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**THE IMPACTS OF BIRD FAECES ON BOAT TEXTILES
AND FINISHING COMPOSITION**

Thesis

**CENTRAL OSTROBOTHNIA UNIVERSITY OF APPLIED
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Thesis Abstract

Department Technology and Business, Kokkola	Date May 2010	Author Lewis Wandah
Degree Programme Chemistry and Technology		
Research problem/Assigned development task The impacts of bird faeces on boat textiles and finishing composition		
Principal lecturer Staffan Borg	Pages 72 +12 APPENDICES	
Supervisor Jana Holm		
Working-life supervisor Liisa Niemi		
<p>This thesis deals with the damage caused by bird faeces to boat textiles and finishing compositions. A survey was conducted to find out from boaters perspective if the bird faeces cause any damage on the boat textiles and the environment or not? Samples of bird faeces were collected from three strategic sites in Kokkola. They were classified using a gas and ion chromatographic techniques, and an atomic absorption spectrophotometer to determine the contaminants content. The detrimental aspects of the contaminants to the boat textiles, hulls and the environment were researched and experimented.</p> <p>A sample of boat canopy damaged by bird faeces was cleaned with different concentrations of 303 fabrics cleaning agent to lay a platform for resource optimization. The colour fastness of the cleaned canopy was assessed following the European Council ISO 105-A05:1996 standard.</p> <p>Some primary and secondary solutions to prevent and manage the impacts of bird faeces on boat textiles, finishing composition and the environment are proposed. The result of this study will form a pathway for the PROBOAT project to lay a foundation for a pro-environmental /ecological finishing composition of boat.</p>		
Key words: Bird faeces, contaminants, boat textiles, anti fouling paint, pro-environmental / ecological finishing		

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LIST OF BOAT TEXTILE TERMINOLOGY

Abrasion resistance: the degree by which a fabric is able to withstand loss of appearance through surface wear, rubbing, chafing, and other frictional actions.

Absorbency: the ability of a fabric to take in moisture ,since it affects many fabric skin comfort, static build-up, shrinkage, stain removal, water repellence, and wrinkle recovery.

Acrylic: a manufactured fibre derived from polyacrylonitrile with soft, wool-like hand, machine washable and dryable, excellent colour retention properties.

Air permeability: the porosity of a fabric as estimated by the ease with which air passes through it.

Anti-bacterial or anti-microbial fabric: a fabric that has been treated with anti-bacterial chemical to make it resistant to or inhibit the growth of micro-organisms

Antifungal: a chemical or any means used to inhibits or kills fungi

Bactericide: a chemical used to kills bacteria.

Bacteriostat: the process of slowing down or inhibiting the rate of bacteria growth.

Bleaching: a process of whitening fibres, yarns, or fabrics by removing the natural and artificial impurities to obtain clear whites finished fabric.

Colour fastness: the change of original colour intensity to a reduced intensity by removing the natural or artificial tailored colour.

LIST OF BOAT STRUCTURE TERMINOLOGY

Bow and stern: the front and rear of a boat respectively

Starboard: the right side of a boat

Port: the left side of a boat

Hull: the body of a boat

Gunwale: the upper edge of a boat's side

Beam: the maximum width of a boat

Freeboard: the distance from water to lowest point of the boat where water could come on board

Draft: the depth of water needed to float a boat

Propeller: the part of the boat that rotates, control and powers a boat forward or backward

Keel: the main centreline (backbone) of a boat or the extension of hull that increases stability in the water

LIST OF ABBREVIATIONS

LC: Liquid Chromatography

GC: Gas Chromatography

IC: Ion Chromatography

AAS: Atomic Absorption Spectroscopy

ppm: part per million

IEC: Ion-exchange chromatography

IPC: Ion-pair chromatography

GC-MSD: Gas chromatography connected to mass selective detector

HC: Hydrocarbon

FWA: Fluorescent whitening agent

DAFF: Dissolved air flotation filtration

FTCs: Freezing-thawing cycles

GHG: Green house gas

UV: Ultra violet

1 INTRODUCTION

The boat building is a traditional work in the Ostrobothnia region. It has evolved from traditional methods to hi-tech methods, leading to the construction of all sorts of sophisticated boats. Fishing boats are built nowadays to resist offshore high waves and hazards. Leisure boats are built to supply the best comfort offshore. Racing boats are built to sustain speed and also protect the racers at high seas waves. Generally, the finishing compositions of offshore sea boats need to be resistant to damage from harsh salty sea water and other pollutants. Little attention is given to the impacts of seabird faeces on the boat textiles, finishing compositions and the environment.

Boaters have faced problems with their boat efficiency and hull durability. Most blame is to the quality of boat material. This is not all what is required for boat inefficiency. It is the owner's responsibility to understand that the quality, efficiency and durability of his or her boat also depend on his or her action actions. These actions include inspecting his or her boat frequently for any fault, strengthening his or her knowledge about parameters that affects the boat. Also, it is his or her responsibility to ensure that his or her boat do not pollute the environment. This is important because the present marine environment sustaining fishing, sailing and leisure at sea is the same environment that will be required for the same and may be more sophisticated sea-life in the future. Pollutants such as CO₂, SO_x, NO_x, Cu and Ni enter the marine environment, pollute it and prevent sustainable development in boating life.

Factors affecting boat efficiency and durability have been underlined by many experts, but the effect of contaminants found in bird faeces have been underestimated for the past. Deterioration of boat hull, fouling impacts, boat textiles and finishing composition degradation are some of the problems highlighted. The impacts of bird faeces on the boat textiles, finishing composition and the environment will be studied in this thesis. The boat textiles under this thesis scope are canopies, cover and other natural or synthetic fabrics used on the boats.

One of the reasons why bird faeces might have been underestimated might be due to the fact that fishing boaters are concerned about their competition for prey (fish) with birds. Bird protection organizations such as Birdlife are concerned about the killing of birds in fishing nets. Seabirds serve fishermen and sailors to locate fish shores and Island respectively. Therefore, there might be concern about the benefits of seabirds to them and not the impacts of bird faeces to their boat and the environment.

This thesis explores the damages caused by bird faeces onto the boat textiles, finishing compositions, and the environment. The objectives of this thesis are to:

1. Identify contaminants in the bird faeces and study their impacts on the boat external textiles and finishing composition, and the environment. Samples of seabird faeces were collected and classified.
2. Determine the optimum concentrations of the cleaning agents that would effectively clean the stains (one of the studied impacts) on the textile without colour fastness. This would ensure resource use optimization. Practically, cleaning the canopy with different concentrations of a cleaning agent gives a clue of the contaminants mechanism of embedment into the textiles and characteristic properties causing impacts. These could aid to postulate prevention and cleaning technique.
3. Underline some solutions used by the boat builders to prevent the studied impacts, investigate the environmental impacts of these solutions and bird faeces.
4. Finally, make a designed-for- the environment proposal for possible solutions that would prevent the impacts of bird faeces to the boat textiles and finishing compositions. This would ensure sustainable development in the boat sector taking its environmental impacts into consideration.

In order to understand the level of these problems from the boat owners, producers and repairers point of view, a survey will be conducted by sending out some questionnaires to them. The responses will analyse and measures will be taken further depending on the response analysis.

This study research questions are: What are the compositions of bird faeces? Are they responsible for the damage inflicted onto the boat textiles and finishing compositions? Via which mechanism are the contaminants absorbed into the highly protective boat synthetic

textiles? How do they affect these boat textiles and the environment? What can be done to prevent their impacts? Has research been conducted in this area and have solutions been suggested to the damage? If yes, have they been successful or have they led to further problems?

Samples of bird faeces will be collected at strategic places and analyzed for possible contaminants. This study is limited to the faeces of birds around Kokkola area. Birds at different places might have different faeces composition depending on what they eat. Their faeces composition might differ from those around Kokkola and would therefore have different impacts on the boat textiles and finishing composition. The season on which the samples are collected plays a role on the composition of the bird faeces. Bird feed on fruits like berries which are available only seasonally.

The sampled bird faeces could not cover all the bird species whose faeces could affect the boat textiles. The samples can only be collected from birds available at the season and in the area of Kokkola. Collecting faeces samples from a wide range of birds could give an overview of the contaminants that could be held responsible for damaging boat textiles, finishing compositions and the environment. Therefore, the composition of all seabirds faeces are assumed to be based on the compounds found in the collected samples.

2 SEABIRDS MIGRATION, FEEDING AND INTERACTION WITH BOATS

The interactions of seabirds and boats lay the pathway through which the bird faeces could reach the boat textiles, finishing compositions and the environment. Seabirds migrate seasonally to other places where they feed on different food source, varying the composition of their faeces. Due to seabird interaction with the boat, these components cause major problems to the boat parts concerned in this thesis.

2.1 Interactions of seabirds and boat

There has been an increase in industrial fisheries around the globe during the 20th century. This has led to an increase in the level of interactions between seabirds and commercial fisheries in both coastal and pelagic systems. This interaction leads to competition between fisheries and seabirds for fish, killing of birds in nets during fishing and seabird feeding on discarded fish and offal. Subsequently, seabird drops their faeces randomly as they interact with the boaters. These faeces cause problems to the boat textiles, finishing composition and surrounding environment. (Sullivan 2010.)

Seabird relationship with fisheries and sailors has advantages and disadvantages to both parties. The advantages includes the use of seabirds used as indicators of fish shoals in water banks that might signify fish stocks; the association of seabirds with lands off shores permitting sailors to locate small land masses; the use of seabirds as source of food to sailors and fishermen off shores, and seabirds such as the cormorant have been used to catch fish. When seabird faeces accumulate in the ground, they mix with the soil to form guano. Guano has been used to increase soil fertility due to the rich nitrogen containing compounds. (Hildén 1997.)

Meanwhile, raiding by seabirds on aqua farming is of negative effect to fishermen. The seabirds flock together with the fishing vessels and sailors, and compete with fisheries for fish. Approximately 70 % of surface eating seabird's total food in certain areas is made up

of discarded fish and offal. The competition between fisheries yields and seabird's food has led to problems in fisheries management. (Hildén 1997.)

This interaction results in frequent disposal of bird droppings on boat textiles. According to Donoho (2010), “left unattended, bird droppings can stain surfaces, and eventually erode materials, not to mention the health risk: bacteria and parasites can also be found in bird droppings”.



GRAPH 1. Bird droppings on boat textile cover (copyright from Meredith Walako 2009.)

2.2 Seabirds as contaminants transmitters

Seabirds are seasonal migratory birds. The timing of the different seasonal stages of their development depends on climate and its variability. In their annual life cycle, this dependence appears directly in the variance of the timing of spring or autumn migration,

breeding period and egg-laying, and indirectly in changes at the population level (Palm, Leito, Truu & Tomingas 2009).

As seabirds migrate seasonally from one place to the other, they feed on different substances and form potential mechanical vectors in transporting chemicals and bacteria from one place to the other via their faeces droplets. Some of these chemicals and bacteria have negative impacts on the boat textiles, finishing composition and the environment. This makes seabird serves as bio-indicators in assessing the toxicological effect of different elements and bacteria in an ecosystem. (Pérez-López, Cid, Oropesa, Fidalgo, Beceiro & Soler 2005.)

Seabird faeces contain contaminants from different migratory or geographical areas. When their faeces touches the boat textiles such as the top cover and canopies, and finishing composition such as the painted hull and the varnished gunwale, the contaminant might penetrate the fabrics and finishing compositions of the boat. Contaminants weaken the fabric strength; leave undesirable marks and stains; and cause colour change, the growth of mould, mildew and fouling organisms. All these have adverse effects on the boat efficiency. The seabird faeces and ornithological soils during freezing-thawing cycles (FTCs) under standard atmospheric condition and nitrogen (N_2) emit carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) which are greenhouse gases (GHGs). (Zhu, Liu, Ma, Sun, Xu & Sun 2009.)

As a consequence of weakening boat textiles (canopies and covers) by bird faeces contaminant, the fabric yarn loosens up. This expands the micro-pores on the fibres and they become more permeable to water, losing their waterproof natures. The acids content changes the brightness of these fabrics and this is known as colour fastness. (ISO 105-A05 1996)

The bacteria content furnish the growth of bacteria, mildew and mould on the textiles. When the contaminants enter the surrounding aquatic environment containing the boat hull, they fertilize the growth of certain living organisms such as algae, barnacles, and weed on boats hull. This is known as fouling and the organisms causing this are called fouling organisms. When fouling organisms grow on boat hulls and propellers, they create backward-drags and frictions. These impacts in turn reduce the boat speed and

manoeuvrability, therefore causing fuel consumption inefficiency and safety at high sea. Anti-fouling paints are used to prevent fouling organisms, although some have been shown to have further effects to the aquatic environment and lives. They leach out toxic biocides into the marine environment causing pollution (Turner, Fitzner, & Glegg 2007).

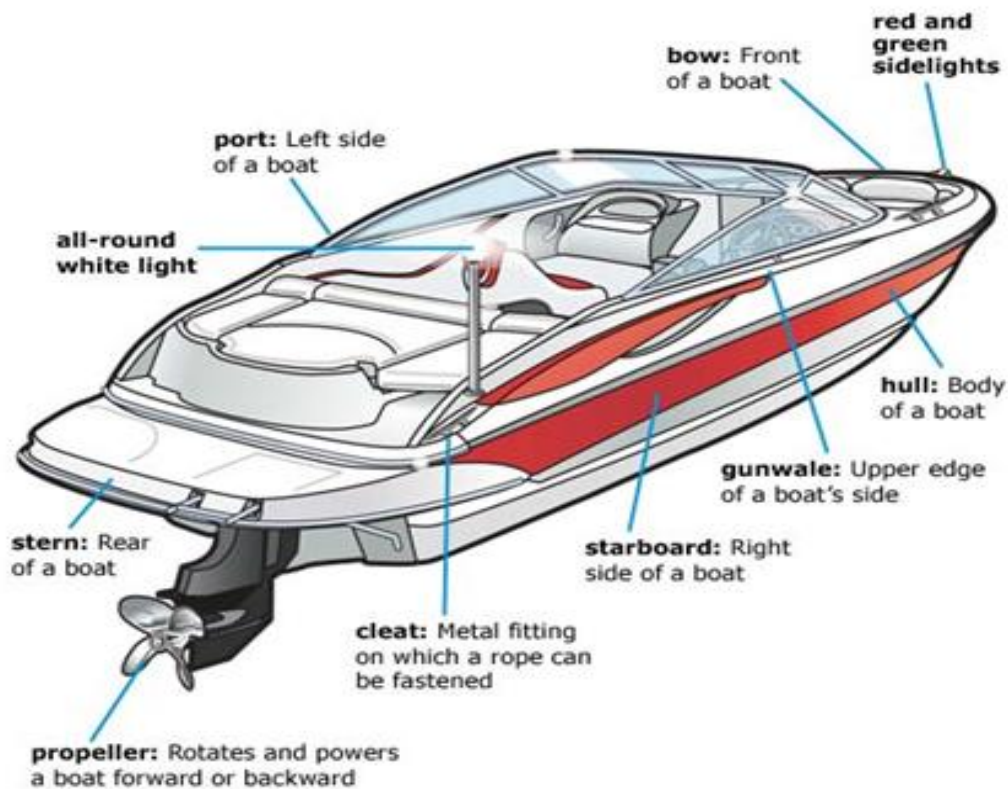
Some measures used by the boat textiles producers, boat finishing paints producers and boat procedures to reduce the damage of bird faeces were discovered to be ecologically unacceptable. Recently, researchers in boat textiles and finishing composition are researching to bring forth environmental and ecological friendly solutions. Some Countries like Sweden and USA among others have put forth strict environmental legislation for boat producers using anti-fouling paints considered to be polluting the environment. (EC Regulation No 1907/2006).

In addition, bird conservation organization such as Birdlife stands firm to stamp out any action that would endanger the birds be it a means to prevent seabirds faeces from damaging boat textiles, finishing composition and the environment or not. Already, some bird species are extinct and some are endangered (Birdlife 2006). Therefore, a symbiotic compromise solution must be reached for the boaters to enjoy life at sea without endangering the seabirds. Also, the solution should seek to prevent the impacts of bird faeces to the boat textiles, finishing composition and the environment.

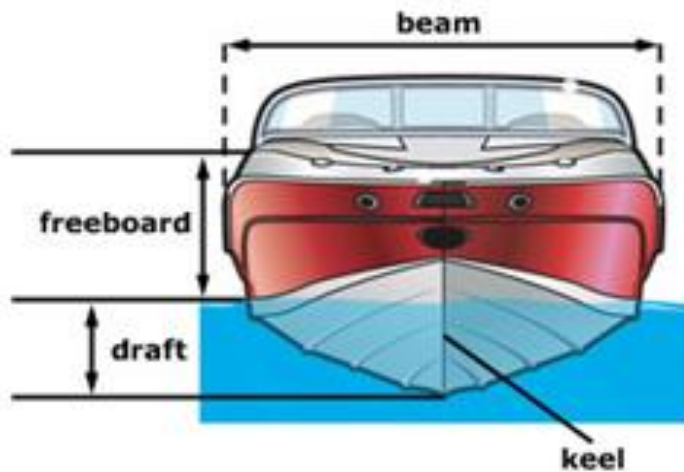
2.3 The boat parts concerned in this thesis

The boat is a composite structure with many parts. Each part has a unique function and it contribute to the boat efficiency. The damage of any boat part affects the overall functionality. There are boats with different shapes and styles, but the different part names remain consistent. In any practical boat, the primary issue is safety at sea, the secondary issue is comfort to be able to sustain life at high sea, and the third issue is speed (McAfee 2009). Bird faeces cause the growth of fouling organisms on boat propeller decreasing its manoeuvring, thereby affecting safety. They also cause diseases to humans. Therefore, bird faeces reduce comfort of humans and reduce the speed of the boat.

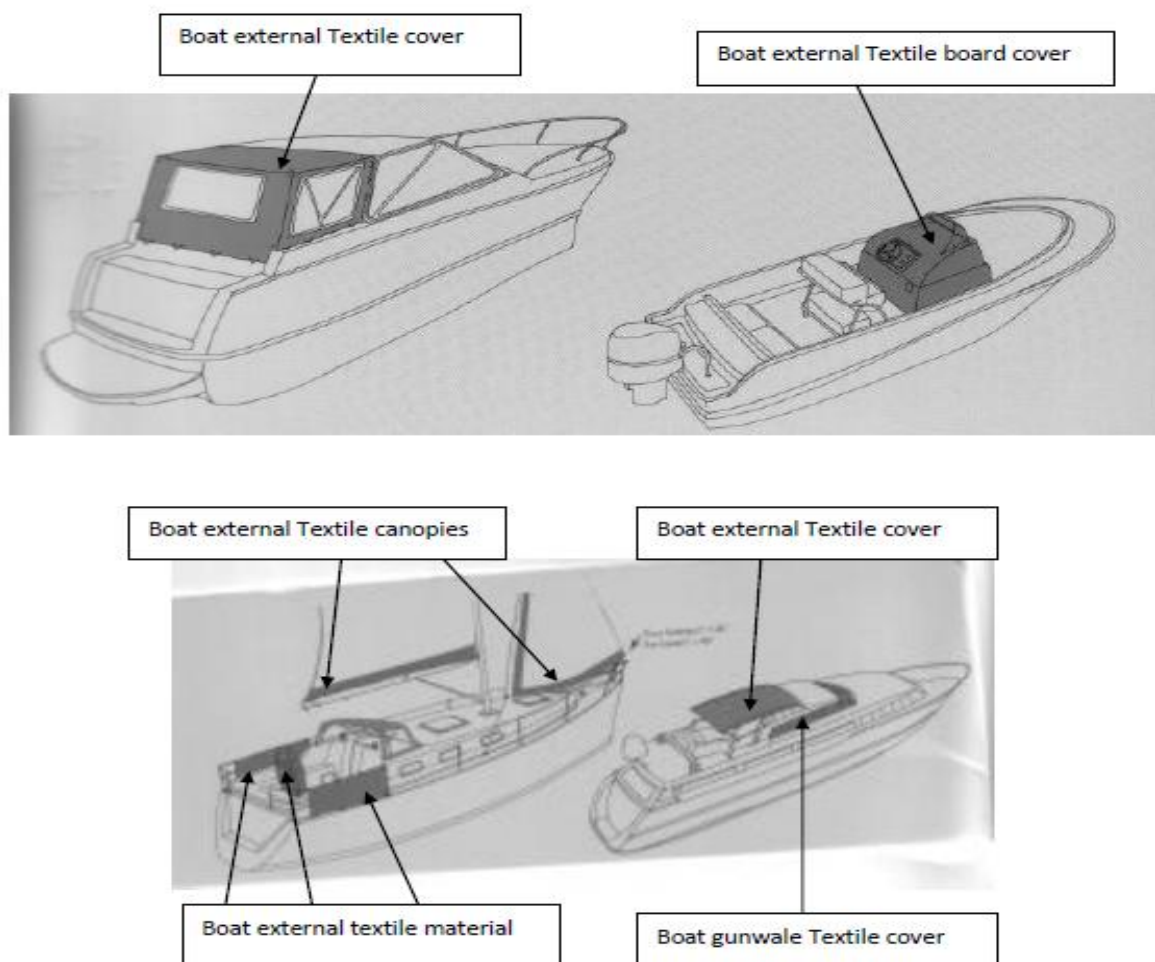
Boat parts and finishing compositions dealt with in this thesis are those exposed to the bird faeces and those affected by bird faeces indirectly. Those parts exposed to them directly are the synthetic textile top, canopy, cover, gunwale, keel, propeller and hull. Those affected indirectly are the internal upholstered seat, seat textile cover, varnished and painted interior as mold and mildew grow to spread rapidly (McAfee 2009).



