TOWARDS A RATIONAL CHOICE OF PRE-TREATMENT AGENTS FOR THE CLEANSING OF OILED WILDLIFE

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Traditional techniques for the cleansing of oiled wildlife are based on the use of dilute surfactant (detergent) solutions (2 - 5% v/v). Over time, such techniques have been highly refined with many successful outcomes at rehabilitation facilities worldwide. In this regard, a number of studies have been reported that systematically optimize related materials and protocols. For example, methods have been developed to subjectively evaluate surfactant efficacy for the removal of petrochemicals from contaminated feathers [1-4]. In some circumstances, the contaminant is resistant to removal by detergent alone and an additional step of applying a suitable "pre-treatment" agent is required [5]. The choice of a pre-treatment agent (PTA) for a given contaminant and feather type, as well as the method of application, are important considerations - since an additional contaminant is being added to the oiled feathers that also needs to be removed. Indeed, there is anecdotal evidence to suggest that, under some circumstances, the inappropriate use of a PTA can actually exacerbate the problem. A wide range of potential pre-treatment candidates are possible and include substances such as olive oil, vegetable oil, methyl oleate and methyl soyate. To our knowledge, there has only been one investigation that evaluates a range of pre-treatment candidates for their ability to facilitate the detergent removal of contaminants from feathers [5]. As is acknowledged by these workers, such experiments are, by their very nature, difficult to carry out and rely on subjective or semi-quantitative evaluations.

For more than a decade, the development of magnetic particle technology (MPT) for environmental remediation and wildlife rehabilitation has been an active area of collaboration between Victoria University and the Phillip Island Research Department, Victoria, Australia [6-9]. This approach to the cleansing of oiled wildlife ("magnetic cleansing") involves the application of contaminant-sequestering magnetic particles to an affected animal, followed by subsequent magnetic harvesting - to simultaneously remove both contaminant and cleansing agent, **Figure 1**. This is effectively a dry cleansing process that may offer some advantages over, or be complementary to, traditional detergent-based methods. One advantage of the magnetic cleansing technique, especially for research purposes, is that it allows the removal of a given contaminant, or a contaminant/PTA mixture, from a given substrate (feathers, fur or rock surface) to be accurately and reproducibly quantified, **Figure 2**. This is very difficult to achieve using detergent-based removal techniques due to the lack of control over the cleansing agent. Furthermore, the MPT process may be mathematically modeled [9] which allows for the possibility of investigating the physical basis of removal and for more accurately assessing relative removal efficacies.

Figure 1: The removal of contaminant-laden magnetic particles from the plumage of an oiled Little Penguin (*Eudyptula minor*) carcass utilizing a magnetic harvesting device.

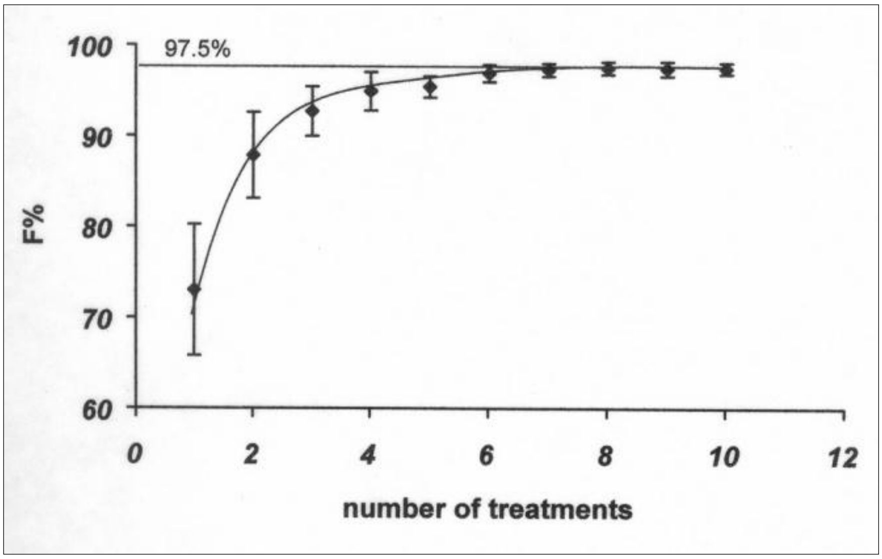

Figure 2: A characteristic “isotherm” representing the percentage magnetic removal of an oil contaminant from feathers, F%, as a function of the number of treatments. Error bars indicate 95% confidence intervals.

