicability and effectiveness of risk mitigation strategies (Table 9) was attained after performing a deterministic model for the scenarios detailed in Table 2 and variables in Table 3. The effectiveness and formulation of each individual mitigation strategy used a calculation approach shown as per the description indicated in Table 10.

Table 9. Effectiveness of Risk Mitigation Strategies by Increasing Efficiency of Effluent Treatment at Various Levels[3].

Strategy		Amount of reduction expected in raw effluent (mg L^{-1} or %)	Increased(%) Efficiencyat Treatment pits	Increased Efficiency(%) at anaerobic lagoons treatment	References and Recommendations to achieve targets.
1.)Reducing contaminant levels in the raw effluents (mg/ l)	-COD -BOD - Cl -Sulphi-de - SS -Cr Grease/ oil	639.9 968.5 829.4 58.6 391.7 10.2 296.7	Remain unchanged	Remain unchanged	- water conservation - reduction of waste, reuse and recycling of process liquors[20,37].
2.)Reducing contaminant levels at treatment pits (%)	-COD -BOD - Cl -Sulphi-de - SS - Cr - Grease /oil	Remain unchanged	52.2 4.4 43.6 94.8 75.8 95.9 91.3	Remain unchanged	Simple technology use of physical-chemical treatment allows removal of 95% of suspended solids and around 70% of BOD[20,21].
3.)Reducing contaminant levels in the final effluents (%)	-COD -BOD - Cl -Sulphi-de - SS - Cr - Grease /oil	Remain unchanged	Remain unchanged	36.7 98.3 46.7 91.2 77.7 70.8 96.3	Tertiary treatment (filtration, stripping, Redox processes[21,38,39].
4.) Combination Of strategy 1, 2 and 3 (%)	-COD -BOD - Cl -Sulphi-de - SS -Cr Grease/ oil	79 80 65 80 74 90 80	47 47 47 47 47 90 60	26 25 22 68.5 22 50 25	Clean technology and rationalisation (recovery and reuse of primary resources) of the operating step s in leather manufacture[20,21,37] and increased efficiencies at the treatment pits and lagoons.

Table 10. Mitigation Calculations for Each Strategy, Which Ensures That the Acceptable Maximum Contaminant Level (MCL's) is Attained (Adopted[3].)

Description	Mitigation calculations
Strategy 1: reduce stressors at raw effluent Levels (Processing)	α = REv – (PMCL/((1- Sefc) × (1 - FEefc /100)))
Strategy 2: Improve efficiency of effluent treatment pits (After general sedimentation)	α2 = 100× (1 – (PMCL/ (REv × (1- FEefc /100))))
Strategy 3: Improve efficiency of Final effluent treatment (After anaerobic lagoons)	α3 = 100× (1 – (PMCL/ (REv × (1- Sefc /100))))
Strategy 4: Combination of strategy 1,2 and 3	α + α2+ α3 = REv× (1 – *REv/100) × (1- *Sefc /100) × (1- *FEefc /100)

* Depicts predicted values to meet target MCL's value

For example using strategy 1; α = REv – (PMCL/((1- Sefc) × (1 - FEefc /100))). To attain the MCL's target for COD which is 1988.4 mg L-1 (mg L-1) corresponding to alpha = 100%.

where $RE_v = 2437.8$ mg L^{-1}
$S_{efc} = 35.22$ (%)
$FE_{efc} = 14.14$ (%)
$P_{MCL} = 250$ mg L^{-1}

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2.4.3. Achieving the Targets towards Mitigation Strategies

The author found out that in achieving the set mitigation strategies there were two principal approaches i.e. operational and waste management factors (Table 11) that formed a fundamental basis if developing ERA. To fathom the idea further the study came up with three main domains which literally incorporated rationalisation through risk assessment model development; leather processing (raw effluent); increasing efficiencies during effluent treatment e.g. chrome stripping, effluent equalisation/sedimentation and final effluent treatment directed towards aerobic or anaerobic lagoons as detailed earlier on in this paper.

Table 11. Two-fold Factors (Operational and Wastewater Management) Towards Achieving Targets in Risk Mitigating Strategies (Modified 20, 21, 37]).

Factors	Interventions
a.) Operational	Use of chemicals having low toxicity or less environmental impact.
	Near 100% utilisation of chemicals.
	Out-of stock or surplus chemicals should be returned to the supplier or stabilized and re-packaged before disposal.
	Product innovation.
	Integration of processes.
b.) Wastewater management	Continuous pH monitoring during the critical phases of oxidation.
	Emission monitoring for hydrogen sulphide.
	Enhanced biological oxidation.
	Nitrification and denitrification (improvement in sedimentation efficiency).
	Chlorination of final effluent.
	Normal sewage type human waste and ordinary waste from office activity, building and repair should never be mixed with the tannery effluent (could complicate biogeochemistry of the efflu- ent in rivers if discharged).

For example the results also concurred with findings related to other investigators in relation to the effluent treatment phase[20,37]. Other areas of interest included different phases of the processing stages where interventions there would impact on the final contaminant load. Appropriate recommendations[37] suggest the re-use of sodium sulphide in an effort to reduce its impact and reduction of enhanced aerobic conditions in the lagoons[21]. Of interest though was the clarity that came out of the study implying that a well strategized intervention was required in particular at the beam house where appropriate mitigation will positively reduce on the final effluent at the tannery. This result was again supported with suggestion that 60% or more of the total pollution in the tannery effluent was associated with Beam-house operation[37].

3. Conclusions

This paper attempted to preview the essentials of ERA as a viable tool, taking a holistic approach on earlier versions that were used to evaluate risks e.g. QSAR, QRA etc. For instance, it would be noted that either the techniques mentioned here-above purely used mathematical approaches or used only chemical analysis. However in this study a new approach which targeted the tanning industry has been formulated. In assessing the impacts all the crucial stages of the tanning industry were involved. This approach assisted in identifying all the stressors in the value chain. Essentially therefore individual levels were ascertained giving the model developed an independent interventional strategy. Most intriguing though was the tremendous achievement attained by the author when he developed different strategies from various processing points. Although the effectiveness and efficiencies were varied at each stage, the use of all the strategies using the mathematical formulation indicated under Table 10 was opportune. In particular there was a reduction of the stressor level at the end of the treatment phase. Categorisation and partitioning of the contaminant load during the processing of leather was important and very fundamental. For example the study clearly indicated that the most prone area that caused high levels of pollution was the beam house than any other place in the leather processing phases. The demonstration of the models has heralded a new frontier in the leather sector where not only can we predict the levels and points prone to contaminant load but also assist in developing strategies to remediate and manage the environmental concern of the tanning process worldwide. The critical area that may need to be integrated is the LCA (Life Cycle Assessment) so as to make the technique of ERA not only in managing the leather processing but also accountable to the environmental impact accruable from leather products developed and its associated lifespan.

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