GRAPH 2. Side view of a boat (copyright from Chesapeake Marine Design LLC Canada 2006)



GRAPH 3. Front view of a boat (copyright from Chesapeake Marine Design LLC Canada 2006)



GRAPH 4. Boat textile parts (adapted from Sunbrella 01/2009 edition)

3 SURVEY TO STUDY THE IMPACTS OF BIRD FAECES ON BOATS

The survey of this thesis is to study the relationship between boaters, birds, and the environment. This will lay the pathway into bird faeces impacts to the boat textiles and finishing composition. The views of the boat users and environmentalists will be used to assess the need for a solution to bird faeces impacts on the boat textiles.

The survey is aimed at studying the damage caused by bird faeces on boat textiles, finishing composition and the environment from the perspective of producers, users and environmentalists. Due to the aim of the survey, the questions will be designed to investigate the relationship between birds and boaters. Also, the questions will strive to realise the impacts of bird faeces on the boat textiles, finishing composition and the environment.

The questions are carefully designed to suit this thesis objective. The author aimed at reaching at least 300 people with the questionnaires. Questionnaires were sent to boat owners, repairers and producers by email. Some questionnaires were distributed randomly to interested people in the city of Kokkola. Their responses were received, analysed and interpreted to evaluate the need for the present thesis work. The questionnaires are attached in the APPENDIX 1/1 and APPENDIX 1/2 at the end of this study.

3.1 Questionnaire responses and conclusions

About 150 questionnaires were sent out and 112 responses were received. Out of the 112 responses received, 87 people fully answered the whole questions. Others did not answer all the questions.

The general percentage response = $\left(\frac{112}{150} * 100\right) = 74.67\%$

The percentage response based on fully answered questions = $\left(\frac{87}{150} * 100\right) = 58\%$

The percentage response based on fully answered questions out of 112 responses received

$$= \left(\frac{87}{112} * 100 \right) = 77.68\%$$

The results of the survey showed that the interaction between the birds and boat owners was obvious at harbours, on-shores and off-shores. Almost 100% of boat owners had seen at least a single type of bird species on or around their boats and hence could lead to the bird droppings on the boat. The fishermen confirmed the competition they faced with the birds for the fish (prey). Approximately 50% of fishermen were less worried about the bird faeces. Meanwhile 95% of them were worried about co-preying with birds and struggling not to kill birds in their nets during long-line fishing.

Based on their boat storage facility, their boats spend almost 85% of their life cycle in water, with 65% in stationery water at the harbours. At the harbours, the bird visits the boat for food remains and some even build their nest on the boat. Hence, there is a high chance of dropping their faeces on the boat external textiles and surrounding water.

Based on the high cost of boat, 80% of the respondents knew the impacts of not cleaning their boat. They clean their boat hull with detergents often and repaint them with anti-fouling paint. Some go further to boat repairers to repaint the boat with antifouling paints every 2-3 years. About 75% of respondents were less informed about the leaching of some chemical from some anti-fouling paints into the aquatic system. Also, the impacts of these leached chemical to the aquatic environment were less known.

In the problem domain, 75% of old boat owners complained of an increase in fuel consumption, growth of mold and mildew, and colour fastness in the textile materials. Approximately 50% of boat owners stated the decreased in the free boat and draft distances, meaning the weight of the boat might have increase to lower the boat more than usual into the water.

Based on the environmental impacts responses, 50% of boat owners did acknowledge their direct behaviour like high fuel consumption and discharges into the water might be contributing to environmental problems. Meanwhile, 50% said they might be contributing indirectly and most environmental damages are direct impacts from the boat producers

leaching their waste and by product into the environment. Responses from the boat producers and repairers showed 90% and 100% of them respectively were aware of the environmental impacts from their production and repair processes. They also state that in the past decades, industrial measures like green chemistry, industrial ecology, end-of-pipe technology and environmental legislation have been revived in the boat production and repair sector.

Responses based on an innovative solution showed 100% needs for a means to produce environmentally and ecologically friendly boat from the boat users, repairers and manufacturers views. All the responses in this aspect showed a definite need for a better solution for boaters to live symbiotically with the birds. The responses confirmed the need for boat finishing composition, textile and productions procedures to be designed for the environment.

This survey result reiterates this thesis research questions further. These questions are the following: What are the content of the bird faeces causing the problems? How do they affect boat textiles and finishing compositions? What could be done to prevent these effects? As a result, these questions raised the need to research into the composition of bird faeces. Bird diet and the metabolic waste gives a clue of what components could be found in their faeces.

4 SEABIRD DIET AND METABOLIC WASTE

The content of the faeces of any animal depends on what the animal consumed and its metabolic activities producing waste. Seabirds are omnivorous scavengers, opportunistic feeders foraging extensively at sea. Their diet is composed of small fish like Baltic herring (*Clupea harengus*), aquatic and terrestrial invertebrates (such as flies, ants, crustaceans, molluscs, and starfish), offal, berries, grains and discarded by-catch. These foods are rich in organic and inorganic compounds. When ingested, they undergo metabolic or non-metabolic processes to provide energy to the bird. The unusable material and by-products of metabolism are excreted. (Encyclopædia Britannica 2010.) Birds prefer the highpoints on a boat, but will also land on a protective canvas resulting to direct droppings onto the boat external textiles materials and surrounding water.



GRAPH 5. Bird feeding on berries (Adapted from Encyclopædia Britannica 2010)

4.1 Seabird excretion

The excretory products of organisms depend on their nutrition, metabolic and non-metabolic activity. Excretion is vital in the health and continuity of life in both unicellular and multi-cellular organisms. Metabolic by-products are toxic in living cells and must be removed at a rate equal to their rate of production. Hence, birds as other living organisms

excrete continually in order to ensure the normal progression of vital chemical events. (De Ruiter 2009.)

Animal faeces are normally made up of 75% water and 25% solid material. Some 30% of the solid matter is made of dead bacteria; about 30% is of indigestible food matter such as cellulose; about 10 to 20% is of cholesterol and others are fats; about 10 to 20% is of inorganic substances and 2 to 3% is made of protein. (Encyclopædia Britannica 2010.)

The main excretory product from the animal body is nitrogenous ammonia (NH_3), derived almost entirely from the proteins of the ingested food. The main excretory product of birds is uric acid because they consumed small amount of water daily to dilute uric acid to soluble urea. The urine and faeces of birds are conducted to the terminal portion of the alimentary canal called the cloaca where it is voided with the faeces. (De Ruiter 2009.)

Therefore, bird droppings come out via one orifice called the cloaca. The faeces are composed of three separate components mixed in the cloaca. The first part is coloured, solid and worm-like faeces depending on what the bird has eaten lately. The second part is a creamy and whitish coloured urate from the digestion and metabolism of proteins in the bird digestive system. The last part is the watery urine made up of uric acids from the kidney. This makes bird faeces watery and can be embedded into any permeable and absorbent substance like the boat textile. These parts are composed of various compounds that have different solubilities and reaction channels with different substances like boat textiles, hull and keel finishing composition and boat surrounding water.

4.2 Bird metabolic toxic waste

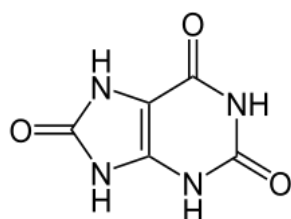
The nitrogen and protein rich bird food undergo metabolic processes to produce energy. The food does not contain the exact amount or mixture of nutrients needed at that time. The proteins digest to produce amino acids. The bird used what they need at that moment to carry out their energy needed processes and the excess are broken down into organic acid which is used in respiration. Respiration produces amine group wastes which piles up with undigested food and are excreted. (De Ruiter 2009.)

The nitrogenous amine waste products from bird are ammonia and uric acids. In seabirds, a high concentration of uric acid can be to blame for the erosion. The acidity can stain canvases, erode materials such as textiles and steels, and discolour paint. These nitrogenous wastes are soluble in water and are very toxic compared to urea due to the fact that birds don't drink sufficient water to dilute its concentration. Uric acid is soluble in water causing eutrophication as a nitrogenous fertility in aquatic environment. It diffuses rapidly to the air and reacts with air moisture to form acid rain. Generally, the content of the waste is dependent of the food consumed and so the effects might be different at times. (Karasov, Phan, Diamond, & Carpenter 2002.)

4.3 Chemistry of nitrogenous wastes

Nitrogenous wastes are produced during protein metabolism via amino acid deamination. During this process, amino groups are removed from amino acids prior to energy conversion. The NH_2 (amino group) combines with a hydrogen ion (proton) to form ammonia (NH_3). Ammonia is converted to uric acid due to less water availability in the bird's metabolic system. Amino groups are converted into ammonia; ammonia is in turn converted to uric acid and secreted via the cloacae. Owing to uric acid break-down releasing ammonia, seabird colonies are a natural source of ammonia to the environment. Ammonia is a potential contributor to nitrogen-cycle and it causes acidification and eutrophication, which has important environmental impacts in the ecosystems. (Wilson, Bacon, Bull, Dragosits, Blackall, Dunn, Hamer, Sutton & Wanless 2004.)

Uric acid or urate is a chemical compound made of carbon, nitrogen, oxygen, and hydrogen ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$). Its molecular structure is in Graph 4.



GRAPH 6. Molecular structure of Uric acid (copyright from Bazari H. Saunders Elsevier; 2007:115)

Preliminary suggestions that seabird faeces would be potential source of ammonia that poses environmental pollution are based on the facts that seabirds:

- Have high dietary nitrogen content from their marine (fish-based) food;
- Have high metabolic rate excreting large amount of nitrogen in the form of Uric acid;
- Naturally lives in large colonies (tens of thousands of birds on a few hectares of land or boat harbour) producing large amount of faeces
- Ammonia vaporizes easily from the bird faeces. (Wilson, Bacon, Bull, Dragosits, Blackall, Dunn, Hame, Sutton, & Wanless 2004.)

5 SAMPLING OF BIRD FAECES AND LOCATIONS

Sampling was done between the periods of July to September 2009 around the city of Kokkola. The choices of the sampling sites were made due to their closed vicinity to boat, lakes, and seabirds. The interaction between the birds and boats was high at these places due to: bird competition with the fishermen and sailor for fish prey, and the availability of forest at boat repair and parking harbours providing terrestrial forest food such as berries. At these sites, boats were parked in stagnant water and fouling organisms were seen growing on boat hulls submerged in water. These characteristics made the sites very suitable for sampling of bird faeces for this thesis.

5.1 Sampling sites

The sites were all chosen around the Kokkola coastline where there are many industrial waste discharge outlets. The outlets samples might enter vital ecosystems that will finally enter the bird food chains. At these sites, the interaction between birds and the boats are high.

5.1.1 Trullevi fish market harbour, Kokkola

Fresh bird faeces samples were collected in mid August 2009 at the Trullevi fish harbour. Trullevi is a fish harbour where fishermen offload their fishing containers in the morning after their overnight fishing. It is situated about 10 km from the city of Kokkola, Finland. During the spring and summer, many species of seabirds follow the fisheries from offshore to this harbour for food. They consumed small fishes and offal rich in nitrogen, hence excreting high nitrogen excretion in the form of uric acid on the fisheries boat external surfaces, canopies, covers and textiles. The samples were collected here between 08:00-09:00 am in the morning when the fisheries are back from offshore and the harbour is busy. The fisheries offload their net, select consumable fishes and throw the small ones back into the sea. At this point, there is a struggle for the small fishes between the fisheries and the seabirds. The dominant seabird species found there were *Larus canus* and *Larus fuscus*.



GRAPH 7. *Larus fuscus* preying on fish (Adapted from Patuxent Wildlife Research Center)

5.1.2 Lahdenperä harbour

The Kokkola Lahdenperä harbour provided a suitable sampling area because many boat production and repair companies are operating around there including Finn Master Oy. Uplifting the boat canopies, covers and interiors for repair provide food remains to the birds. Bird faeces sample was collected on the boat textile canopy here on the 27th of August 2009. Lahdenperä boat harbour is situated about 6 km from Kokkola city. This place offers a good sampling area because many boats are built and repaired here. The nearby seas provide a breeding area for the seabirds as sailors bring their boat to the harbour. They seabirds here feed on food remains from the sailors as the repairers dismantle the boat and on the forest berries surrounding the area. The dominant seabird species found there were *Larus fuscus* and *Larus argentatus*. At this site, fouling organisms were seen growing on the stored boat anchored in the sea sides.



GRAPH 8. *Larus argentatus* (Adapted from Patuxent Wildlife Research Center)

5.1.3 Öja lake

The third sampling was done in a small island in Öja lake area is situated about 15 km from Kokkola city in the month of August. This place was considered a tangible sampling area because they were many recreational boats parked at the harbour during this period. Some were partly submerged in water, and the growths of fouling organisms were observed at the bottom of the boats in the shallow water. There are summer cottages around and most of the owners own a boat as well. The lakes around provide a good source of fish as food for the seabirds. The neighbouring forests provide variety of terrestrial food sources with carboxylic rich berries. The samples collected here were fresh and from the species *Larus canus*, *Larus argentatus* and *Larus focus*



GRAPH 9. *Larus canus* (Adapted from Patuxent Wildlife Research Center 2004)

Generally, the presence of a boat, the seabirds and food sources such small fishes, food remains from boat owners and berries (rich in carboxylic acids) lead to the production of bird faeces which are deposited onto the boat external surfaces, canopies, covers and textiles. Approximately 32% of the nitrogen excreted is volatilized into ammonia-nitrogen under favourable condition of temperature and moisture. Ammonia might also be found in the seabird faeces as a result of the breakdown of uric acid or urea in the bird's biological activities (Wilson et al.2004). The samples were collected boat fresh and dried. Some were actually collected from boat external surface. The samples were stored in the school laboratory fridge awaiting analysis.



GRAPH 10. Satellite map of sampling sites (adapted from google 2010 satellite view of Kokkola city)

5.2 Sampling method and taking a representative sample

It was assumed that the bird species above have same migratory and scavenger feeding character, and represents all seabirds' species. Hence, their droppings contain the same contaminants that pose problems to the boat external textiles and finishing composition. Therefore a representative sample of all the collected samples was taken by stratified random sampling method. The three samples collected at different locations were divided into three strata. Each was mixed and a random 10 gram was collected and mixed together

again. The samples were completely mixed with an electric tubular mixer to a homogenous mixture.

The final mass of 30 grams sample collected formed a random representative sample assumed to contain all the necessary contaminants from the three bird species. The bacteria, algae, fungi or micro organisms content of the samples were researched. Small amounts of the sample were collected and analyzed for inorganic and organic compounds.

6 CLASSIFICATION OF BIRD FAECES

The content of animal faeces is dependent on what the animal recently consumed and its metabolic processes producing the faeces. The seabirds are primary consumers in both aquatic and terrestrial environment including the forest. They migrate seasonally and are placed at the higher trophic level in the marine and terrestrial food chain. Hence, they might feed on heavy metal samples and petroleum product like polycyclic aromatic hydrocarbons (PAHs) during tanker wrecks in cases of accident. (Pérez López et al. 2005.) Traces of these heavy metals might be found in their body and faeces. Seabirds forage the sea and land extensively for food, meaning their faeces might contain remains and waste products from digested marine and terrestrial foodstuffs.

Due to seabird food sources and their metabolic processes, it was suggested that their faeces would contain both organic and inorganic compounds like nitrates, sulphates and phosphates. Seabirds drink salty seawater (NaCl) which draws water from the bird's digestive system due to high osmotic pressure difference. This result in urine concentrated with uric acid and chlorides. The samples were collected in autumn when the birds might have eaten forest red and blue berries from the sampling sites forests. Some traces of carboxylic acid, alcohols, ketones and ester from berries were suggested to be found in the samples. These compounds occur either naturally in plants and fruits or might enter the bird food chain from nearby industries waste outlets. Companies producing or using these chemicals directly or indirectly might have some traces in their outlets.

If the compounds listed above are found in the bird faeces, then some might have direct impacts on the boat external textiles, finishing composition and the environment. Also, these compounds further reactions and by-products might have effects on the boat textiles and the environment.

6.1 Chromatography techniques to analyse samples

Gas chromatography is a separation method where the analyte is confined within a gaseous mobile phase, pumped via a stationary phase. The gaseous mobile phase and the stationary phase are immiscible. The chromatography separation technique depends on the

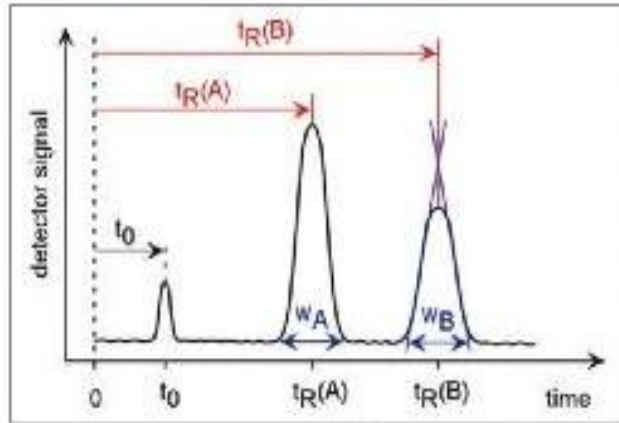
differential distribution of sample components between these two immiscible phases. When the sample components are separated, they can be identified base on their specific characters. (Patnaik 2004.)

The gaseous mobile and the stationary phases are immiscible because one of them is hydrophilic and the other is lipophilic. The components of the analyte interact in different ways within these two immiscible phases. Based on the components polarity, they spend more or less time interacting with the stationary phase resulting to greater or lesser extends of residence time or retardation. Therefore, the components present in the sample are separated according to their residence time. Each sample component elutes from the stationary phase at a specific time (known as its retention time). The eluting component passes through the detector, producing signals which are recorded and plotted in a chromatogram form. (Patnaik 2004.)

6.1.1 Differential distribution

When an analyte is placed in a system containing two immiscible phases, the analyte distribute itself between the two phases in a specific manner depending on each phases' affinity for its components. The manners in which it distributes at equilibrium depend on parameters like system pressure, temperature, nature of the two phases and the analyte. In gas chromatography, a gas is one phase (the mobile phase) and a low volatility liquid is the second phase (the stationary phase). (Patnaik 2004.) For chromatographic reasons, a distribution coefficient k_d is defined by Nernst equation:

$$k_d = \frac{\text{Concentration of component in the stationary phase}}{\text{Concentration of component in the mobile phase}}$$



GRAPH 11. Typical chromatogram of two components sample (adapted from Patnaik 2004)

Where:

t_0 = time for unretained component

$t_R(A)$ = retention time for component a

$t_R(B)$ = retention time for component b

w_A = width at base for peak a

w_B = width at base for peak b.

6.1.2 Selectivity factor α

The selectivity factor α explains the relative velocities of the analytes with respect to each other in the phases. It describes how well a chromatographic method can distinguish between two analytes.

$$\text{selectivity factor } \alpha = \frac{K'_B}{K'_A} = \frac{t_R(B) - t_0}{t_R(A) - t_0}$$

6.1.3 Capacity factor

Due to different time required by each component in the sample in interacting with the mobile and stationary phase, the relative velocity of each component between the two phases gives the capacity factor. The average velocity of a sample component depends on how much time it spends in the mobile phase. Based on Graph 7, capacity factor k' is given by:

$$\text{Capacity factor } k' = \frac{t_R - t_o}{t_o}.$$

If $k' \ll 1$, (much smaller than 1), then the analyte speed is very fast and the elution time will be short and an exact determination of t_R will be difficult. If the sample moves too slowly, the separation time will be very high. According to Patnaik (2004) “a good value for k' would be between 1 and 5”.