As with detergent-based methods, the magnetic removal of a contaminant from feathers is found to be generally improved by applying a suitable PTA, **Figure 3**. Notably, it is found that different PTAs vary in their effectiveness for a given contaminant and feather type. This variance is statistically significant and is suggestive of a means for conveniently quantifying relative PTA efficacy.

Based on the observation that different PTAs accelerate the removal process to different extents, an assay may be devised whereby an arbitrary “effective number of treatments", N_{99} in this case, may be defined that denotes the effective number of treatments whereby 99% contaminant removal is achieved. This is represented graphically in **Figure 4.** Note that the lower the N_{99} value is along the horizontal axis, then the more efficient is the PTA for a particular application. In other words, this PTA allows 99% removal (of both PTA and contaminant) to be achieved relatively faster. Therefore one can stipulate a qualitative and quantitative ordering of relative PTA efficacies for the facilitation of oil removal - which in this case is the removal weathered bunker oil from duck feathers, **Figure 5**.

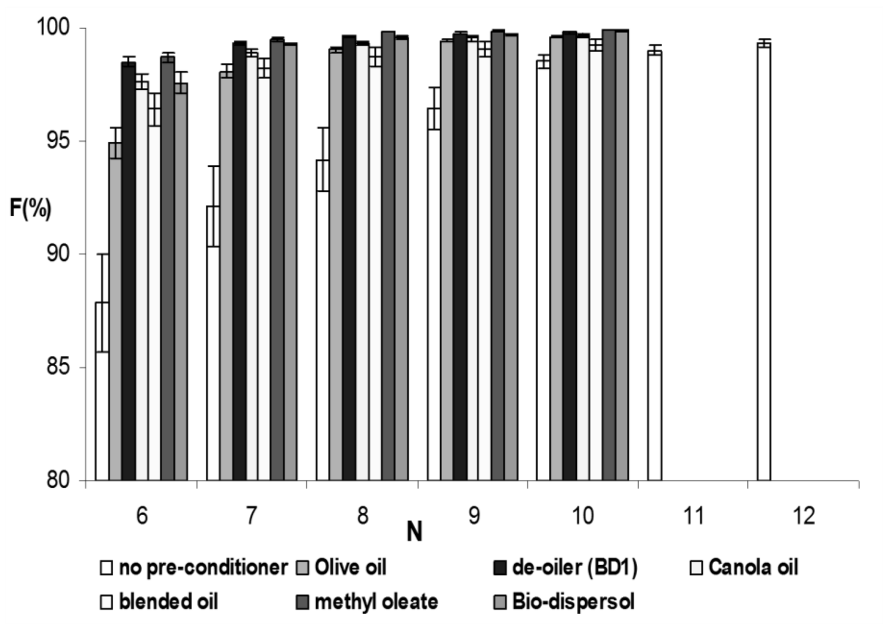

Figure 3: A comparison of the percentage removal, F%, of weathered bunker oil from duck feathers with and without the use of various pretreatment agents upon N successive treatments with magnetic (iron) particles. Error bars represent the SE for five replicates.