6.1.4 The efficiency of chromatographic separation

The efficiency of a chromatographic separation is dependent on its band broadening. If the band broadening is large, peaks might overlap and resolution will be lost. Band broadening for a column of length L is quantitatively expressed using the height equivalent concept of a theoretical plate H , or simply using plate numbers, N . The larger the number of plates and the smaller the plate height is, the better the chromatographic efficiency. (Patnaik 2004.)

$$\text{Platenumbers } N = 16 \left(\frac{t_R}{w} \right)^2,$$

$$\text{Plate height } H = \frac{L}{N}.$$

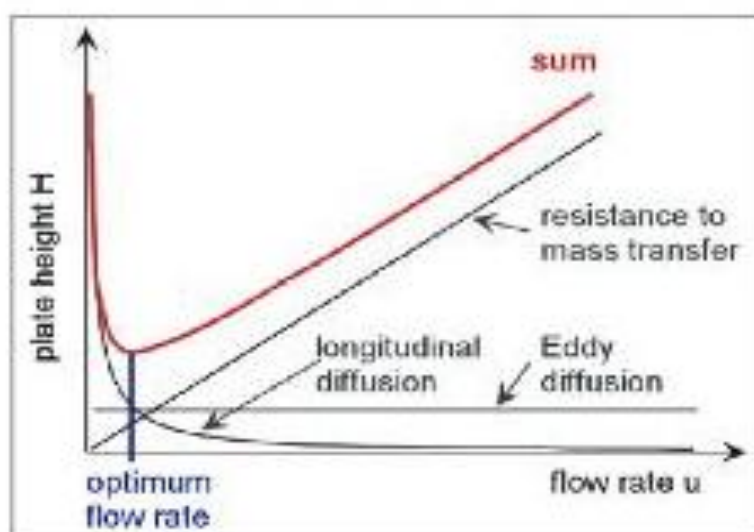
6.1.5 Band broadening

The parameters that influence band broadening can be approximated by the van Deemter equation which is valid for gas and liquid chromatography as well as capillary electrophoresis.

$$\text{van Deemter equation } H = A + \frac{B}{u} + C \cdot u.$$

H is the height of theoretical plates (given as a sum of three terms). A describes the influence of the column packing on band broadening. This is called Eddy diffusion. It is constant for a given column and independent of the flow rate. B/u describes the longitudinal diffusion in or opposed to the direction of flow and inversely proportional to the flow rate u. C*u describes the resistance to mass transfer between the stationary and mobile phase which is directly proportional to the flow rate. (Patnaik 2004.)

By plotting H as a function of u, the optimum flow rate for a chromatographic separation can be determined as presented in Graph 12.



GRAPH 12. A van Deemter plot for the determination of the optimum flow rate (adapted from Patnaik 2004)

6.1.6 Resolution

Chromatography separates or resolves one component from another, therefore the resolution R of the components is important in differentiating them. The resolution can be calculated using any of the equation below;

$$1. \text{ Resolution } R = \frac{2 * \left[\frac{t_R(B) - t_R(A)}{w_A + w_B} \right]}{w_A + w_B}$$

$$2. \text{ Resolution } R = \frac{\sqrt{N}}{4} (\alpha - 1) \left[\frac{k'}{1 + k'} \right]. \quad \text{This equation is valid for } \alpha < 1.2$$

$$3. \text{ Resolution } R = \frac{\left[\frac{t_R(B) - t_R(A)}{w_A + w_B} \right]}{\frac{1}{2} (w_A + w_B)}$$

Above, k' is the capacity factor and N is the number of plates. This shows the capacity factor has an influence on the resolution. The components in the sample have a wide range of values. If conditions are optimized so that the first components to elute have values between the optimum of 1 and 5, then the other compounds with higher k values elute much later. This results in excessive band broadening. Again, if conditions are optimized for the later eluting compounds, the resolution will be poor for the compounds that elute first. This general elution problem can be overcome by decreasing k during the separation. If $R=1.5$, therefore peaks of identical area will overlap by only 0.3% and If $R= 1$, the peak overlap will be 4 %. Peak resolution can be optimised by increasing the selectivity and minimising band broadening. (Patnaik 2004.)

In LC, the composition of the mobile phase can be altered during the separation. This is known as gradient elution opposed to an isocratic elution, where the composition of the mobile phase remains unchanged throughout the separation process. (Patnaik 2004.)

In GC, instead of operating under isothermal parameters, a temperature gradient can be applied during separation. Generally, the first step in order to achieve a good separation of the component in the mixture is to choose a suitable stationary phase with which the analyte can interact. Thus, the composition and gradient of the mobile phase can be chosen to optimize the capacity factor and resolution. (Patnaik 2004.)

6.2 Determination of inorganic compounds

The determination of inorganic compounds was divided into two, namely, anionic compounds and cationic metal ions. To achieve a better efficiency, an IC and AAS analytic equipments were used to determine the anions and the cations respectively.

6.2.1 Determination of inorganic anions

Due to the seabird nutrition, diet and metabolic activity, these ions NO_3^- , PO_4^- , SO_4^- , and Cl^- were suggested to be present in their faeces. Carbon, nitrogen, sulphur, phosphorus and chlorine compounds are the compositions of bird diet. These compounds undergo metabolic activities during digestion to produce contaminant that could be held responsible for the impacts of bird faeces to the boat textile and finishing composition. These compounds were analyzed in the bird faeces sample collected using the ion chromatography (IC).

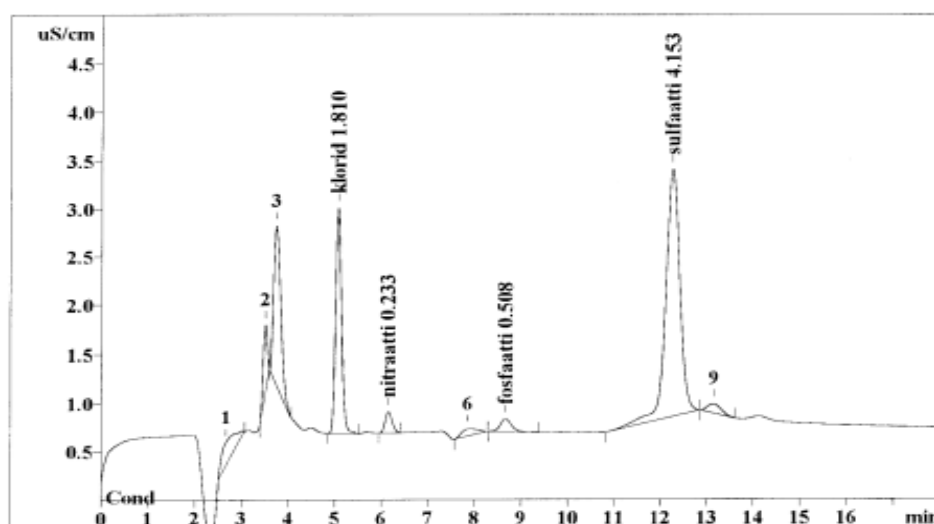
Ion chromatography is a technique use to separate and detect ions based on their charges. In IC, ionic or charged species in the mobile phase are separated by selective exchange with the stationary phase either by ion-exchange chromatography (IEC) or ion-pair chromatography. Therefore, IC is used to analyze only charged molecules. Standard solutions of known compounds can be analyzed in the IC and their peaks can be stored inside the equipment as standard peaks. These standard peaks are then used to compare and detect the presence of an unknown injected sample producing the same peaks. Retention time is the time required by the mobile phase to convey a solute from the point of injection onto the stationary phase, through the stationary phase, and to the detector. (Manz, Pamme, & Iossifidis 2003.)

Exactly 339 mg of NaCO_3 and 84 mg of NaHCO_3 were weighed and placed into a 1 l beaker. It was raised to 0.7 l with distilled water. One stirring bar was placed inside and stirred for 10 minutes on the magnetic stirrer. The solution was transferred into a 1000 ml volumetric flask. The beaker was rinsed several times and poured into the flask till it reached 0.9 l. The volumetric flask was placed in an ultrasonic bath for 15 minutes (to break the salt, dissolved them and remove gases). The content was raised to 1 l and filtered

with a 0.45 μm mesh size filter to remove dust, unreacted NaCO_3 and NaHCO_3 , and solid impurities in the solution. This effluent solution was used in the ion chromatography process. It was later made up to 1l with distilled water. With an automatic delivery, 1000 μl was taken and diluted to 10 ml.

Exactly 0.1 g of sample was weighed and placed into a 25 ml volumetric flask. A volume of 15 ml of the prepared effluent solution was added and placed in the ultrasonic bath for 5 minutes. It was set to vibrate at very high frequency, broke the solid particles into smaller sizes that could easily dissolve in solution. A magnetic bar was placed inside and stirred on the magnetic stirrer for 10 minutes. The 25 ml volumetric flask was filled to the lower meniscus with an effluent solution. A volume of 1000 μl was measured and diluted to 10 ml with the effluent solution. This solution was filtered with 0.45 μm syringe filter and was the analyte to be analyzed in the ion chromatograph for the presence of NO_3^- , PO_4^- , SO_4^- , and Cl^- ions.

Standard solutions were run in the IC, their peaks and retention time were determined. The sample was injected into the IC and its peaks were compared to those of the standard solution and the corresponding compounds were classified. Graph 13 presents the compounds whose peaks and retention time corresponded with those from the standard solutions.



GRAPH 13. Chromatogram of bird faeces anions from IC

The compounds with their corresponding retention time, height and concentration in the bird faeces sample were determined and presented in Table 1.

TABLE 1. Data of detected anions in bird faeces sample

Compounds	Retention time (min)	Height ($\mu\text{S}/\text{cm}$)	Concentration (mg/l)
Chlorides	5.06	2.33	1.810
Nitrates	6.15	0.22	0.233
Phosphates	8.66	0.14	0.508
Sulphates	12.25	2.56	4.153

The concentrations from IC are given in mg/l, which should be in mg/g sample. It implies:

$$1. \text{ Conc. of } \text{Cl}^- \text{ in mg/g sample} = \left(\frac{1.810 \text{ mg/l} * 50 * 10^{-3} \text{ l}}{0.1 \text{ g}} \right) = 0.905 \text{ mg } \text{Cl}^- / \text{ g sample}$$

$$2. \text{ Conc. of } \text{NO}_3^- \text{ in mg/g sample} = \left(\frac{0.233 \text{ mg/l} * 50 * 10^{-3} \text{ l}}{0.1 \text{ g}} \right) = 0.1165 \text{ mg } \text{NO}_3^- / \text{ g sample}$$

$$3. \text{ Conc. of } \text{PO}_4^- \text{ in mg/g sample} = \left(\frac{0.508 \text{ mg/l} * 50 * 10^{-3} \text{ l}}{0.1 \text{ g}} \right) = 0.254 \text{ mg } \text{PO}_4^- / \text{ g sample}$$

$$4. \text{ Conc. of } \text{SO}_4^- \text{ in mg/g sample} = \left(\frac{4.153 \text{ mg/l} * 50 * 10^{-3} \text{ l}}{0.1 \text{ g}} \right) = 2.0765 \text{ mg } \text{SO}_4^- / \text{ g sample}$$

Based on the overall result, there is a higher concentration of sulphates ions, followed by chlorides ions. High concentration of sulphates might be due to the fact that the sample was collected in the Ostrobothnia region where the birds feed on the high sulphates concentrated soil and soil organisms. In the Ostrobothnia area especially in Kokkola, there is an annual land lifting from the sea. When the land rising from the sea, water reacts with the sulphur to produce sulphate and sulphuric acid, which in turn lowers the area pH. (Peltonen, Haanpää & Lehtonen 2005.) The chloride might be due to the salty sea water which underwent dissociation to release chloride. Also, the bird feed on the marine food which might be highly concentrated in chloride swept into the lakes from road salt (NaCl and CaCl_2) used in melting snow in the region. The peak with downward trough between the time 2 and 3 minutes was due to the presence of some traces of distilled water left in the test tube during analysis.

6.2.2 Determination of inorganic cations

The AAS technique was used to classify the metal ions in the sample. As a result of metal production and usage in the Kokkola industrial park plants, some metal ions were suspected to be found in the surrounding air, terrestrial and aquatic ecosystems. They could enter the seabird food chain. The suspected metals ions were Zn, Fe, Cu, Na and Ni. These metals are very reactive and hence do not occur naturally in their atomic forms. The metals easily give out their outermost shells electrons, behaving as reducing agents and forms bonds with other reactive, oxidising elements. In this experiment, the following compounds were used to prepare standards solutions of their respective metals: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

The AAS a technique compares the concentration curves from standard solutions with the curves from samples with unknown metal content and concentration. In this method, a source of radiation, a sample, and a device for detecting and analyzing radiation are needed. The absorption spectrometer employs broadband radiation emitters followed by a monochromatic to provide a signal of very narrow frequency content as source. The monochromatic source signal then passes through a sample contained in a cell and onto a detector designed to sense the source frequency being used. The resulting spectrum is a plot of intensity of absorption versus frequency. (Hurst 2010.)

A mass of 1 g of bird faeces sample was measured and placed into a 50 ml volumetric flask. Conc. HNO_3 acid of volume 20 ml was measured, added onto it and connected in a reflux cooling tube. It was heated to boil for 90 minutes on an electric heater under the hood. This was intended to help dissolve the solid particles and remove NO_2 from the solution. Brown fumes of NO_2 were observed from the boiling solution. It was allowed to cool, then filtered and raised to 50 ml. This was used as the sample to be classified using the atomic absorption spectroscopic technique.

Stock solutions of 1000 ppm for the different metals were prepared as follows;

A mass of 4.396 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was weighed and placed in a 1000 ml volumetric flask. Distilled water of volume 100 ml was measured and added into it, stirred and raised to 1000 ml with distilled water.

A mass of 3.560 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was weighed, placed in a 1000 ml volumetric flask and 100 ml of distilled water was added to it. The solution was stirred and raised to 1000 ml with distilled water.

A mass of 3.329 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was weighed, placed in a 1000 ml volumetric flask and 100 ml of distilled water was added to it. The solution was stirred and raised to 1000 ml with distilled water.

A mass of 4.479 g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was weighed, placed in a 1000 ml volumetric flask and 100 ml of distilled water was added it. The solution was stirred and raised to 1000 ml with distilled water.

The above were 1000 ml stock solutions, from which 100 ppm working solutions were prepared. Concentrated HCl of volume 1 ml was measured and added to each of the 100 ppm working solution. From each of the working solution: 1 ppm, 3 ppm, 5 ppm and 10 ppm solutions were prepared. These solutions were injected into the AAS and the plots of their absorption intensity versus frequency were used as standard curves for known metal samples and concentration in the equipment. The bird faeces sample was injected into the equipment and tested for the presence of each of the elements. For each of the metals, the curve produced was compared to that of the standard solutions.

The following elements and concentrations in ppm were present in 50 ml prepared bird faeces sample. For Zn-213.8, Fe-248.3, Ni-232.0 and Cu-324.8, the detected concentrations were 4.83, 8.8, 0.35 and 0.69 in ppm. This classification showed that the suggested metal ions were present in the bird faeces. Metals are known to be highly reactive; they could cause adverse reactions on the boat textiles and leave undesirable reaction products and impacts such as colour fastness and stains.

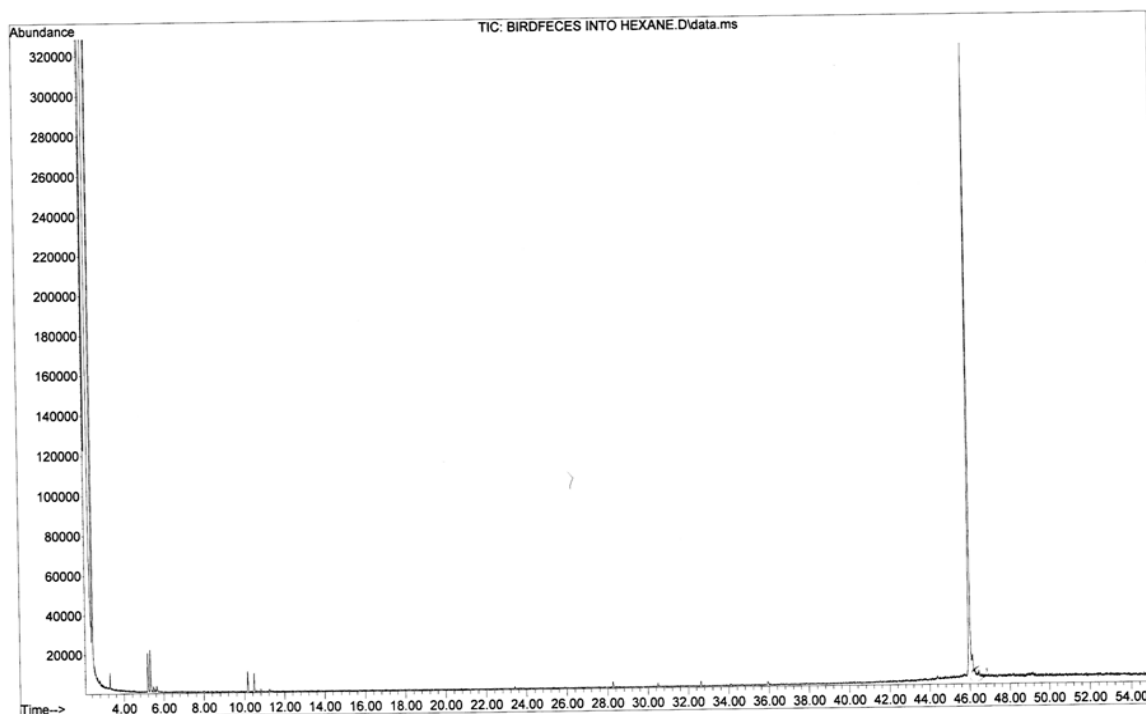
6.3 Determination of organic compounds

Gas chromatography was applied because the volatile substances in the bird faeces were considered to be heat-stable and cannot be thermally destroyed before vaporization. The samples were analyzed using high efficiency gas chromatography connected to mass selection detector. The sample components were vaporized and their bonds fragmented. Each component produced a specific characterized fragmentation pattern that was compared to those in the equipment library to identify them.

For gas chromatographic purposes, each component distribution coefficient depends only on the stationary phase and operating temperature. Each component in a sample distributes itself differently; hence its distribution coefficient (k_d) is independent of other component k_d in the sample. Thus, at a specific temperature and carrier gas flow rate, the retention time of the component is a function of its time spent in the stationary phase (Patnaik 2004). A compound with a lower k_d will spend less time in the stationary phase than one with a higher k_d , and each will spend the same amount of time in the mobile phase. As a result, the component with lower k_d will elute faster and be separated.

The equipment used was a gas chromatography connected to a mass selective detector (GC-MSD), ultrasonic bath, balance, test tubes, magnetic stirrer and an electric heater. The reagents were hexane and bird faeces sample. The bird faeces sample of mass 0.1 gram was collected and mixed in 3 ml of hexane in a test tube and capped. The test tube was placed in an ultrasonic bath for 10 minutes. Later, it was shaken manually for 5 minutes and placed on the ultrasonic bath for 10 minutes again. The sample was shaken again for 3 minutes and taken through a 0.45 μm filter into a test tube. This formed the sample analyzed with the GC-MSD for organic compound.

The samples were analyzed in a 761 compact GC-MSD with 250 columns. They were vaporized, cooled to 50 °C and pumped through a 30 m coiled column where stepwise heating of 5 °C per minute was taking place. It was heated to 200 °C. The bonds in the various components were fragmented forming patterns that were unique to specific compounds. These fragmented pattern or peaks of the analyte were detected in the gas stream as they exits the column by flame ionization. They were compared to the GS-MSD library with patterns or peaks of some 300000 compound to detect which compounds were present in the analyte with same peaks. The total retention time in the process was 55 minutes. The organic compounds present in the bird faeces sample produced spectrum similar to those of specific standard organic compounds in the GS-MSD library. Graph 14 presents the spectrum of the organic compound determined in the sample.



GRAPH 14. Spectrum of organic compounds in the bird faeces sample

The specific organic compounds identified in the bird faeces sample and their corresponding retention times in the GC-MSD are presented in Table 2.

TABLE 2. Data of organic compounds in bird faeces sample detected with GC-MSD

Compounds identified	Retention time in minutes
Heptane	3.295
3-Hexanone	5.188
2-Hexanone	5.318
2-Hexanol	10.465
1,3-Propanediamine	28.253
1,2-Benzenedicarboxylic acid	45.973

As shown in Graph 14, the chemicals were found in small levels that could not cause harm to the birds whose physiological processes regulate them. Their continuous accumulations into the environment might have harmful effects on humans, the environment and other occupants including the boat external surfaces when in higher amounts. (EU Risk assessment 2001.) These bodies do not have self regulating systems to control the harmful level of the chemicals.

The most significant peak was that of 1,2-benzenedicarboxylic acid, also known as phthalic acid. The source of this was estimated to be the forest berries. The samples were collected in the middle of July and end of August when there were enough berries in the forest on which birds feed on. (Drew & Frangos 2001.) Blue and red berries of the natural forest contain traces of this chemical. Other forest plants like *Ajuga bracteosa* contain traces of phthalic acid (Singh, Mahmood, Kaul, & Jirovetz 2006, 593-597).

The compound 1,3-propanediamine is a clear colourless liquid with an ammonia-like odour. It does not occur in nature, but is derived from the reaction of ammonia (NH_3) with an aliphatic organic group. In the bird faeces, the nitrogenous waste (NH_3) may react with the organic waste (remains of fish food) to produce 1,3-propanediamine. It is soluble in water, with health and environmental effects when in high concentrations (Environment Australia 2001).

The compounds 2-hexanone and 3-hexanone are ketones; 2-hexanone is also known as methyl n-butyl ketone and is a clear, colourless liquid with a sharp odour. Its traces are found in oranges, grapes and vinegar, but its primary sources are the industries that manufacture it or use it in production. These include the chemical, rubber, pharmaceutical, semiconductor, varnish, paints and plywood industries. Most of these industries are located on the Ostrobothnia region, and hence could be potential sources of 2-hexanone. (Hamilton-Kemp, Archbold, Loughrin, Collins & Byers 1996.)

When 2-hexanone is released from the industries to lakes, air and soil, it dissolves very easily. It has also been found in drinking water and soil near hazardous waste sites (EU Risk assessment 2001). Birds become exposed to it as they drink and feed on contaminated water and soil. The compound 3-hexanone is a volatile compound. Its traces could be found in the strawberry fruit on which the bird feed on. (Hamilton-Kemp et al. 1996.)

Heptane or n-heptane is the straight-chain alkane with the chemical formula C_7H_{16} . It is insoluble in water but does burn explosively. Heptane is a hydrocarbon and is found in the carbohydrate-based food that birds feed on.

6.4 Theoretical determination of micro organisms in bird faeces

The two main types of bacteria in the intestinal tract of birds are the aerobic and anaerobic bacteria. Other organisms found in the intestines are the yeast, fungi and sometimes single celled protozoa. Few bacteria are found in the stomach due to stomach acidic property that kills them. The stomach acid kills most bacteria, but the stomach acidity is neutralized by bicarbonate from the pancreas as food passes into the small intestine. Therefore, both living and dead bacteria can be found in the faeces. Bacteria constitute about 50% of the content

of several organisms' faeces. These residents of the intestinal tract are always in a state of flux: new bacteria are continuously being produced and old bacteria are being flushed out in the moving intestinal contents and later in the faeces. (Shawn 1991.) Fungi, yeast and protozoa in bird faeces accelerate the growth of other micro organisms such as mold on boat textiles and fouling organisms on the boat hull when the faeces are deposited on boat external surfaces and surrounding water respectively.

The results of the analyzed sample showed that the content of bird faeces was made of many chemicals, metabolic remains and waste. The compounds suggested were all found, although in small concentrations. It was established that the bird faeces are rich in nutrients (nitrates, sulphates and phosphates). These nutrients act as fertilizers in the growth of plants. Hence, they would fertilise the growth of fouling organisms on the boat hull submerged and stationary in water, and other aquatic vegetation or phytoplankton. This would reduce water quality and level of oxygen as a result of eutrophication causing survival problem to fishes and other water diffused oxygen dependent organism (Cloern, Krantz, & Duffy 2007).

Micro organisms contained in the bird faeces reproduce rapidly and can invade a suitable environment in a short time possible. Some are biological catalysts that increase the rate of some other chemical reactions under suitable conditions like pH and temperature. (Wilson et al. 2004.) The bacteria will increase the rate of formation of mold and mildew under moisture. Reproducing rapidly by sporulation, mold will produce thousands of spores and invade the boat moist textile material in the shortest time possible.

7 CLEANING OF DAMAGED CANOPY

Finn Master Oy Kokkola uses Sunbrella fabrics from the company Va Varuste Oy in Kuopio, Finland. The practical work of this thesis was done in Finn Master Oy, Kokkola. A boat canopy with mild and stubborn stains from bird faeces was cleaned with the chemical called 303 fabrics cleaner. Apart from the stains on the canopy, there was mold and mildew growing on it.

The canopy was made of synthetic polyester fibres with thin film coating and laminated by superimposing and bonding of two or more fabrics during finishing. Polyester resists colour changes due to chemicals, heat and sunlight (Eberle, Hermiling, Hornberger, Menzer & Ring 1999). Several boat textiles used by Finn Master are from a company called Sunbrella. According to Sunbrella, their fabrics are: produced with latest innovations, of impeccable quality and best-in-class warranties. During the production process, they begin with proprietary polymer chemistry, applies technical precision in fibre formation, yarn manufacturing, weaving and finishing to produce resistant to colour fastness and greater water repellence textiles with high breathability. Their textiles are used for boat decorating needs, interior and harsh outdoors conditions. (Sunbrella 2008.)

When the bird faeces chemical and bacteria content are sucked into polyester, if they are not immediately clean, they will affect the brightness and strength of the polyester, enhance mildew and mold growth. The compounds classified in the bird faeces behave differently on the boat textile material, finishing composition and surrounding water. Their behaviour depends on their characteristic properties. The compound 1,2-benzenedicarboxylic acids is a natural substance from forest berries that the bird feed on during the berry season. The faeces are greasy and sticky; therefore they make a strong grip on the boat textiles. This produces a stubborn stain on it when the particles are hooked within the textiles fibres. The chlorides bleach the textiles when their concentrations and retention time are sufficient enough (Eberle et al. 1999).

Bird waste ammonia content diffuses rapidly into the air, is highly soluble in water, and escapes easily into the external medium. Bird ammonia is converted into compound less harmful in its body via detoxication. Birds excrete nitrogen in the form of uric acid, which

is highly insoluble in water as well (Birdlife 2008). This thick, acidic suspension, which easily diffuses ammonia, sticks on the boat textiles in two folds: the thick suspension sticks firmly on the textiles and the ammonia easily diffuses into the fibres by capillary action. The compounds 3-hexanone, 2-hexanone and ethanol found in the bird faeces diffuse easily into the textile fibres reacting with it. They are organic compounds, and hence will react with the boat synthetic textiles that are organic in nature as well. The outcome might either be a stubborn stain, mild stain or strength weakening of the textiles fibres. These soften the fibres, to be eaten up by mold and mildew. The bulk of matter from bird faeces that remains as loose dirt on the boat textile could accommodate microbes to grow on the fabric.

In the practical textile cleaning process, the boat cover damaged by bird faeces content was the California dodger type. It had mild, heavy stains, mildew and mold growth. The original colour was navy blue. The red colour type in Graph 15 was adapted to express the outlook and type of textile, and not the original colour.



GRAPH 15. California Dodgers boat covers (adapted from Sunbrella 2008 magazine)

The reagents used in the practical cleaning process included 950 ml 303 fabrics cleaner and 950 ml 303 High Tech Fabric Guard (from Rosenquist Oy, Turku), distilled water, mild soap and lukewarm water. The high tech fabric guard was insoluble in water and could not be diluted to optimized resource. The chemical 303 fabrics cleaner was solution in water and hence different concentrations of it was made. The different concentrations helped to determine which concentration was efficient in cleaning the fabric without side effects. Therefore, optimization of resources was studied rather than using 100 % concentrated solution in cleaning the textile.

From 303 fabrics cleaner, the following five solutions of different concentrations were prepared:

1. A 10% solution of 303 Fabric cleaner. A volume of 10 ml 303 Fabric cleaner was measured and diluted in 90 ml distilled water;
2. A 25% solution of 303 Fabric cleaner. A volume of 25 ml 303 Fabric cleaner was measured and diluted in 75 ml distilled water;
3. A 50% solution of 303 Fabric cleaner. A volume of 50 ml 303 Fabric cleaner was measured and diluted in 50 ml distilled water;
4. A 75% solution of 303 Fabric cleaner. A volume of 75 ml 303 Fabric cleaner was measured and diluted in 25 ml distilled water;
5. A 100% solution of 303 Fabric cleaner. A volume of 100 ml 303 Fabric cleaner was measured and used directly.

The solutions were used to clean the California dodger cover starting with the 10 % solution to the 100% solution.

7.1 Cleaning of the California dodger cover damaged by bird faeces

The California dodger cover is a typical type of textile material used on the boat top. It protects the boat's interior and occupant from rain and sunlight. Practical cleaning of the California dodger cover in this study showed the intensity of the damage caused by bird faeces to the boat textiles. Stubborn stains were deeply embedded into the yawned fibres. Some of the stubborn stains were dark and some were whitish in colour, confirming to what the bird fed on and the coloured composition of its faeces. Mild stains were white in colour and most loose dirt. The growth of mildew and mold created dark and greyish spots on the cover. Some spots were already eaten up by the mold digestion.

The loose dirt was brushed off. A solution of water and ivory snow mild soap was prepared. With a soft bristle brush, the cleaning solution was spread on the cover, allowed to soak into the fabric, rinsed completely and air dried for one day. The next day some spots were observed to contain stubborn greasy-like stains and mildew.

Therefore, heavy cleaning with the prepared solutions of 303 fabrics cleaner was necessary. The areas were isolated and cleaning started with 10% solution. Samples of this solution were poured on the stubborn spots, allowed to soak in to the fabrics for 25 minutes and cleaned with a soft bristle brush. Spots were rinsed with enough lukewarm water to remove soap residue and air dried. Persistent stains were cleaned with the next solution of higher concentration. This was done stepwise from lower to 100% concentrated solution.

When all the stains were cleaned, the fabric was tested for waterproof or its water repellence characteristic. It was clipped and suspended at the extreme edges on four vertical feet pillars to completely spread it out. Water was poured on the whole cleaned surface.

It was observed after cleaning that the canopy colour was not uniform; some spots showed whitish while others were unchanged from its original colour. When water was poured on the surface, there were leakages on the bottom part at whitish spots. This shows that the fabric was bleached and its original protective, smooth coatings were removed, reducing the fabric's waterproof property. This will expose the rough surfaces of the textile fibres which are more penetrable to liquid contaminants from bird faeces. The rough surface will provide mechanical compartments to grasp and host weightless mold spores from air and dirt will embedment into it. The fabric was later tested for colour change (colour fastness) to determine the gray scale rating according to the EN ISO 105-A05:1997 standard.

7.2 Colour fastness test of the damaged California dodger cover

The colour fastness test was done according to the instrumental assessment of colour fastness for determination of grey scale rating of European Committee for Standardization of textiles and textiles products (ISO 105-A05 1996).

The colour fastness test is an instrumental assessment of the colour change for the treated fabric comparable to its untreated colour. It was carried out using a spectrophotometer which assessed the colour fastness in the damaged and cleaned sample; compared it to the original sample. Some calculations were undertaken to convert the instrumental measurements into grey scale rating. The gray scale rating gave a view of how much of the

original finishing coatings or colours of the textile have been washed away during cleaning into the waste water. (ISO 105-A05 1996.) This also showed the waste water containing the bleaching agent and fabrics finishing compositions such coating chemicals and fabric particles needed further treatment before disposal, else it will cause environmental damages if disposed without treatment.

The California dodger cover and an identical undamaged specimen were used in this experiment. Their colours were measured instrumentally, CIELAB coordinates for lightness L , chroma C_{ab} and hue h_{ab} were determined. Their CIELAB differences ΔL , ΔC_{ab} and ΔH_{ab} were calculated and converted into grey scale rating with the help of equations in the spectrophotometer.



GRAPH 16. Spectrophotometer used for colour fastness test (Copyright from Central Ostrobothnia University of Applied Sciences textile and fur department)

The test sample was the washed California dodger boat cover and the untreated sample was an identical unwashed California dodger boat cover. Both specimens' single layers were back with an opaque white material containing no fluorescent whitening agent (FWA). The untreated sample was kept as a reference to each spot on the tested sample. Firstly, the equipment was placed over the untreated sample; Ultra Violet (UV) lights were emitted from the equipment on to the untreated sample. A specific amount of the light was reflected back to the equipment. The amount reflected was read and compared to the amount emitted in order to calculate the amount absorbed or that have gone through the material. Secondly,

the spectrophotometer was placed on a spot (labelled) on the California cover. UV light was emitted, the amount reflected back was noticed and used to calculate the amount absorbed or that have gone through the spot. The amounts absorbed or that have passed through the labelled spot on the California cover was compared to that of the untreated sample. Starting with the untreated sample, followed by the test sample, measurements were done at 20 different spots on the test sample.

Each time, a CIE tristimulus values was obtained using CIE illuminant D65 and 10° observer in the equipment. The values for CIELAB coordinates for lightness L, chroma C_{ab} and hue h_{ab} were calculated for both the test sample and untreated sample as specified in ISO 105-J03:1995. The differences in lightness ΔL , ΔC_{ab} and ΔH_{ab} between the untreated sample and test sample gave subsequent colour change mean values (ΔE_F). Determination of grey scale rating (GS_c) for colour change was done based on the Table3.

TABLE 3. Range of colour change mean values (ΔE_F) to determine grey scale rating (GS_c)

Range of ΔE_F	GS_c
<0.40	5.0
$0.40 \leq \Delta E_F < 1.25$	4.5
$1.25 \leq \Delta E_F < 2.10$	4.0
$2.10 \leq \Delta E_F < 2.95$	3.5
$2.95 \leq \Delta E_F < 4.10$	3.0
$4.10 \leq \Delta E_F < 5.80$	2.5
$5.80 \leq \Delta E_F < 8.20$	2.0
$8.20 \leq \Delta E_F < 11.60$	1.5
≥ 11.60	1.0

The various spots colour change values (ΔE_F), grey scale rating (GS_c), mean of colour change and mean square values were calculated in order to calculate the variance and standard deviation of the colour fastness on the California cover damaged by bird faeces.

TABLE 4. Data of colour fastness test on California dodger boat cover

Test sample Spot	ΔE_F mean (X)	GSc	$X - \bar{x} = \frac{\sum X}{n}$	$\left(\frac{\sum X}{n}\right)^2$
Spot1 = dcl +10% ca	1.15	4.5	-2.87	8.21
Spot2 = dcl+10% ca	1.23	4.5	-2.79	7.76
Spot3 = dcl+10% ca	1.33	4.0	-2.69	7.21
Spot4 = wch+75% ca	4.22	2.5	0.20	0.04
Spot5 = wch+25% ca	2.35	3.5	-1.67	2.77
Spot6 = wch +50% ca	4.35	2.5	0.33	0.11
Spot7= dcl +10% ca	1.35	4.0	-2.67	7.10
Spot8 = wch +75% ca	8.25	1.5	4.23	17.93
Spot9 = wch +75% ca	8.62	1.5	4.60	21.20
Spot10 = wch +25% ca	2.35	3.5	-1.67	2.77
Spot11= dch + 25% ca	3.34	3.0	-0.68	0.46
Spot12= dch + 25% ca	3.34	3.0	-0.68	0.46
Spot13= wch+50% ca	5.65	2.5	1.63	2.67
Spot14= wch +50% ca	4.38	2.5	0.36	0.13
Spot15 = dch100% ca	6.25	2.0	2.23	4.99
Spot16= wch +50% ca	4.85	2.5	0.83	0.70
Spot17= dch50 % ca	3.45	3.0	-0.57	0.32
Spot18 = dch100% ca	5.84	2.0	1.82	3.33
Spot19 = wcl+25% ca	2.34	3.5	-1.68	2.81
Spot20= wch +50% ca	5.67	2.5	1.65	2.74
Sum	80.31			93.72

$$n=20$$

$$\text{Mean } \bar{x} = \frac{\sum x}{n} = 4.02$$

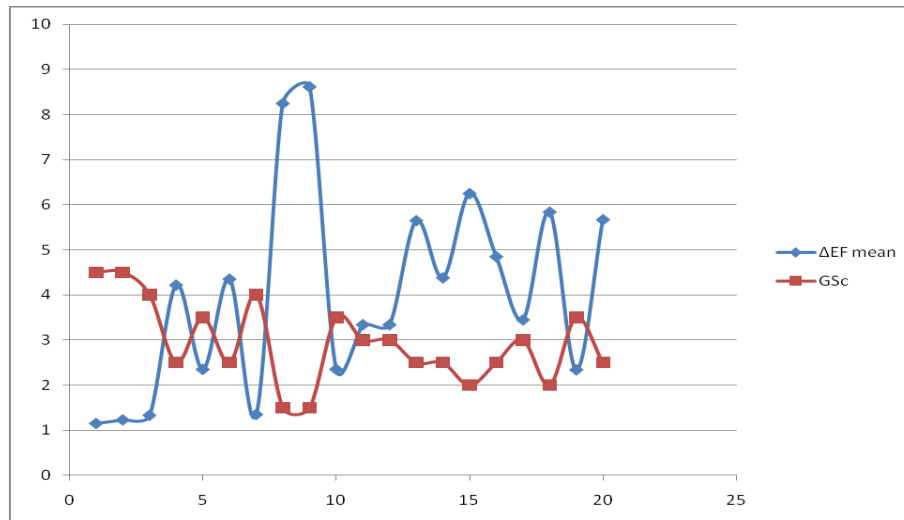
$$\text{Sample variance } s^2 = \frac{\sum (x - \bar{x})^2}{n-1} = 93.72 / (20-1) = 4.93$$

Implies standard deviation (s) = 2.22

Key:

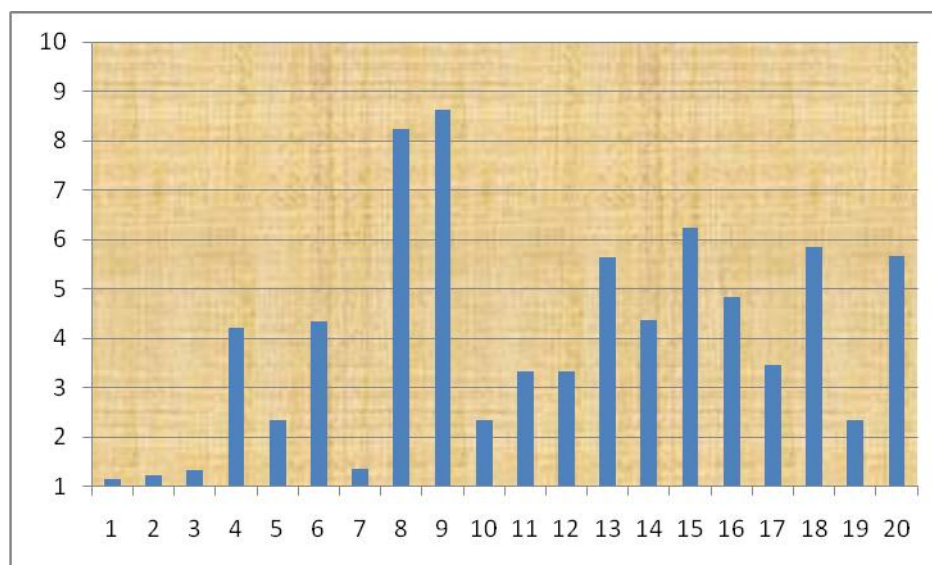
- Spot1 = dcl +10% ca means spot 1 was dry when the bird faeces dropped on the canopy (dc=dry canopy) and it was a light stained spot, cleaned with 10% concentrated solution of 303 fabric cleaner.
- Spot4 = wch+75% ca means spot 4 was wet when the bird faeces dropped on the canopy (wc) and it was a heavy stained spot, cleaned with 75% concentrated solution of 303 fabric cleaner.
- Spot11= dch + 25% ca means spot 11 was dry when the bird faeces dropped on the canopy (dc) and it was a heavy stained spot, cleaned with 25% concentrated solution of 303 fabric cleaner.
- Spot19 = wcl+25% ca means spot 19 was wet when the bird faeces dropped on the canopy (wc) and it was a light stained spot, cleaned with 25% concentrated solution of 303 fabric cleaner.

The mean colour change values (ΔE_F) showed to vary with standard grey scale ratings (GS_c). Their variation was plotted in Graph 17. It shows that the higher the ΔE_F value, the smaller was the GS_c value, meaning the two variables are inversely proportional. The least grey scale value showed the highest colour change took place at that spot. Firstly, this meant the bird faeces and their content caused a stubborn stain that was heavily washed. Secondly, the 303 fabric cleaner concentration was likely too high and resulted in cleaning and bleaching the spot as well.



GRAPH 17. Variation of mean colour change (ΔE_F) versus standard grey scale rating (GS_c)

A bar chart of the mean colour change values at the 20 labelled spots on the California dodger textile cover was drawn to show which spots were underwent much colour change. Also, the spots which underwent much colour changes were the spots which were heavily stained by bird faeces and hence required heavy cleaning with higher concentrations of the 303 fabric cleaner. Graph 18 shows the bar chart: the vertical axis is the mean colour change values and the horizontal axis is the spots on the California cover.



GRAPH 18. Bar chart for the mean colour change values ΔE_F mean at various spot on damaged canopy

Based on Table 4, it can be concluded that when the bird faeces drop on the canopy when it is dry, they simply stain the canopy mildly. This type of stains can be clean lightly with a 10% of 303 fabric cleaner concentrated solution. In this case, less colour fastness will occur at that spot, therefore a high grey scale value. On the other hand, when bird faeces drop on a wet canopy, the bird faeces chemicals content are sucked into the fabrics by capillary action (due to water polarity) and are embedded into the fabrics. This will create stubborn stains, which in turn requires heavy cleaning using higher concentrations (75% or more solution) of 303 fabrics cleaner. If the acids concentrations in the bird faeces are high, they can erode and bleach the textile fibres causing colour fastness as well. Bleaching of textiles by acid in bird faeces coupled with bleaching caused by heavy cleaning at spots with stubborn stains will result in higher colour fastness, therefore a smaller grey scale values. Some heavy cleanings were caused by greasy and stubborn contaminant like the greasy 1,2-benzenedicarboxylic acid and hydrocarbon compounds classified in the bird faeces samples.