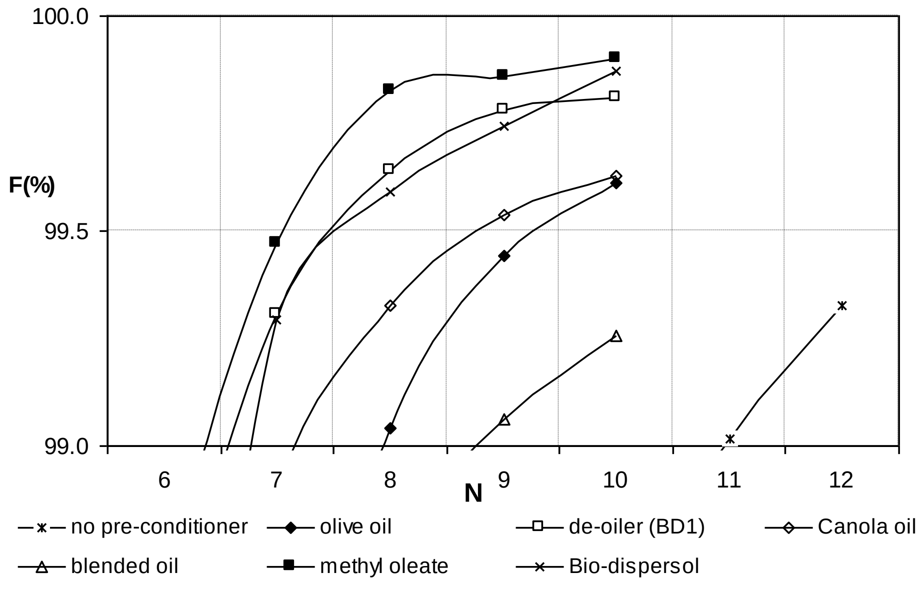

Figure 4: Percentage MPT removal, F%, of weathered bunker oil from duck feathers, showing the relative values of N_{99} (the intercepts along the horizontal, N-axis) for the six PTAs tested, compared to the value in the absence of a PTA.

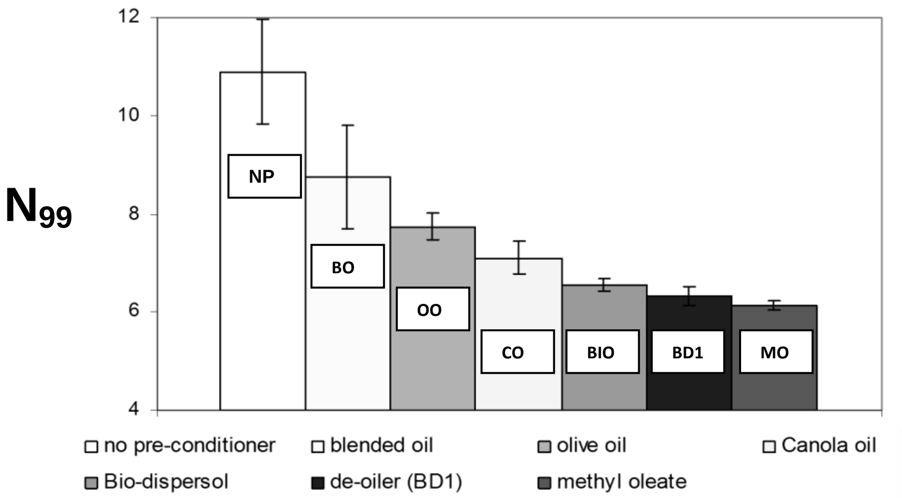

Figure 5: Relative average values of N_{99} for the six pre-conditioners tested compared to the average N_{99} value in the absence of a pre-conditioner. Error bars represent the SE for five replicates. Note that MO is better than BD1 > BIO > CO > OO > BO > NPC – for this scenario, i.e. MPT removal of weathered bunker oil from duck feathers.

An important consideration for this work is the extent to which the relative PTA efficacies - as determined by the MPT assay, carry over with fidelity to PTA-assisted detergent based methods. Intuitively, one would expect this to be the case since the forces between the substrate, the contaminant and the PTA are the same irrespective of the removal mechanism. Experiments have therefore been designed and conducted in order to test this notion for eight different PTAs, listed in **Figure 6**. Thus, parallel, semi-quantitative detergent-based and fully quantitative MPT-based experiments have been conducted as follows; for the PTA assisted removal of a representative contaminant (a Bunker Oil) from feathers (Mallard Duck, *Anas platyrhnchos*).

The data shown in **Figure 6** represent the outcome of an experiment in which three independent assessors, utilizing a Likert Scale (1 [good] – 5 [bad]), have scored the removal of the contaminant from single feathers with successive PTA-assisted detergent treatments (up to 14). Derived scores (i.e. relative semi-quantitative assessments, RSQAs), corresponding to each PTA, were obtained by quantifying the relative decline rates of the curves, **Table 1.**

The data for the parallel PTA-assisted MPT experiment, utilizing the same feather type and contaminant, is represented in **Figure 7**. The corresponding N_{99} values have been converted to $P_o\%/N_{99}$ values, where $P_o\%$ represents the final (optimal) removal. The $P_o\%/N_{99}$ value is considered to be an improved representation of the removal efficacy since it incorporates both the final removal as well as the acceleration of removal. This parameter is also listed in **Table 1** for all PTAs tested. When the MPT data, as represented by $P_o\%/N_{99}$, are plotted against the detergent-based data, as represented by the RSQA values, **Figure 8**, a high correlation of 0.906 is achieved. This suggests that the MPT quantitative assay for PTA efficacy does indeed carry over to detergent-based cleansing. It should also be noted that the qualitative assessments according to both methods are effectively identical; i.e. MS better than MO > EO > IO > BIO > BD1 > OO > CO> NPC.