The averages of ΔE_F and GSc are 4.02 and 2.93 respectively. This means the averages distribution of colour fastness over the canopy was 4.02. According to the greyscale rating system, this value corresponds to GSc value of approximately 3. The original sample with no damage had a GSc of 5. This implies washing the California dodger canopy damaged by bird faeces with 303 fabric cleaner chemical caused colour fastness from 5 to 3. This was estimated to be the average colour fastness on the canopy's whole surface from taking 20 ΔE_F readings from 20 different spots on it.

7.3 Retreating the damaged fabric

The cover was retreated with the 303 high tech fabric guards. Firstly, a thin layer of the solution in its 100% concentration was sprayed evenly on half of the fabric surface area in a ventilated area. It was evenly coated and allowed to dry for two days. A second thin, evenly coated layer was applied again on that same area and allowed to dry for two days. On the other half, a thick evenly coated layer was applied on the fabric surface area and allowed to dry for four days. Later, the two halves were isolated, labelled and tested for

water repellence. The two light coatings proved to be effective in restoring fabric water repellence than a single thick coating.

The best observed concentrations to be used depending on the nature of the stains are 25% solution for heavy stains and 10% solution for light stains. These concentrations cleaned the stains sufficiently and prevent the impact of the colour fastness. Also, these concentrations do not damage the textile's original polyurethane coatings; in turn do not reduce the waterproof property of the textiles. Hence, the waste water resulting from cleaning with these concentrations do not contain residues of polyurethane paints and synthetic fibres pieces that would pollute the environment. This implies such waste water would not require further treatment to reduce its pollutant concentration to accepted standard by environmental legislation before disposal. Meanwhile, the concentrations above these will produce these adverse conditions and will require further treatment. Else, they will pollute the environment on which they will be deposited.

8 IMPACTS OF BIRD FAECES ON BOATS

Bird faeces have impacts on the boat parts exposed to it as well as environmental impacts. Impacts of bird faeces stretches to human and other living organisms as a result of mold and mildew spores to human health.

Fouling, mold and mildew are potential problems facing boaters since their boat usually stays in all kinds of weather (including salty water) with all sort of dirt and chemicals (including bird faces contaminants). The bird faeces play a vital role in the growth of the organisms causing these effects. The boat part submerged in water will accommodate fouling organisms under favourable water nutrients supplied by the bird faeces. Mildew and mold growing grows on the boat textile as a result of bird faeces content and moisture. Mold and mildew affects the boat textiles (cover and canopies) meanwhile fouling affect boat parts submerged in water (hulls, anchors, fishing gear, propellers and lines).

8.1 Fouling

Fouling is the growth of micro and macro organisms on the boat hull immersed in water. The process is initiated by nutrients such as nitrogen, phosphorus and sulphur compounds in the water. The classification of the bird faeces confirms the presence of these nutrients and some micro organisms. When these components in the bird faeces dissolve into the boat surrounding water, they nourish the growth of slimes or bio films (fouling organisms) in the boat lower layer. Nitrates, sulphates and phosphate compounds act as fertilizers. Therefore, they contribute to the growth of plant both terrestrially and in the aquatic environment. (Pacheco-Ruíz, Zertuche-González, Arroyo-Ortega & Valenzuela-Espinoza 2004.) If the boat is stagnant, then the slime may host other sea plants and organisms such as mussels, barnacles, algae, sponges and sea squirts, and the mass will increase with time.

Organisms causing fouling are divided into two main groups namely: primary slime film forming micro-organisms such as bacteria, diatoms and algae, and secondary macro-fouling organisms such as barnacles, molluscs, sea squirts, sponges, sea anemones, bryozoans, tube worms, polychaetes and weeds.

8.1.1 Factors influencing the growth of fouling organisms

Parameters such as nitrates, sulphates and phosphates available in water, and the water quality determine the growth of fouling organisms and hence, their attachment onto the boat hulls and keels. Water quality depends on temperature, pH, water flow velocity, shade, pollution and material inflows into the water. The bird faeces contain the nutrients, uric acid altering surrounding water pH, fertilizer (nitrates, sulphates and phosphate) and if the boat remains stagnant, with lukewarm temperature, fouling organisms would grow effectively.

8.1.2 Fouling Organisms

When mussels and barnacles attached to boat hulls and keels submerged in water, they produce millions of larvae in water during their reproduction. The larvae feed on the nutrients from the bird faeces in surrounding water. When the boat is stationary in the water such as in winter, the larvae will attach to the boat hulls, propellers, and anchors and would feed efficiency. Fortunately for them, the boat stays stagnant for almost 90% of its live history in water. (CRC Reef Research Centre 2001, 8.)

Weeds are capable of attaching themselves to static boats and feed on available nutrients supplied by bird faeces in the stagnant water surrounding the boat. The upper surfaces of the boat provide a suitable shade for the growth of weeds. Some seaweeds stay firmly attached to the boat at high speed whereas some fall off. In any case, their presence in the water where boats sail provides a suitable breeding environment where they will one day find stationary boat hull to attach on. (CRC Reef Research Centre 2001,8.)

Algae grow and reproduce in stagnant water with nutrients to form a large colony called slime. With enough nutrients from bird faeces, the algae grow and host other organisms that would form a slippery mass attached to the boat hull which is submerged in water. (CRC Reef Research Centre 2000, 5.)

8.1.3 Impacts of fouling on boat

The growth of fouling organisms on the boat hull and keel increases the weight of the boat. Hence the boat draft and the freeboard parts become more submerged into the water than normal. During motion, this extra weight slows down the boat speed as it drags in opposite direction. This increases the time normally required to cover a specific distance. Also, high acceleration will be required to initiate motion. These lead to high fuel consumption, increasing energy cost and producing higher amount of emissions such as NO_x and SO_x resulting from fuel combustion in the boat to the environment. Fouling organisms entangle the propeller of boats, making the boat manoeuvrability difficult.

Fouled hulls will increase the overall weight of the boats, causing the boats to lower in water than normal. This will cause the hulls not to respond quickly at helm, reducing their sea worthiness. According to the U.S. Coast Guard's Boating Safety Division 2007, "The most critical issues in the boat are safety and efficiency". Boat safety is affected by growth of fouling organisms because they increase the boat weight thereby reducing the draft and freeboard distance. Draft is the depth of water needed to float a boat and freeboard is distance from water to the lowest point of the boat where water could come on board.

When fouling organisms stay for a longer time on a stagnant boat, it can damage the paints, fabrics and cause deterioration. They produced natural glues to attach themselves to the boat and the natural glues can damage wood, textiles and glass fibres. Deterioration caused by fouling weakens the safety level of the boat hull. (Environment Canada 1993.)

Summarily, a fouled running gear, propeller and hull coupled with increased weight will provide a dragging force reducing boat manoeuvrability, speed and efficiency. Therefore more residues of fuel combustion such as NO_x and SO_x would be emitted to the environment, thereby increasing environmental pollution.

8.2 Mildew and mold growth

Mildew and mold are fungi, in other words simple microscopic organisms that grow anywhere there is moisture. Their presence is shown by greyish or white fuzz seen on

surfaces. Mildew and mold are necessary in the environment as they cause leaves to decay and enrich the soil (digest organic matter: dead animals and plants). Mildew and mold assist in composting, reduce dead and unpleasant things that would pile up on the earth and hence cleaning the environment. Mildew and mold are tough and numerous, forming essential tools for natural cleaning of the environment. It is their ability to destroy organic materials including boat textile material. However, that makes mold a problem to the boat textiles made of organic materials and human bodies as they digest and destroy organic tissues. (FEMA Publications 2002.)

Mildew, an early stage of mold and mold grow on wood products, ceiling tiles, cardboard, wallpaper, carpets, drywall, fabric, plants, foods, insulation, decaying leaves and other organic materials. They digest organic material, eventually destroying the material they grow on, and then spread to destroy adjacent organic material. Mold growths, or colonies, can start to grow on a damp surface within 24 to 48 hours. Their spores are tiny, tough, lightweight seeds-like matter that can hang and travel in the air for days and drift far in the wind. They can survive when frozen for 40 years. It is estimated that one square foot of dry wall can contain 300 millions mold spores when fully colonized. (McAfee 2002.)

Additionally, mildew and mold can cause from mild to severe health problems to humans. In 1991 the Mayo clinic in North America estimated that 40 million people in the U.S suffered from sinus infections caused by mold and mildew. Rapid rise in asthma over the past 20 years is attributed to mold. (US EPA 2005.) The mildew and mold spores contain DNA to reproduce. They require moisture and food (nutrients in bird faeces) to grow and perform their activities. On the boat textiles, mildew and mold get their moisture from water vapour in the air or from boat textiles stored wet.

Mold spores are tough and swing in the air. When the spores approach a wet or moist textiles material, they hang into it and will hatch egg-like structures that begin to grow into arm-like structures called hyphae. These grow into octopus-like structures that begin to feed on microscopic dirt and nutrients from bird faeces, dead organic matter and paint on the boat. More arms grow out if there is enough dirt, paint and moisture on the boat textiles.

8.2.1 Mold spore diseases

There are three mechanisms for the pathogenesis of human disease caused by mold which include infection, allergy, and toxicity.

Mold (fungal) infections of humans are often localized to the skin or lungs. Tissue abscesses or disseminated diseases in any organ are more apt to occur as opportunistic infections in the immune compromised host. The presence of candidiasis, cryptococcosis, aspergillosis, mucormycosis, and other infections are likely under these conditions. Opportunistic infections also occur in diabetes, alcoholism, and neutropenia during the course of corticosteroid therapy, as well as with the use of broad-spectrum antibacterial drugs. These include infections by actinomycetes (*Nocardia* and *Actinomyces* species) and by the dimorphic fungi such as histoplasmosis, coccidioidomycosis, blastomycosis, paracoccidioidomycosis, sporotrichosis, and penicilliosis. (Abba 2003, 221-226)

Respiratory diseases are caused by inhalation of mold spores coordinated by allergic mechanisms. They encompass only four known diseases: atopic asthma, hypersensitivity pneumonitis, allergic bronchopulmonary aspergillosis (ABPA), and allergic fungal sinusitis. Inhalation of mold spores might produce respiratory allergy. Individual fungal species contain 40 or more distinct allergens for human beings. There are thousands of species of mold, although only about 200 of them are known allergens. (Rabito, Iqbal, Kiernan, Holt & Chew 2004)

There are poorly defined seasonal patterns for mold sporulation in contrast to the pollination of plants. Identification of spore is difficult and the allergen changes expression both within the same species and among different species, which is often dependent on culture conditions. This makes allergen extraction complicated. Few purified allergens are currently available for research purposes or clinical use. Inhalation of mold spores has been implicated and it does happen as part of a mixed flora with bacteria and other microorganisms. (Abba 2003, 223-226.)

All microorganisms generate chemicals that are necessary for their survival and nutrition. These chemical moieties are both toxic and nontoxic. Their toxic or nontoxic characters depend on the substrate like tissue, organ, and whole organism, including the human being,

the dose and route of exposure. Airborne mold also causes chronic fatigue and upper respiratory tract illnesses. *Stachybotrys atra* is an indoor mold, greenish-black saprophytic mold. It requires substantial humidity to grow on cellulose with low nitrogen content. It grows on synthetic substrate such as polyester if moisture is available and causes putative illness. (Abba 2003, 224-226; Rabito et al. 2004.)

8.3 Mild and stubborn stains on boat external textiles

When the faeces drop on wet boat textiles, volatile gases from it easily diffuse and embed into the textile fibres forming stubborn and coloured stains. Some of the components dissolve in the water forming solutions that moves through the textiles fibres by capillary action. When the faeces drop on the dry boat textiles, the faeces stick onto the textile l, but due to the fact that there is no water or moisture for which most of the chemicals are soluble, they remain as mild stain. The textile canopy cleaning experiment showed that mild stains are easier to clean than stubborn stains. Intensive cleaning of stubborn stains leaves significant impacts such as bleaching and reducing the waterproof nature of the textile. The solid substrates from bird faeces stay on the textiles are mild dirt.

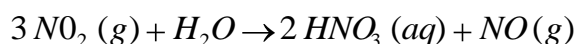
The bird faeces contain chlorides which are bleaching agents. If the concentration is high enough, then it can bleach the boat textile covers and canopies causing colour fastness. The organic compounds classified in the bird faeces create stubborn stains on the textile material. Stubborn stains require heavy cleaning and result in bleaching and colour fastness. These reduce the bright and elegant colour of boat textiles, reducing its quality.

9 ENVIRONMENTAL IMPACTS OF BIRD FAECES

The environmental impacts of bird faeces are linked to its chemical content and the reactions they undergo in the nature. Some of the chemical content reacts with water vapour to form acid rains. Some of the antifouling paints used on boat hulls further leaches into the aquatic environment posing pollution.

9.1 Acid rains formation and environmental impacts

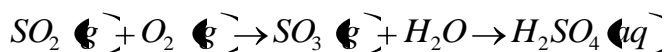
Nitrogenous compounds in the bird faeces occur in the form of uric acid, NO_3^- and ammonia. Uric acid is converted to ammonia. Ammonia gas is oxidized to nitric oxide and nitrogen dioxide by air. The nitrogen dioxide is a green house gas contributing to green house effect and global warming. It also reacts with water vapour in the atmosphere to form nitric acid which is an acid rain.



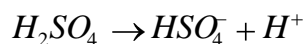
GRAPH 19. Variation of pH with acidity of NO_x Acid rain (adapted from Casiday & Frey 1998)

Nitric acid dissociates in water, producing hydrogen ions and nitrate ions (NO_3^-), and lowering the pH of the solution. The lower pH means the lake acidic strength is increased, making the lives of fishes and other marine organisms depending on higher pH difficult. (Casiday & Frey 1998.)

Sulphates in bird faeces produce SO_2 which also reacts with water vapour in the atmosphere to form acid rain.



Sulphuric acid is a strong acid, it readily dissociates in water to produce H^+ ion and an HSO_4^- ion

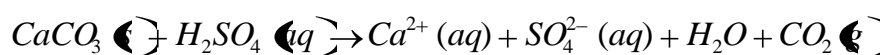


The HSO_4^- ion may dissociate further to produce H^+ and SO_4^{2-} .



Hence, acid rain such as H_2SO_4 causes the concentration of H^+ ions to readily increase, lowering the pH of rain water to harmful levels.

Acid rain triggers inorganic and biochemical reactions in natural systems with deleterious environmental effects. Marble and limestone consist of calcium carbonate ($CaCO_3$). Buildings and outdoor monuments made of these materials are gradually eroded away by acid rain. A chemical reaction between calcium carbonate and the primary acid component of acid rain (H_2SO_4) results in the dissolution of $CaCO_3$ to give aqueous ions, which is in turn washed away in the water flow. (Stryer 1997, 332-339.)



Acid rain degrades soil minerals producing metal ions that are washed away by runoff into the lakes causing the release of toxic ions, such as Al^{3+} into the lakes. It washes important minerals such as Ca^{2+} , NO_3^- from the soil, killing trees and retarding plant growth. (Casiday & Frey 1998.)

NO_2 and SO_2 form fine particulates which cause respiratory problems to humans. They form toxic air pollutants, and contribute to stratospheric ozone depletion, climate change and acid rain. (Driesen 2002, 3.) These compounds pollute the air and harms future generations who will depend on the air, lakes and forest.

Some boat anti-fouling paints and lacquers, paint strippers, and textile fabrics cleaning agents may emit volatile organic compounds (VOCs). The alcohol and ketones classified in the bird faeces are VOCs. VOCs cause eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. VOC reacts in

the air to form ozone. Ozone damage lungs tissue and triggers asthma attacks. (US EPA 2009.)

The source of chlorides into water is not only from winter road salt as de-icing agent. Bird faeces chlorides are contributing to the total chlorides in the water in certain areas. Increased of chloride concentrations in the lakes from bird faces threaten the quality of surface waters as primary drinking water sources. Conventional pollutants such as phosphorus, nitrogen and chlorides have a significant impact on water quality and the ability of aquatic organisms to survive. High chloride concentration stresses aquatic organisms (CEPA 2009). Phosphorus and nitrogen are nutrients necessary for plant growth in lakes. Increased amounts of nitrogen and phosphorus from bird faeces can lead to reduced oxygen levels, and limit fish ability to survive. (Amirsalari & Li 2007.)

9.2 Boat antifouling paint and environmental impacts

Colonisation of boat hulls and other areas in water by fouling organisms is prevented by applying anti-fouling paints. Some anti-fouling paints contain triorgantin compounds and metals ions which are toxic to non-target organisms in the water. Cu in the form of Cu_2O is a major inorganic biocidal component of most anti-fouling paints used nowadays. Ships, yachts and motor boat may leach excess Cu of 2 kg per year and some are washed directly into the environment and therefore supplies Cu to the coastal environment. This lowers aquatic biodiversity, salinity and limits food webs. Species such as bladderwrack and fucus vesiculosus are very sensitive to high Cu concentrations in the water (Karlsson, Ytreberg & Eklund 2009).

Water and sediment contamination by Cu in harbours and boatyards has been reported. In these areas, particulate contaminations is of great concern from boating activities, paint chips or flakes from hull pressure-hosting cleaning or boat scrapping processes such as shot blasting, sanding and stripping (Turner et al. 2008).

Due to the toxic effect of Cu-leaching anti-fouling paints, some new anti-fouling paints containing zinc are entering the market. These were claimed to function by physical means and not releasing toxic substances. A main component is zinc oxide with physical and

chemical mode of action and functions as binder and as pigment (Singh & Turner 2008). This means zinc based anti-fouling paints on boat hull would supply Zn into the aquatic environment. Zn is toxic to bacterium, alga and crustaceans. Cu and Zn are used in enzymes carrying out metabolic processes. They are toxic when their concentrations are above what is needed physiologically. (Karlsson et al. 2009.) These metals concentration in boat hull pressure wash water do exceed the required concentration for fish and other aquatic organisms (Environment Canada 2006).

10 REMEDIATIONS TO THE IMPACTS OF BIRD FAECES ON BOAT TEXTILES AND FINISHING COMPOSITION

Fouling is a problem in shipping as well since it causes economic loss due to speed reduction and higher costs for both fuel and for hull maintenance (Champ 2000). Methods such as pitch, tar, and copper sheathing have been used to prevent fouling (Karlsson et al. 2009). Recently introduced anti-fouling paints and their residues contain biocides such as tributyl tin (TBT), Irgarol and high concentrations of leachable copper and zinc, considered toxic to aquatic organisms, including salmon and shellfish (Almeida et al. 2007). Research has shown that even biocide free boat paint such as Micron Eco produces toxic leachates. This means other toxic substances rather than biocides are present in the paint.

Waste water and solid residues from washing, scraping, sanding and blasting of antifouling paints on boat hulls contain deleterious substance. Environmental legislation forbids the release of these wastes to the natural environment (Council Directive 89/677/EEC). Some commercially used anti-fouling paint used on ships and leisure boat are Anti-fouling Olympic 86 951 (AO) and Interspeed 617 (IS), and Fabi and Micron Eco (ME) respectively. Based on these problems, methods to prevent and manage the impacts of bird faeces onto the boat textiles and finishing compositions, and environment are emphasized below. (Karlsson et al. 2009.)

10.1 Primary methods to protect boat textiles and toxic hull leaching

The best and ideal strategies encompassed in the primary method would be to:

- Prevent boat textiles and hulls from bird faeces. This can be done by coating the boat textile material with a polyurethane compound. This method will prevent bird faeces contaminants from entering the textiles, and subsequently the textiles will require mild cleaning when stained.
- Use non toxic anti-fouling paints on boats hulls. If this becomes successful, it will prevent Cu and Zn leaching from boat hull into the aquatic environment. This method will not prevent the addition of nutrient into the lakes from bird faeces.

10.1.1 Coating textile surface with breathable waterborne polyurethanes (PUs)

Coating the surfaces of the fibres on boat textiles with breathable waterborne polyurethane (PU) consisting of alternate soft and hard segments will smoothing the textile surface. Fairly smooth and coated surface of textiles prevent bird faeces contaminant entering the fabrics by sorption-diffusion-absorption mechanism. Therefore, stubborn stains will not be formed on or entangled into the boat textiles. Smooth and coated surface of textiles easily bounds off air floating mold spores when they contact each other, limiting the attachment and growth of mold and mildew. It implies intense cleaning of boat textiles with high concentrated solutions of cleaning agent will not be required. In turn, no colour fastness and boat textile fibres weakening will occur.

The two fundamental properties of boat textiles that will suit this study are breathability and ability to prevent the diffusion and absorption of bird faeces contaminants into the fabrics. Boat textile breathability is its ability to transmit water vapour from the boat interior by diffusion to the exterior to facilitate evaporative cooling. If water vapours are trapped in the interior, the relative humidity of the boat internal environment will increase. This will increase the heat conductivity of the insulating air inside creating uncomfortable situations. (Meng, Lee, Nah & Lee2009.)

Breathable waterproof boat textile could be produced using micro-porous or hydrophilic nonporous films waterborne PUs. Micro-porous films will prevent water and bird droplets from the external environment to penetrate the fabric coatings into the inside, but allow water vapour to penetrate from inside and escape outward. Hydrophilic nonporous films allow water vapours from the interior to penetrate the fabric coatings to the exterior via the hydrophilic segments by a sorption-diffusion-desorption mechanism. Hydrophilic waterborne PUs coatings adhere firmly to textile surfaces and would prevent water droplets and bird droppings from entering fabrics from the exterior. (Meng et al. 2009.)

10.1.2 PUs, PUs films and PUs coating synthesis

According to Meng et al., cationic waterborne polyurethanes can be synthesis with diols. Diol such as polytetramethylene ether glycol (PTMEG) was melted at 60 °C. Polypropylene glycol (PPG) and dimethylol butanoic acid (DMBA=4.5 wt% based on prepolymers) were dissolve in N-methyl-2-pyrrolidone (NMP) and added into round bottomed, 4 neck separable flask containing a mechanical stirrer and a thermometer. Under gradual stirring, the mixture was heated to 90 °C for 1 hour. It was cooled to 60 °C and isophorone diisocyanate (IPDI=NCO/OH at the ratio of 1.85) was added. The mixture was heated to 80 °C and allowed for 3 hours to obtain NCO-terminated prepolymers. The polymers were cooled to 50 °C and neutralized with triethylamine (TEA). After 30 minutes, it was cold again to 35 °C and emulsified with distilled water under vigorous stirring. The polymer chain was neutralised by adding EDA solution and 1, 4-butanediol (molar ratio 1:1) in water. The reaction was allowed to continue until the NCO groups reacted completely. Other diols such as polyethylene glycol (PEG) and polycaprolactone (PCL) can be use to prepare cationic waterborne PUs. (Meng et al. 2009.)

Using PUs films and coatings on the surface of textiles makes them fairly smooth and tailors balance between breathability and waterproof properties of the textile. The films enhance the thermal and tensile properties meanwhile the coating control the mass transfer properties of the fabric. Generally small molecules such as the contaminant from bird faeces are transported through uncoated rough textile surface via sorption-diffusion-desorption mechanism. The molecules are first absorbed by the synthetic textile polymer membrane, followed by the diffusion through the membrane when they become embedded as stubborn or mild stain with diverse damages on the textiles. This mechanism via which water and bird faeces enter the textile membrane is prevented by PUs films and coatings.

To prepare a thin film that could be placed on the surface of the textiles, mix a 1:1 (w/w) waterborne PUs and distilled water and pour it on the boat textile fabrics. Allow it to dry at room temperature. Later, dry the film for 12 hours at 80 °C. Keep it to dry again in vacuum at 50 °C. The duration after which it could be re-applied be experimented and prescribes in manual of instruction. This could re-enforce breathability, waterproof nature and prevent bird faeces from interring the boat fabrics by adsorption, sorption or diffusion.

10.1.3 Non toxic boat hull antifouling paint

The use of nontoxic anti-fouling paint functioning by physical means rather than biological and chemical means can prevent toxic biocide leaching into the environment. Toxic anti-fouling paints function by leaching toxic biocides (Cu and Zn) slowly into surrounding water. The toxic biocides keep away the fouling organisms from attaching to the boat hull and keel. Meanwhile, nontoxic anti-fouling paints do not leach toxic compounds to prevent organisms from attaching to boats' hulls. Their slippery natures simply reduce the attaching strength of the natural glue that fouling organisms produce in order to attached themselves to boat hulls. The slippery nature of silicone coatings allows for fouling organism growth to be wiped off easily. Frequent hull cleaning would be needed to clean off fouling organisms about to attach to boat hulls. Non toxic anti-fouling paints are more durable than toxic paints. This is because the effectiveness of toxic paints depends on toxic compounds which leach out of the paints over time. Non-toxic hull coating paints may be silicone based, water based, epoxy-based, or polymer-based due to their coating slippery character. This method will eliminate leachable biocides, and hence no environmental pollutions from the waste water from anti-fouling paints

10.1.4 Other primary measures

Boat fabrics should be made of anti-bacterial or anti-microbial material. To keep the textiles in good looking conditions and delay deep or vigorous cleaning, bird faeces and other dirt should simply be brushed off immediately before they becomes embedded in textiles fabrics. Spills should be wiped up as soon as they occurred, stained spots should be cleaned soon after stains occurred, wet and moist boats textiles should be dried before storage. These will limit conditions enhancing the growth of mold and mildew, and absorption of contaminants. Boat hulls and keels should be cleaned frequently. Boats should not be allowed submerge in water when not in use. Boats should be stored in dry places or surrounded with slip liner. Companies should control their outlets for compounds that can easily enter bird and fish food chains in terrestrial and aquatic ecosystems.

Methods to keep the birds off the boat without endangering them would be a solution as well. Birds usually land on high points on a boat where they can locate prey and predators.

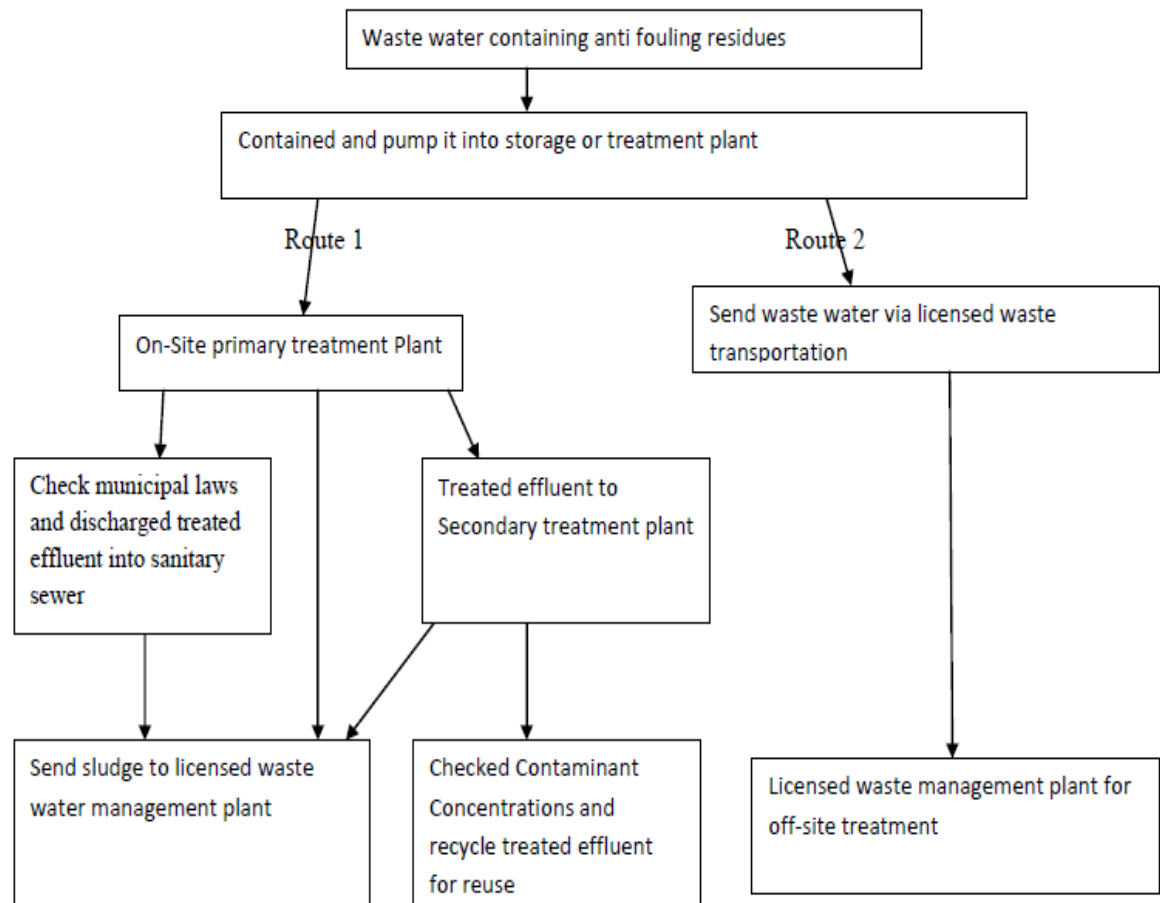
Treating high points on boat with visual or physical deterrents will discourage the bird from landing and the birds will move on to a more suitable location off the boat. Bird deterrent designs such as the solar repeller and the bird spider creates inconvenience for birds to choose a boat as a perch. When the solar repeller is mounted on the boat top, it uses battery energy to spin continuously. The continuous spinning keeps the birds off the boat. Bird spiders contain arms that sway in the wind, discouraging birds from landing on the boat tops. (Donoho2009.)

10.2 Secondary methods to protect boat textiles and hulls toxic leaching

Secondary methods are those management schemes applied to control mostly the environmental impacts of toxic leachates from boats hull caused by toxic anti-fouling paints and boat textiles infected by mold in case the primary methods fails. This method ensures that wash water with deleterious anti-fouling residues does not enter the aquatic environment. It also limits the spread of lighter mold spores. Also, this method ensures that environmentally friendly anti-fouling paints are used carefully. Fouling organisms and fouled residues should be disposed in the landfill.

According to McAfee (Sunbrella 2010), "when mildew and mold affects any fabric that fabric should be junked or tossed". Usually, objects that resist the growth of mold and mildew are constructed with materials that resist mold. Often, these materials are used on the outer surface and not the interior of the objects because claims are made that only the surfaces are exposed to mold spores and moisture for sporulation. Unfortunately, threads used in stitching these materials are not made with mold resistant. Therefore, molds easily digest the stitchings and find their way into the interior where all the conditions are favourable for rapid digestion.

In case of washing a boat hull painted with anti-fouling paint or boat textile material, the waste water should be managed properly. The flow chart below gives guide on the management system of waste water with textiles fibres, PUs coatings, strong detergents and anti-fouling deleterious residues.



GRAPH 20. Boat hull waste water management scheme (adapted from Environmental Canada)

The first step is to contain and collect the wash water. The water can then be preliminary and primary treated on-site or off-site. Non proper containment of antifouling paint residues can result in deleterious substances being released into the aquatic environment.

In preliminary treatment, screens can be used to remove the larger solid inorganic particles, followed by the removal of particles such as grit and silt which are abrasive to plant equipment. Later, primary treatment is applied. The wastewater is passed through a primary sedimentation tank to remove solid particles of organic material from the suspension by gravity settling. The effluent can be sent to the secondary treatment plant. In the secondary treatment stage, a biological process called activated sludge could be applied to break down dissolved and suspended organic solids using naturally occurring

micro-organisms and supplied by oxygen for mixing and aeration. Depending on the concentration of contaminant and the intended purpose of the water, it can be deposited to the environment or sent further to the tertiary treatment plant.

In the tertiary treatment, a disinfectant such as chlorine is applied to reduce pathogenic micro-organisms which can pose a risk to human health. Other tertiary treatments such as dissolved air flotation filtration (DAFF) could be applied depending on the purpose of the final treated water.

Generally hi-tech fabric should be used to make boat textiles. The finishing compositions of boat hull should be monitored. To prevent the damage caused by bird faeces, the fabric should be:

- Water resistant (utilizing a durable polyurethane undercoating), the durability of its breathable characteristic should be enhanced,
- Able to retain its original colour (resist colour fastness) and superior strength from any damage that the bird faeces might caused,
- Able to provide healthy interior air quality,
- Able to persist stain and mildew, easy to clean, resort to bleach for stubborn stains
- Able to resist the growth of mold and mildew,
- easily dried to prevent moisture which nourished mildew and mold growth,
- able to prevent the absorption, diffusion and embedding of chemicals and liquids

In certain cases, the primary and secondary methods should be applied together to ensure greater efficiency. The primary method will prevent the diffusion and absorption of contaminants from bird faeces to enter the boat textiles. Also, primary method will create just mild stains that can be easily brush off, preventing colour fastness and the bleaching of boat textiles. This will further reduce the amount of textiles particles that can be found in the waste water. Hence, less treatment will be required of the waste water in the secondary method. In the secondary method, besides choosing textile materials with specific characteristics, the treatment of the waste from anti-fouling paints, fouled and molded objects are of critical importance to the environment.

11 DISCUSSIONS

Birds are important for their aesthetical values in the biosphere. Their variations are important to bird viewers and birds species continuity. The interaction of birds with boaters has both advantages and disadvantages. Birds depend on food rich in compounds that undergo metabolic and non metabolic processes. These processes produce faeces that contain contaminants. During the interaction of birds with boaters, bird faeces drops on the boat textile, finishing composition and surrounding water. The contaminants in the bird faeces damage these boat part exposed to them.

Based on the short survey made at the beginning of this research work, it is shown that bird faeces posed impacts like fouling, mold and mildew, colour fastness and bleaching on the boat. The effects might be environmentally under estimated due to the small amount of waste produce per isolated bird. When the birds are in large colonies, the effects might be observed significantly due to the large amount of faeces produced. Until recently, there has been interest on bird faeces (guano) as fertilizers due to the high amount of nitrates, sulphates and phosphates content.

When the bird faeces sample was classified, it was shown to contain nitrate, sulphates, phosphates and chlorides as well as other organic compounds and metals. The nitrates, sulphates and phosphates diffuse faster into the air and easily break down to their oxides in the soil by nitrogen fixing bacteria, desulphurization and dephosphate reactions respectively. They are polar compounds; hence dissolve in water to produce compounds with fertiliser potentials. This increases the growth of sea plants causing eutrophication and risking the lives of aquatic organisms that depends on dissolved oxygen in the water. In the air, they react with water vapour to produce acid rains with damaging environmental effects on building and statues made with limestone. The chlorides have bleaching effects on the boat textile material. Hence, the compositions of the bird faeces are actually responsible for the damage caused by bird faeces to the boat textiles, finishing compositions and the environment.

Synthetic textiles used in the boat external surface are mostly polyester or acrylic. These organic polymers are non permeable to water, and resistant to mold, heat and acids. When

the bird faeces contaminant dissolved in water, they diffuse into the fibres. Organic compounds are mostly partially or non polar and dissolves in each other. The organic contaminant in bird faeces would react with polyester organic molecules, producing undesirable effects. Also, the inorganic and metal components of bird faeces react with the boat textiles and composition of the boat hull, and are embedded into the textile fibres and finishing paints respectively. The components react to leave different undesirable effects like stains, colour fastness and deterioration on the boat textiles and finishing composition. These impacts are considered to be the damages caused unto the boat textiles and finishing composition by bird faeces.

Some of the bird faeces chemicals do not occur naturally in the bird food chains and metabolic waste. They are mostly from industrial outlet into the air, water and soil. From there, they enter vital food chains until the metabolic pathway of bird and finally into the bird faeces on the boat textiles and surrounding water. On the boat textiles, the chemicals manifest the effects studied in the impacts of bird faeces sector. Meanwhile in water, they increase the growth of fouling organisms on the boat hull, as well as causing eutrophication. Hence, they are called contaminants.

There are many chemical companies and other production plants in Kokkola. These companies are situated in the Kokkola Industrial Park by the sea side. Strict environmental regulations on the content of companies' outlets put in order by the Kokkola environmental office obliged the outlets content to meet accepted and environmentally viable standards. The companies have updated their technologies on waste management. The regulations put forth obliged the companies to deposit waste to landfills, and those to be dispose in the water and air should contained concentrations that are considered safe to the environment. Nevertheless, some small concentrations of their waste and by-products may enter vital food chains. Even the concentrations considered safe to the environment may accumulate in the air, water and soil, and enter important food chains.

This means in order to prevent some of the damages of bird faeces on boats, there should be continuous research and development on boat textiles and finishing compositions. This would also protect the environment that is sustaining present lives to be able to sustain future generation lives. Experts have used anti-fouling paints on boat hulls to prevent the growth of fouling organisms. The anti-fouling paints contain metals like Cu. The Cu

content gradually leaches into the aquatic environment causing pollution. Researchers are still underway to produce anti-fouling paints that do not function by leaching out metals.

The PU textile, PU film and PU coatings could be researched and experimented in detail to understand the various effects on using different diols or a combination of diols. The PU films and coatings could be applied on textiles in three different manners to verify which would be efficient to prevent the penetration of bird faeces contaminant, and mold and mildew growth. The three application manners might include spraying the outer surface of the knitted or woven fibres, spraying the fibres before spinning them into yarn to be knitted or woven (Eberle et al. 1999; 39-65) and spraying the fibres before spinning into yarn and spraying the outer surface again. The third method reinforces the protecting coat property.

From these, the breathability and waterproof properties of the textile would be reinforced and the one with the best equilibrium efficiency would be used to protect boat textiles. In the same line, nontoxic boat hull antifouling paints should be produced in line with environmental legislations. This might require extra frequent hull preparation and cleaning, but would sustain the environment on which we solely depend.

Coating the PU textile with PU films and coatings, implementing industrial ecology and green chemistry during boat production processes, and using end-of-pipe technology in waste management would save bird species, protect the boat and reduce environmental pollution.

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APPENDIX

The purpose of this survey is to study the impacts of the bird faeces on to the boat textiles, finishing composition and the environment. The findings of this survey will help the author to understand public views on this issue and research what could be done to prevent these impacts. The questions were subdivided into different segments which include:

- I. Interaction with birds
 1. How often does your boat interact with the birds?
 2. What do you do when birds faeces fall on your boat?
 3. Are you aware of the impacts on your boat textiles and finishing composition?
 4. Are you worried of bird presence and their faeces on your boat?
 5. How do you manage the birds and your boat interaction?
- II. Boat Storing facility
 6. Where do you keep your boat during winter and summer when not in used?
 7. How is the storage environment (moist, humid or dry)?
 8. How long do your boat stay stationery submerged in water at harbour per year and per its life span?
- III. Care and maintenance
 9. Do you repaint your boat hull, re-varnish the wooden parts or retreat the fabrics?
 10. If yes, how often and which paint has been used?
 11. Do you dry your boat textile materials after contact with sea salty water?
 12. How often do you clean your boat hull, keel deck and fabrics?
- IV. Problems
 13. Have your boat fabrics ever been affected by mildew and mold?

14. Have you had difficulties in your boat manoeuvring and propeller functioning?
15. If yes, what do you do with it?
16. Do you take it serious?
17. What is fouling? Do you used anti fouling paint on your boat?
18. Have there been any increased in the boat draft and freeboard length?
19. Have you ever realized an increase in fuel consumption in your boat?
20. Have you ever realized fabrics colour fastness on your boat fabrics? Are you worried of it?

V. Environmental impacts

21. What are the environmental impacts of using and caring for your boat?
22. Have you ever undergone any non-environmental friendly activity on your boat like hull and textile material washing, using antifouling paints and varnish?
23. Are you aware of the impacts of some anti fouling paints?
24. How do you manage the wastewater from washing your boat fouled hull, boat fabric affected by mold and mildew?

VI. Innovative solution

25. Are you interested in any form of environmental friendly and non toxic paint, varnish and fabrics guard that would prevent bird's faeces contaminant, mildew, mold and fouling organism from embedding into the fabrics?
26. What would you suggest to research institutions and projects like CENTRIA and Proboat project?

Bird faeces samples were analyzed with the IC to determine the presents of inorganic anions. The anions present gave a chromatogram with peaks comparable to those in standard solutions of chlorides, nitrates, phosphates and sulphates. The chromatogram for the various compounds (element) and their concentrations in mg/l is presented below.