These results represent an important proof of principle, i.e. the finding that MPT-based recommendations for PTAs carry over with fidelity to PTA-assisted detergent-based treatments. This is a significant advance since the quantitative MPT assay may now be conveniently applied to the systematic exploration of a wide range of PTAs and PTA blends for various types of contaminant and for a wide range of feather types.

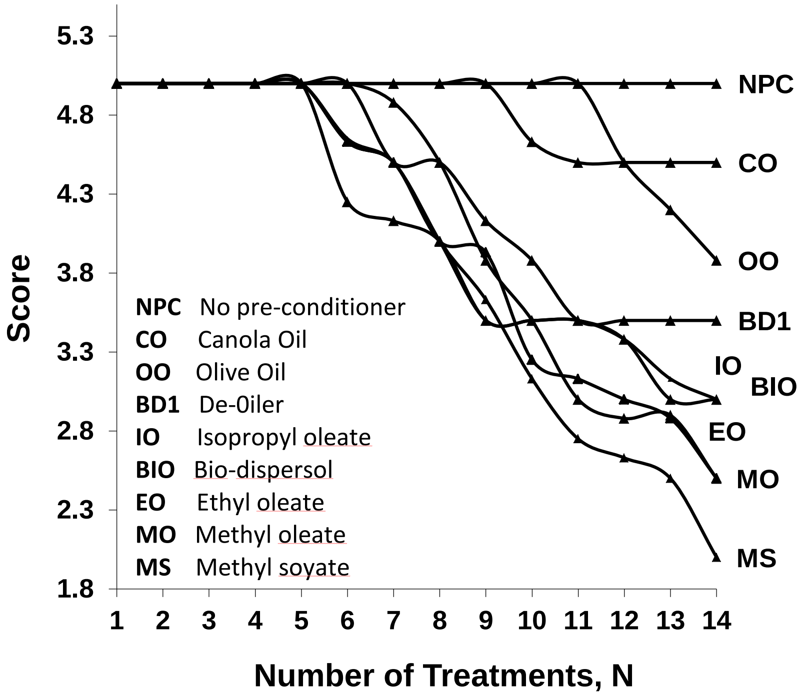

Figure 6: The improvement in oil removal from feathers with successive detergent treatments. The score is based on a Likert scale: 1 [good] – 5 [bad]. The detergent was 5% v/v Divoplus V2, Johnson Diversy, NSW, Australia.

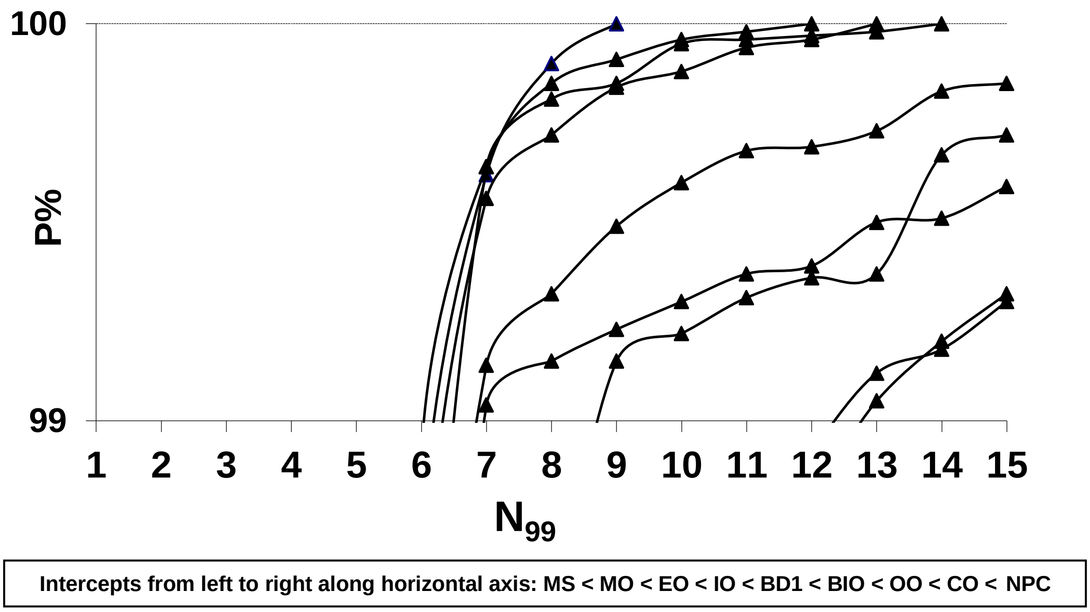

Figure 7: Percentage MPT removal, F%, of bunker oil from duck feathers, showing the relative values of N_{99} (the intercepts along the horizontal, N-axis) for the eight PTAs tested, compared to the value in the absence of a PTA.