Report date: 26/03/2010 13:46:04
 Printed by:

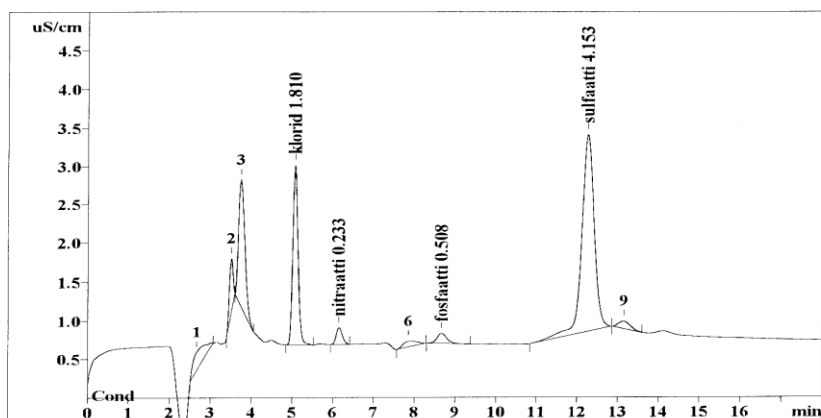
Ident: birdfaeces2
 Analysis from: 26/02/2010 15:11:25
 File: u2261511.chw Last save: 26/02/2010 13:29:
 Modified:
 Method: ASUPP5_150_riikka.mtw Last save: 15/01/20
 Run operator:
 Analysis number: 1686

SAMPLE: 0.1 g into 25 ml
 : dilution 1:100
 Vial number: 0
 Volume: 20.0 µl
 Dilution: 1.00
 Amount: 1.0000

COLUMN: METROSEP_asup5_150
 Size: 4.0 x 150 mm
 Number: 10590056
 Part.size: 7.0 µm

ELUENT: 3,2mM Na2CO3
 1,0mM NaHCO3

Flow: 0.70 mL/min
 Temperature: 20.0°C
 Pressure: 8.8 MPa



Quantitation method: Custom

No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	5.06	2.33	20.803	1.810	klorid
2	6.15	0.22	2.305	0.233	nitraatti
3	8.66	0.14	2.265	0.508	fosfaatti
4	12.25	2.56	54.453	4.153	sulfaatti
4	18.01	5.26	79.826	6.705	

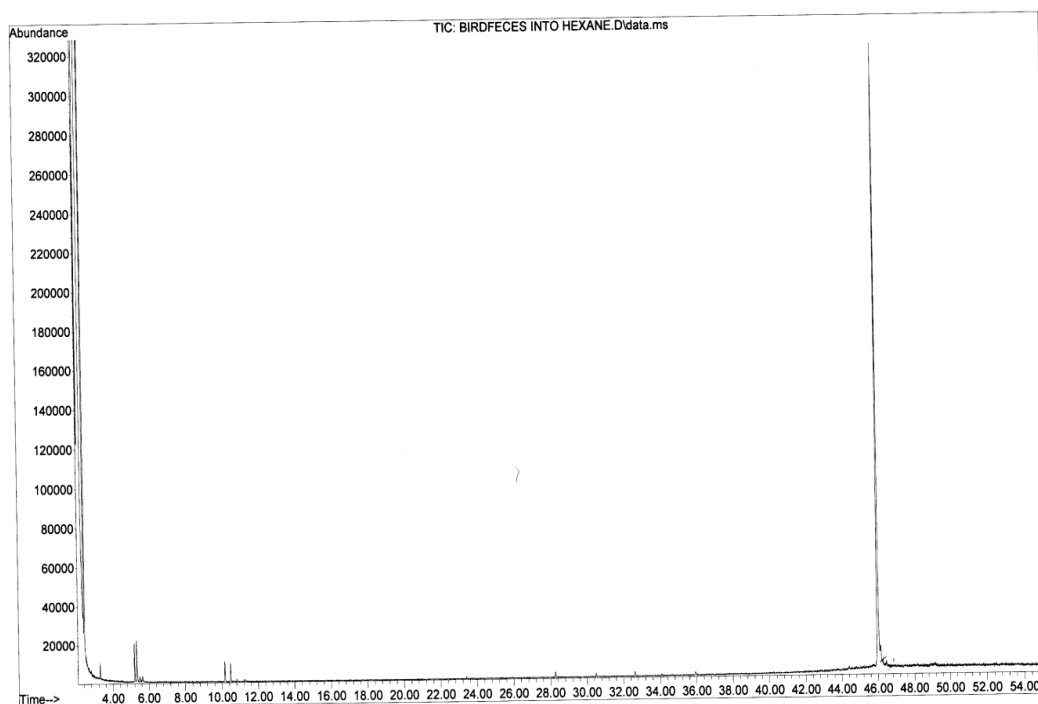
This report has been created by IC Net

Chromatogram of anions in bird faeces sample from IC

The organic content of the bird faeces sample was determined using the GC-MSD. The chromatogram of the compounds present corresponds with those of certain compounds stored in the equipment library. The diagram below shows a general view of the organic compounds chromatogram present in the bird faeces sample.

whale

```
File       :C:\msdchem\1\DATA\Fischer-Tropsch\BIRDFECES INTO HEXANE.D
Operator   : hr
Acquired   : 26 Jan 2010 14:41   using AcqMethod Diesel.M
Instrument  : 5975_Demo
Sample Name:
Misc Info  :
Vial Number: 3
```



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Report date: 26/03/2010 13:46:04
 Printed by:

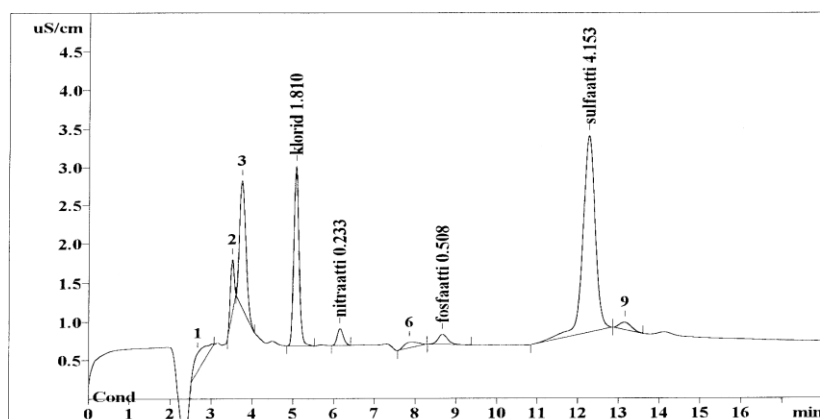
Ident: birdfaeces2
 Analysis from: 26/02/2010 15:11:25
 File: u2261511.chw Last save: 26/02/2010 13:29:
 Modified!
 Method: ASUPP5_150_riikka.mtw Last save: 15/01/20
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 Volume: 20.0 µl
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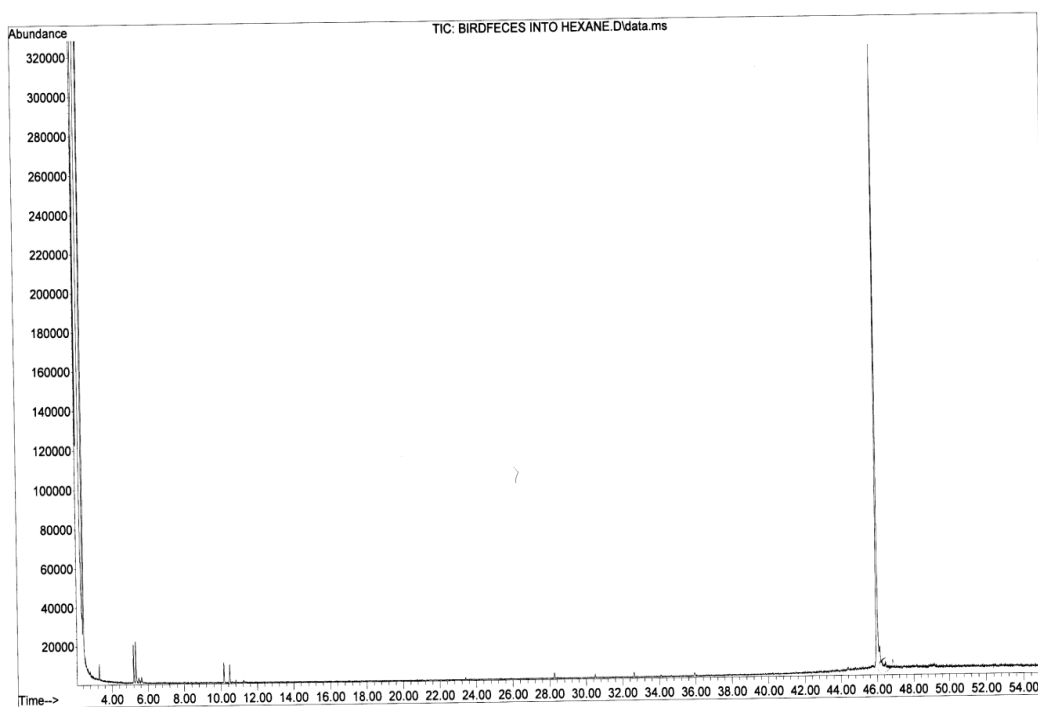
This report has been created by IC Net

Chromatogram of anions in bird faeces sample from IC

The organic content of the bird faeces sample was determined using the GC-MSD. The chromatogram of the compounds present corresponds with those of certain compounds stored in the equipment library. The diagram below shows a general view of the organic compounds chromatogram present in the bird faeces sample.