Table 1: Detergent-based efficacy parameters (relative semi-quantitative assessments – **RSQA** values) and the corresponding MPT efficacy parameters (**P_o%/N_{99}**) for eight different PTAs obtained for the removal of Bunker Oil from duck feathers.

PTA	MS	MO	EO	BIO	IO	BD1	OO	CO	NPC
RSQA	1.97	1.62	1.63	1.30	1.31	0.97	0.74	0.33	0
P_o%/N_{99}	16.39	16.13	15.87	14.43	15.38	14.68	11.73	8.07	7.76

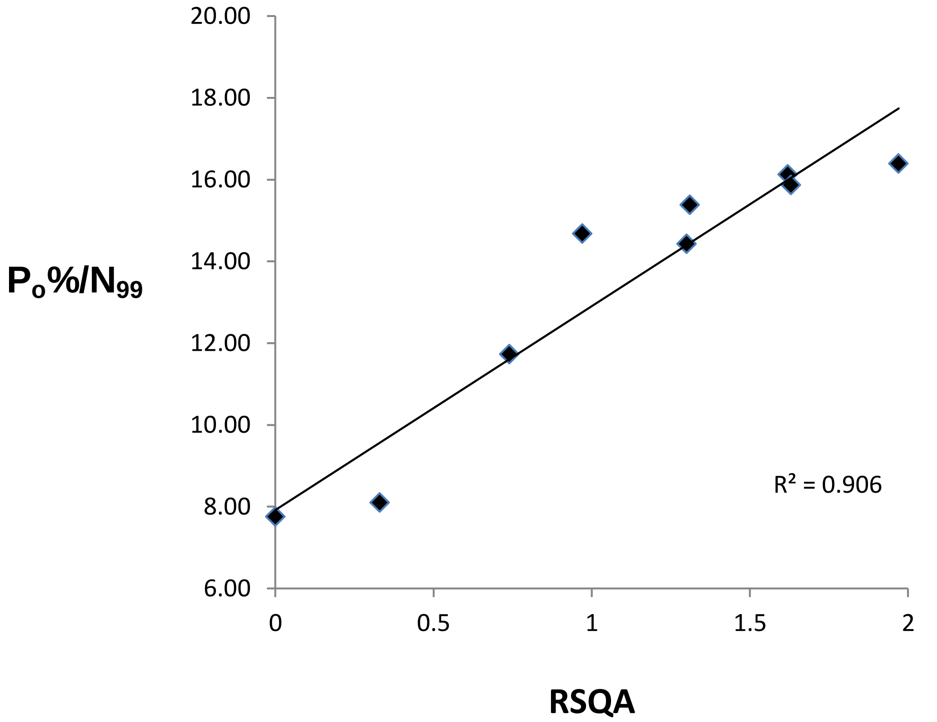

Figure 8: The correlation between the (parallel) MPT assay and semi-quantitative detergent assay for the PTA-assisted removal of Bunker oil from duck feathers.

The MPT assay described in this research offers a more accurate and convenient method for systematically screening PTAs for the removal of contaminants from oiled wildlife than detergent-based methods. Using this assay, our investigations to date show that PTAs are both feather and contaminant specific and what is applicable for one species and/or one contaminant type might not be recommended for another. For example, we have previously demonstrated that methyl soyate is a preferred PTA to methyl oleate for the removal of crude oil from the feathers of the Little Penguin and that both are preferable to the use of olive oil. Other considerations that are under investigation include the most appropriate point of PTA application and the relative efficacy of different blends of commonly used PTAs. The potential for this assay to be used for the screening and rational development of a wide range of pre-treatment candidates, for various feather types and contaminants, will lead to a database of recommendations that could prove useful to wildlife rehabilitators in the field.

1. Brydnza, H.E., Foster, J.P., McCartney, Lundberg, B and J.H., Lober, J.C. 1991, Surfactant efficacy in removal of petrochemicals from feathers. The effects of oil on wildlife: research, rehabilitation and general concerns, J. White and L. Frink (eds.). The Sheridan Press, Hanover, Pennsylvania, pp. 78-94.

2. Brydnza, H.E., Foster, J.P., McCartney, J.H., Lober, J.C. and Lundberg, B. 1995, Methodology for determining surfactant efficacy in removal of petrochemicals from feathers, Wildlife and Oil Spills: Response, Research and Contingency Planning, L. Frink (ed.), Tri-State Bird Rescue & Research, Inc., Newark, Delaware, pp. 69-86.

3. Miller, E.A., Bryndza, H., Milionis, C., Meenan, K. and Simmons, M. 2003, An evaluation of the efficacy of eighty-six products in the removal of petrochemicals from feathers, Proceedings form the 2000 Effects of Oil on Wildlife Conference, H. Stout (ed.). Tri-State Bird Rescue and Research, Inc., Newark, Delaware, pp. 52-66.

4. Miller, E.A., Keller, J and Bryndza, H. 2006, An evaluation and comparison of some current products for the removal of petrochemicals from feathers, Proceedings of the Eighth International Effects if Oil on Wildlife Conference, K. Evans and R. Dunne (eds.), Tri-State Bird Rescue and Research, Inc., Newark, Delaware, pp. 85-99.

5. Tegtmeier, S. and Miller, E, 2007, A subjective evaluation of suggested products to facilitate contaminant removal from feathers, Proceedings of the Ninth International Effects of Oil on Wildlife Conference, K. Evans and R. Dunne (eds.), Tri-State Bird Rescue and Research, Inc., Newark, Delaware, pp. 192-210.

6. Orbell, J.D., Tan, E.K., Coutts, M.C., Bigger, S.W. and Ngeh, L.N. 1999, Cleansing oiled feathers-magnetically, *Marine Pollution Bulletin*, 38, 219-221.

7. Orbell, J.D., Ngeh, L.N., Bigger, S.W., Zabinskas, M., Zheng, M., Healy, M., Jessop, R. and Dann, P. 2004, Whole-bird models for the magnetic cleansing of oiled feathers, *Marine Pollution Bulletin*, 48, 336-340.

8. Orbell, J.D., Dao, H.V., Ngeh, L.N., Bigger, S.W., Healy, M., Jessop, R. and Dann, P. 2006, Magnetic cleansing of weathered/tarry oiled feathers - the role of pre-conditioners, *Marine Pollution Bulletin*, 52, 1591 – 1594.

9. Bigger, S.W., Ngeh, L.N. and Orbell, J.D. 2010, A Mathematical model for the sequestering of chemical contaminants by magnetic particles, *J. Environmental Engineering*, 138, 1255 - 1259.

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Professor John Orbell is a Professor of Chemistry within the School of Engineering & Science and a Professorial Associate of the Institute for Sustainability & Innovation at Victoria University, Melbourne, Australia. He completed a PhD in Chemistry at the University of Auckland, New Zealand, in 1979 and held a Postdoctoral Fellowship at the Johns Hopkins University, U.S.A. from 1980 to 1981 and at the University of Trieste, Italy, in 1982. He has held research positions at the University of Maryland, U.S.A., the Flinders University of South Australia and St. Vincent's Institute of Medical

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Kasup Munaweera Kasup is currently in the final stages of a PhD degree on an ARC Linkage scholarship, in collaboration with the Phillip Island Nature Parks. The title of his research project is: "The rational development of improved pre-conditioning agents for removal of oil contamination from wildlife and rocky foreshore". As part of this project he has also been involved in the adaption of magnetic particle technology to the provision of a "quick clean" to oiled wildlife in the field. Prior to his PhD program, Kasup completed a Master of Science in Environmental Management at Victoria University with research in the area of "Environmental Management in the Aviation Industry". Kasup has also worked at Victoria University as a research assistant on the application of magnetic particle technology to the removal of oil contamination from rock surfaces. Prior to his arrival in Australia, Kasup completed an Honours degree in Geography at the University of Colombo, Sri Lanka, in the area of "Rice Cultivation and It's Problems in Ibbagamuwa Divisional Secretariat, Kurunegala District, Sri Lanka".