what

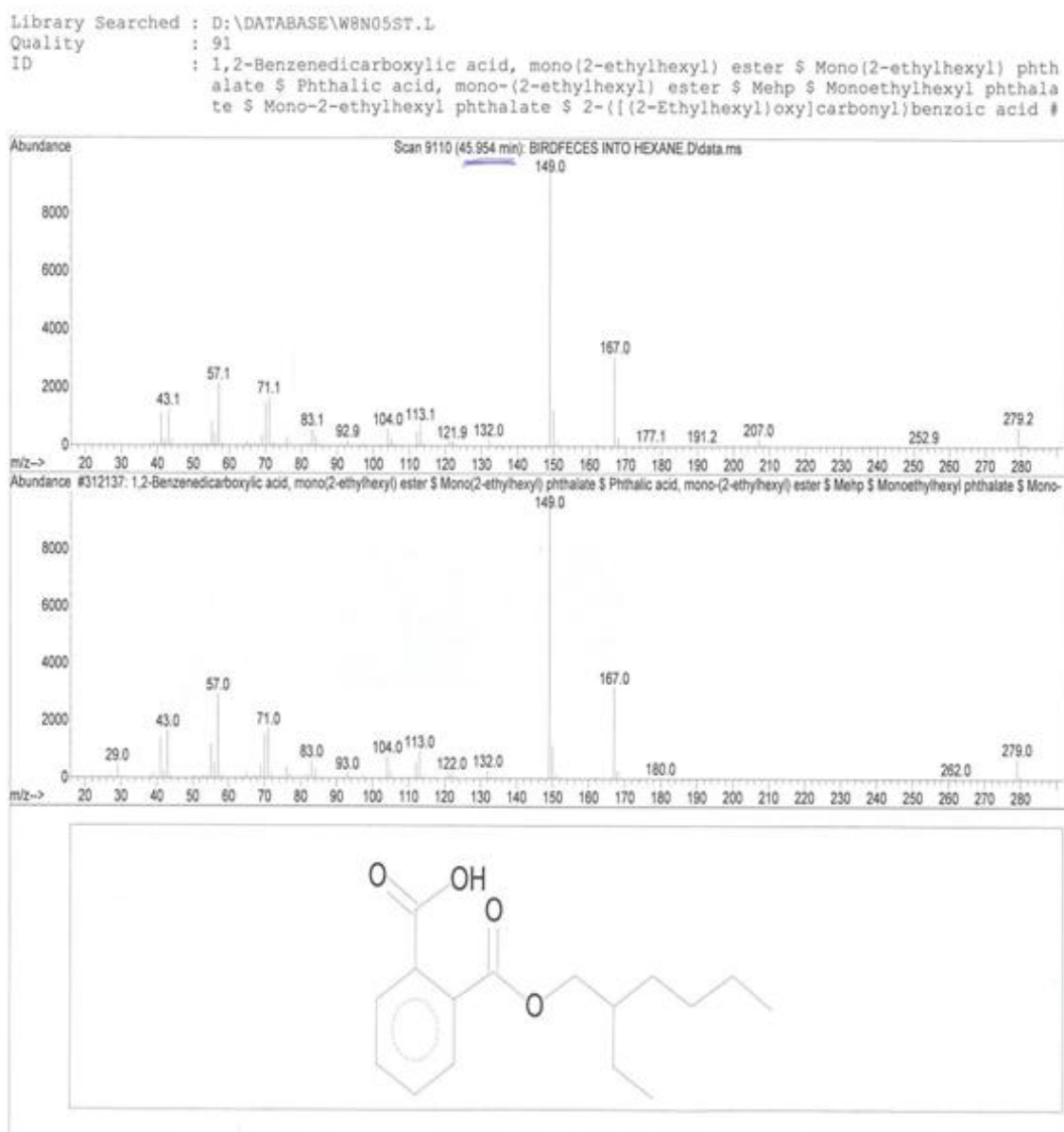
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Operator   : hr
Acquired   : 26 Jan 2010  14:41      using AcqMethod Diesel.M
Instrument  : 5975_Demo
Sample Name:
Misc Info  :
Vial Number: 3
```



Chromatogram of organic compounds in bird faeces sample from GC-MSD

The organic compounds that were found in the bird faeces sample with GC-MSD had individual retention time. The following compounds and their percentage abundance versus retention time graph were found inside the bird faeces sample:

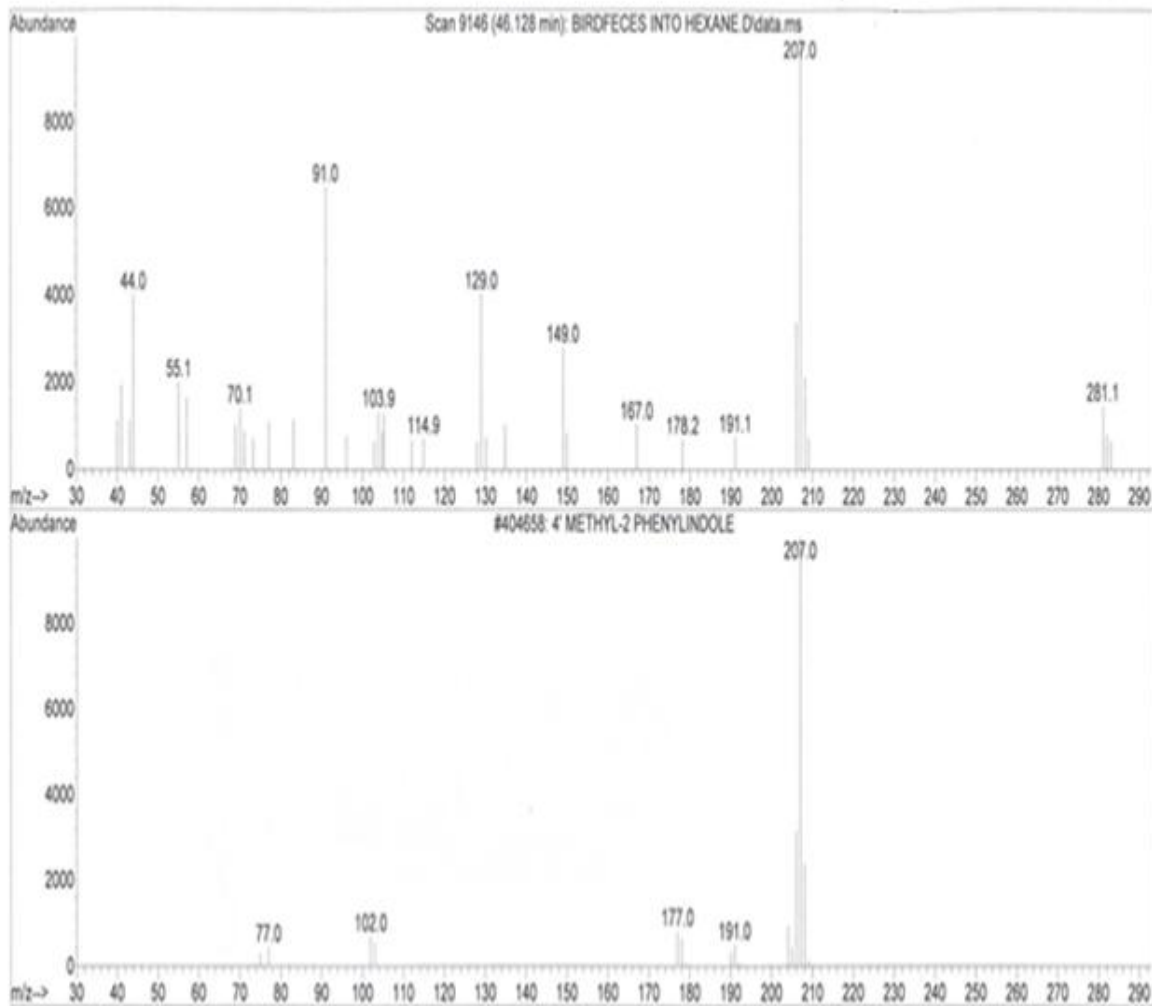
1. 1,2-benzenedicarboxylic acid



Chromatogram of 1,2-benzenedicarboxylic acid from GC-MSD

2. 4-methyl-2-phenylindole

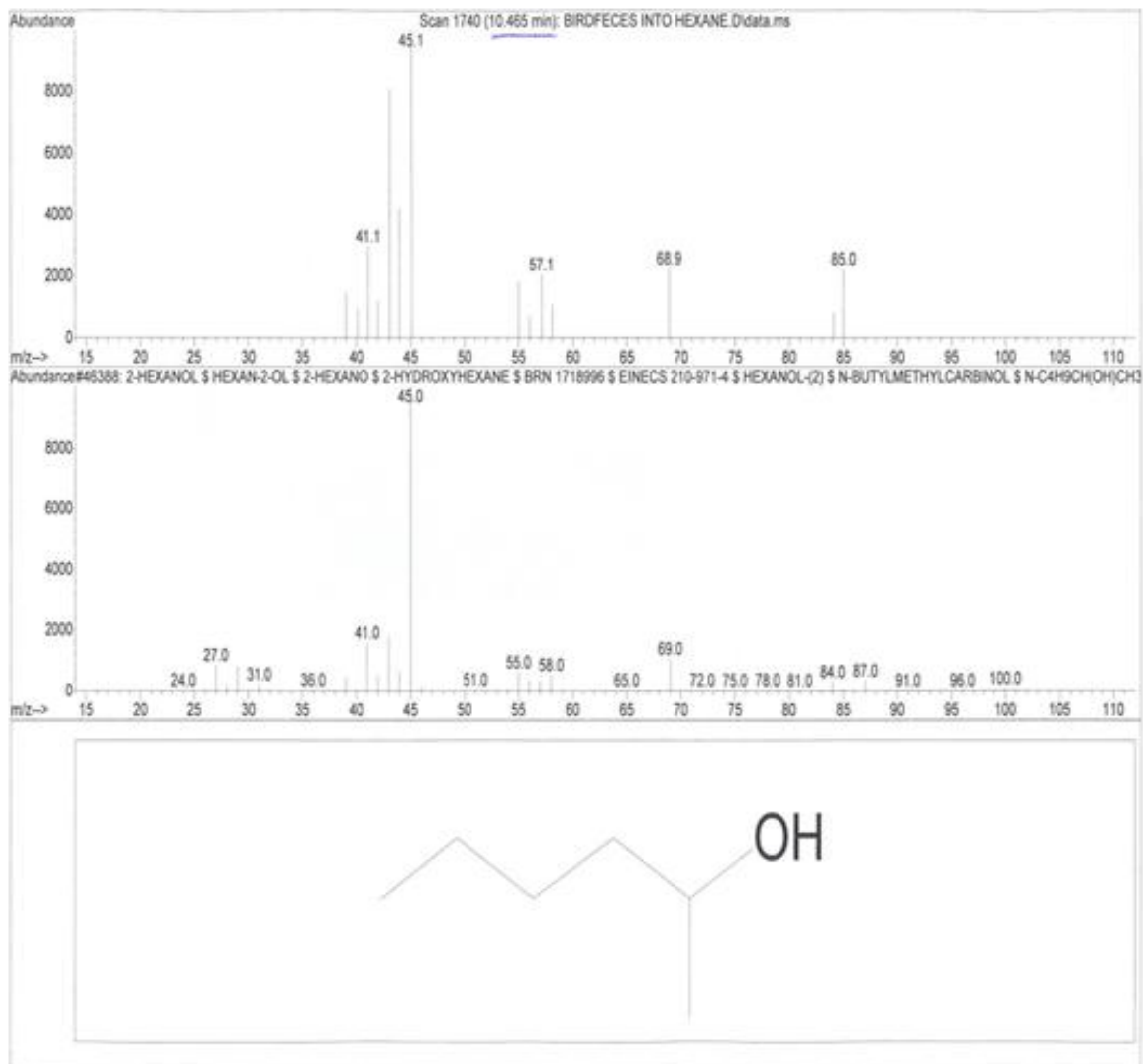
Library Searched : D:\DATABASE\W08N05ST.L
Quality : 46
ID : 4' METHYL-2 PHENYLINDOLE



Chromatogram of 4-methyl-2-phenylindole from GC-MSD

3. 2-hexanol

Library Searched : D:\DATABASE\W8N05ST.L
Quality : 25
ID : 2-HEXANOL \$ HEXAN-2-OL \$ 2-HEXANO \$ 2-HYDROXYHEXANE \$ BRN 1718996 \$ EINECS 210-971-4 \$ HEXANOL-(2) \$ N-BUTYLMETHYLCARBINOL \$ N-C4H9CH(OH)CH3 \$ N-HEXAN-2-OL \$ NS C 3706 \$ SEC-HEXYL ALCOHOL



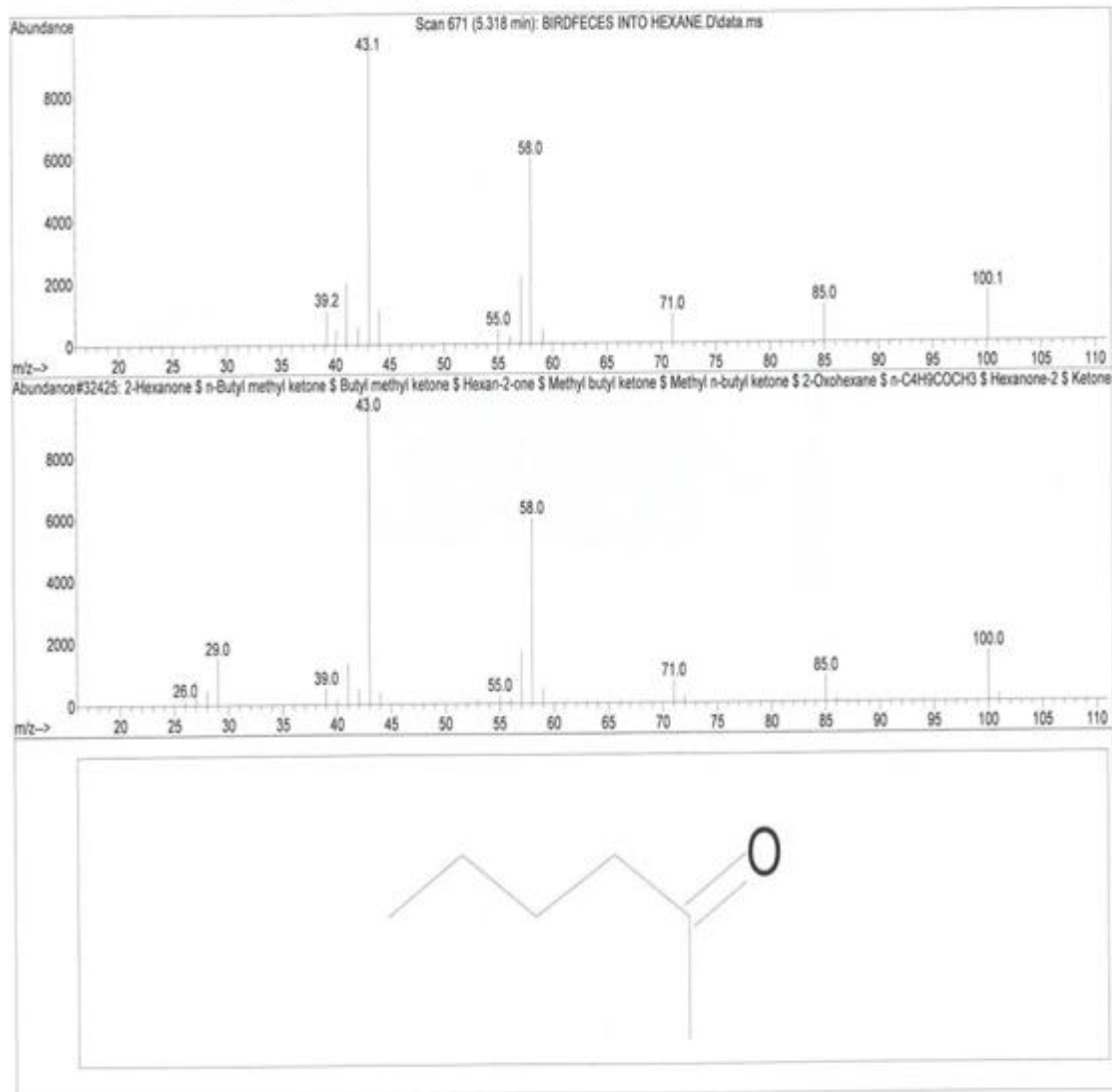
Chromatogram of 2-hexanol from GC-MSD

4. 2-hexanone

Library Searched : D:\DATABASE\W8N05ST.L

Quality : 91

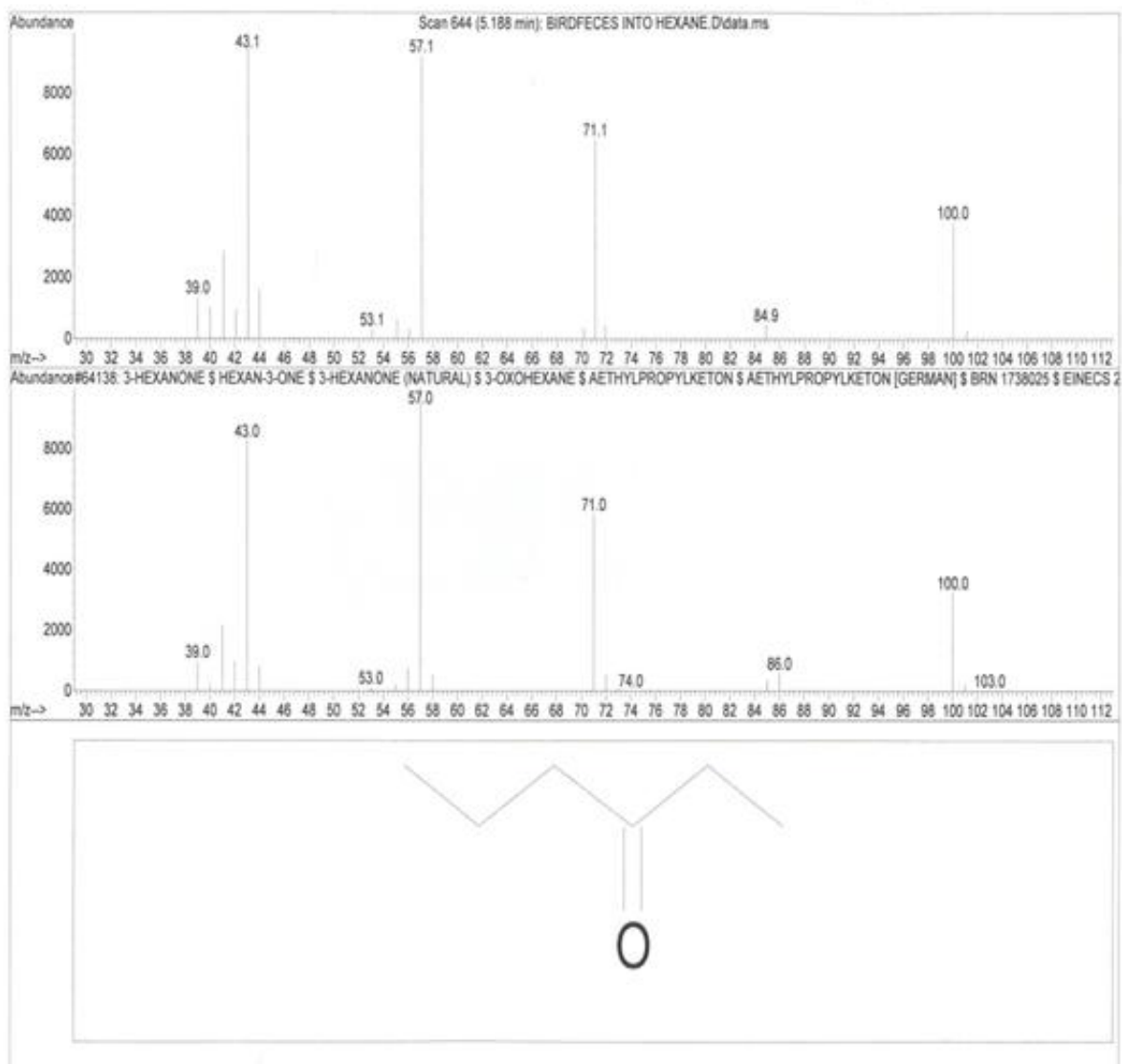
ID : 2-Hexanone \$ n-Butyl methyl ketone \$ Butyl methyl ketone \$ Hexan-2-one \$ Methyl
butyl ketone \$ Methyl n-butyl ketone \$ 2-Oxohexane \$ n-C4H9COCH3 \$ Hexanone-2 \$
Ketone, butyl methyl \$ MBK \$ MNBK



Chromatogram of 2-hexanone from GC-MSD

5. 3-hexanone

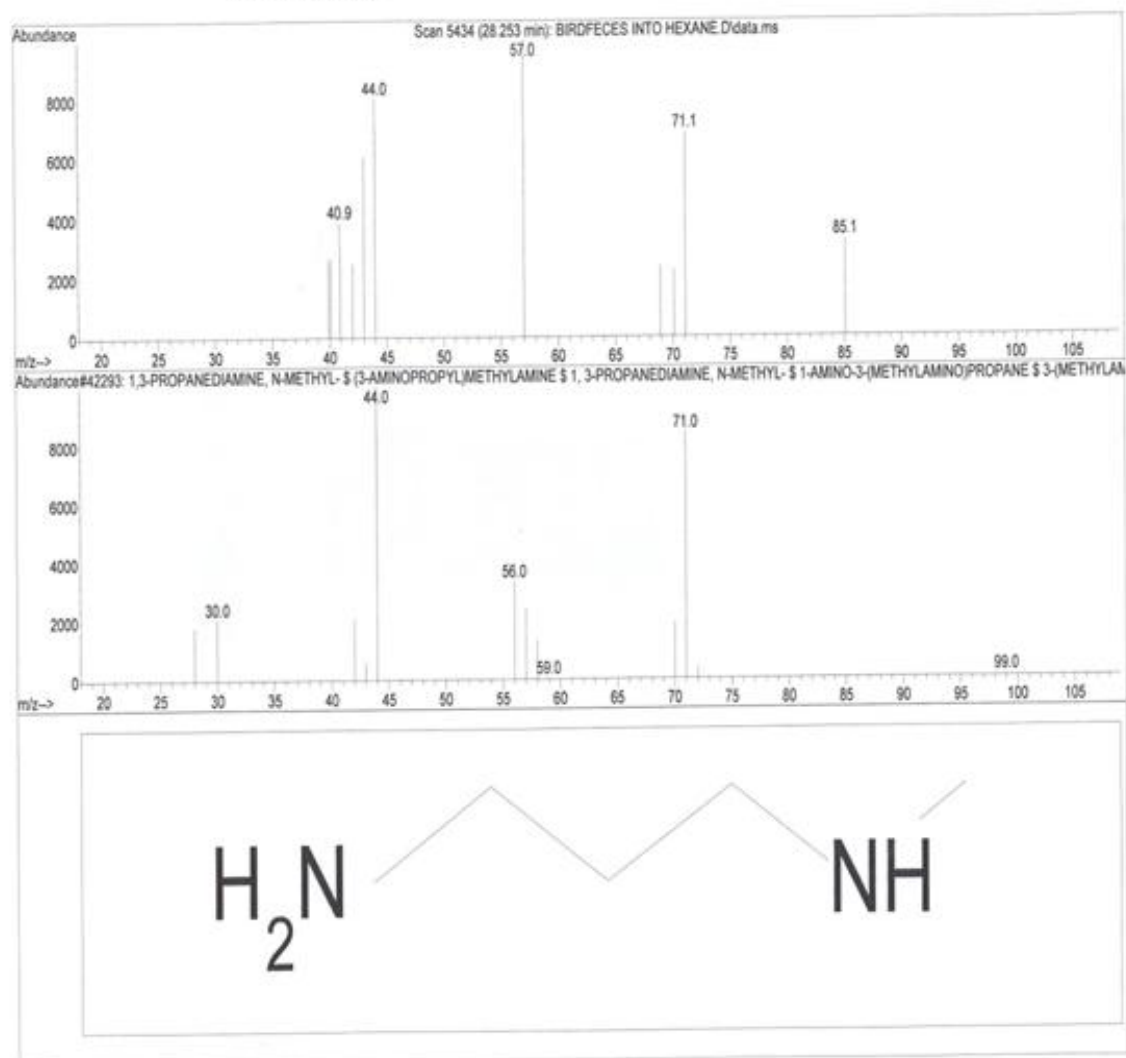
Library Searched : D:\DATABASE\W08N05ST.L
Quality : 91
ID : 3-HEXANONE \$ HEXAN-3-ONE \$ 3-HEXANONE (NATURAL) \$ 3-OXOHEXANE \$ AETHYLPROPYLKETO
N \$ AETHYLPROPYLKETON [GERMAN] \$ BRN 1738025 \$ EINECS 209-645-4 \$ ETHYL N-PROPYL
KETONE \$ ETHYL PROPYL KETONE \$ FEMA NO. 3290 \$ HEXANONE-(3) \$ N-C3H7COC2H5



Chromatogram of 3-hexanone from GC-MSD

6. 1, 3-propanediamine

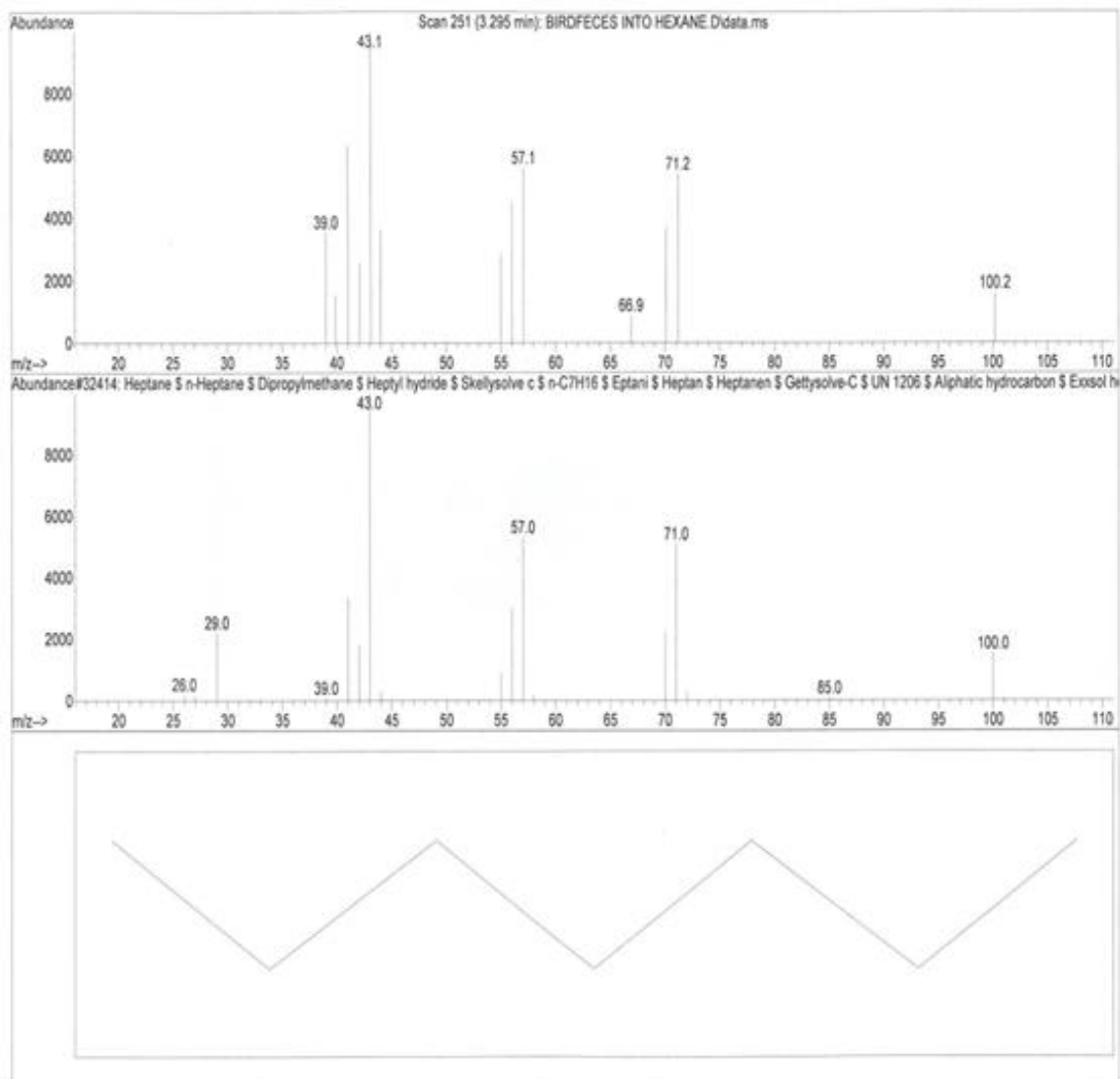
Library Searched : D:\DATABASE\W8N05ST.L
Quality : 39
ID : 1,3-PROPANEDIAMINE, N-METHYL- \$ (3-AMINOPROPYL)METHYLAMINE \$ 1, 3-PROPANEDIAMINE
, N-METHYL- \$ 1-AMINO-3-(METHYLAMINO)PROPANE \$ 3-(METHYLAMINO)PROPYLAMINE \$ 3-AM
INO-1-(METHYLAMINO)PROPANE \$ 3-AMINOPROPYLMETHYLAMINE \$ 3-METHYLAMINOPROPYLAMINE
\$ AI3-25443 \$



Chromatogram of 1,3-propanediamine from GC-MSD

7. Heptane

Library Searched : D:\DATABASE\W8N05ST.L
Quality : 86
ID : Heptane \$ n-Heptane \$ Dipropylmethane \$ Heptyl hydride \$ Skellysolve c \$ n-C7H16
\$ Eptani \$ Heptan \$ Heptanen \$ Gettysolve-C \$ UN 1206 \$ Aliphatic hydrocarbon \$
Exxsol heptane



Chromatogram of heptane from GC-MSD

Colour fastness test was performed on the California dodger canopy destroyed by bird faeces. The test result gave a clue to determine the grey scale rating at different spots on the canopy depending on the spot ability to absorb and reflect light from the spectrophotometer. Spots that underwent heavy cleaning due to heavy stains from bird faeces could not reflect most of the light. Comparing the amount of light reflected by a spot to those reflected by the original and undamaged sample, their differences were used to calculate the mean values for range of colour change and hence its grey scale rating determined. The mean values for range of colour change at specific spots are shown below.

P17		8M17D 21:37	
(n= 10)		8M17D 21:37	
MAX	Y	3.32 x	.2484 y .2396
MIN	Y	3.89 x	.2447 y .2344
MEAN	Y	3.26 x	.2473 y .2376
SD	Y	0.06 x	.0012 y .0017

P08		8M18D 01:29	
(n= 10)		8M18D 01:29	
MAX	Y	3.35 x	.2479 y .2398
MIN	Y	3.27 x	.2468 y .2374
MEAN	Y	3.30 x	.2473 y .2383
SD	Y	0.02 x	.0003 y .0004

P17		8M17D 21:37	
(n= 10)		8M17D 21:37	
MAX	Y	3.32 x	.2484 y .2396
MIN	Y	3.89 x	.2447 y .2344
MEAN	Y	3.26 x	.2473 y .2376
SD	Y	0.06 x	.0012 y .0017

ORIGINAL

P10		8M17D 21:39	
(n= 10)		8M17D 21:40	
MAX	E	5.89	
L	+4.90 a	-0.77 b	+0.61
MIN	E	2.33	
L	+2.20 a	-1.45 b	-0.03
MEAN	E	4.35	
L	+4.17 a	-1.22 b	+0.35
SD	E	0.95	
L	0.92 a	0.23 b	0.19

P09		8M18D 01:32	
(n= 10)		8M18D 01:33	
MAX	E	1.98	
L	+1.06 a	-0.37 b	+3.25
MIN	E	1.40	
L	+1.32 a	-0.60 b	-3.02
MEAN	E	1.65	
L	+1.59 a	-0.44 b	+0.12
SD	E	0.14	
L	0.15 a	0.06 b	0.09

P10		8M17D 21:39	
(n= 10)		8M17D 21:40	
MAX	E	5.89	
L	+4.90 a	-0.77 b	+0.61
MIN	E	2.33	
L	+2.20 a	-1.45 b	-0.03
MEAN	E	4.35	
L	+4.17 a	-1.22 b	+0.35
SD	E	0.95	
L	0.92 a	0.23 b	0.19

TEST 1.

SFS-EN ISO 105-A05

TEST 1.

4.

1.1

2.5

P00		8M17D 21:56	
(n= 10)		8M17D 21:56	
MAX	Y	3.29 x	.2481 y .2395
MIN	Y	3.09 x	.2459 y .2361
MEAN	Y	3.22 x	.2471 y .2374
SD	Y	0.07 x	.0007 y .0011

P02		8M17D 22:04	
(n= 10)		8M17D 22:04	
MAX	Y	3.34 x	.2478 y .2383
MIN	Y	3.21 x	.2465 y .2371
MEAN	Y	3.25 x	.2472 y .2378
SD	Y	0.04 x	.0004 y .0004

P06		8M17D 22:12	
(n= 10)		8M17D 22:12	
MAX	Y	3.36 x	.2478 y .2376
MIN	Y	3.28 x	.2443 y .2341
MEAN	Y	3.31 x	.2456 y .2368
SD	Y	0.02 x	.0008 y .0010

P01		8M17D 21:58	
(n= 10)		8M17D 21:59	
MAX	E	4.28	
L	+4.10 a	-0.75 b	+0.17
MIN	E	2.66	
L	+2.54 a	-1.24 b	-0.12
MEAN	E	3.63	
L	+3.51 a	-0.91 b	-0.01
SD	E	0.48	
L	0.47 a	0.14 b	0.10

P03		8M17D 22:06	
(n= 10)		8M17D 22:07	
MAX	E	4.34	
L	+4.20 a	-0.80 b	+0.13
MIN	E	3.47	
L	+3.36 a	-1.12 b	-0.11
MEAN	E	3.93	
L	+3.82 a	-0.96 b	+0.02
SD	E	0.34	
L	0.33 a	0.10 b	0.10

P07		8M17D 22:15	
(n= 10)		8M17D 22:15	
MAX	E	4.10	
L	+3.95 a	-0.68 b	+0.46
MIN	E	2.49	
L	+2.34 a	-1.06 b	+0.17
MEAN	E	3.39	
L	+3.25 a	-0.99 b	+0.34
SD	E	0.56	
L	0.56 a	0.13 b	0.08

TEST 2.

1)