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EVALUATION AND INTERPRETATION OF ENVIRONMENTAL DATA ON ENDOSULFAN IN ARCTIC REGIONS

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Compiling Authors: N. Mackay, D. Arnold
Cambridge Environmental Assessments-ADAS

LANCASTER UNIVERSITY

UNIVERSITY of GUELPH

Contributors:
C. Halsall, Lancaster University, UK
B. Herbert, Lancaster University, UK
L. Jantunen, Centre for Atmospheric Research Experiments, Canada
D. Muir, National Water Research Institute, Environment Canada
J. Small, University of Guelph, Canada
K. Solomon, University of Guelph, Canada
J. Weber, Lancaster University, UK

Environment Canada Environnement Canada

Cambridge Environmental Assessments
Battlegate Road
Boxworth
Cambridge CB3 8NN
United Kingdom

Email: enquiries@cea-res.co.uk

Cambridge Environmental Assessments

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SIGNATURE PAGE

Author: **Date: 14 October, 2005**

Neil Mackay

Date: 14 October, 2005

Dave Arnold

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EXECUTIVE SUMMARY

The classification of compounds as Persistent Organic Pollutants (POPs) under UN ECE Executive Body Decision 1998/2 and in the UNEP Stockholm Convention is based upon toxicity, semi-volatility, persistence and bioaccumulation characteristics. Under Article 1 of the Protocol agreed by the Executive Body of the UN ECE LRTAP Convention, POPs are defined as:

'...organic substances that:
(i) possess toxic characteristics;
(ii) are persistent;
(iii) bioaccumulate;
(iv) are prone to long-range transboundary atmospheric transport and deposition; and
(v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.'

UN ECE Executive Body Decision 1998/2 sets out more detailed criteria for identifying potential POPs in the form of requirements for a risk profile (the text of this Decision is reproduced in Section 1.5). Criteria *iv* draws heavily upon evidence from monitoring programmes in Arctic/remote region. Detections alone, however, are not evidence of that a chemical is *"likely to cause significant, adverse human health or environmental effects"* (Criteria *v*). A number of factors should be evaluated before making such a determination:

- Temporal trends
- Spatial trends
- Transport mechanisms
- Distribution within the food chain (potential for bioaccumulation/biomagnification)
- Associated ecotoxicological risks due to background and food chain exposure
- Associated human dietary risks, primarily due to potential marine bioaccumulation

A first draft dossier was prepared in support of a proposal for endosulfan to be considered as a candidate for inclusion in the UN-ECE LRTAP protocol on persistent organic pollutants. The draft dossier focused on the specific numeric criteria for the inclusion as a POP, but also presented the findings of endosulfan in remote and Arctic areas in support of the argumentation.

The primary objective of this research exercise is to assemble a broader basis for evaluation of behaviour and exposure of endosulfan by gathering and interpreting monitoring data in key locations, compartments and links within the Arctic food web. Finally, the residues profile within both abiotic and biotic compartments is considered within an ecotoxicological and human health risk context.

Air

- **The temporal trend in endosulfan residues in the air in the Arctic appears to be stable in agreement with its actual use during the 1990 – 2000 decade. The mean concentrations are very small, amounting to approximately < 1 – 15 pg/m^3.**
- **A distinctive seasonal profile (summer reductions in α-endosulfan concentrations with spring and fall peaks) probably results from a combination of complex environmental fate processes described by Hung, et al. (2002).**

- Analysis of air trajectories indicates that continental/southerly air masses in North America are likely to be more significant contributors to Arctic contamination than Asian sources.

Seawater

- The endosulfan levels in seawater were typically approximately < 1 – 10 pg/L
- Results of seawater monitoring are highly consistent despite wide geographic separation and analysis being undertaken by a range of institutes.
- The Central Asian Arctic is poorly represented, presenting uncertainties regarding potential riverine routes of entry for endosulfan into the Arctic.
- There are no geographical trends that may suggest that transport from the Pacific Ocean through the Bering and Chukchi seas may be occurring - as observed for other persistent organochlorine pesticides.
- A net air to seawater exchange appears to dominate in some locations (Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) but is reversed at others (Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea), highlighting uncertainties of the trace levels detects in air and water and a potential seasonal sensitivity to ice pack conditions.
- Compounded uncertainties (trace seawater analysis, reliance on a spatially limited air monitoring database and absence of a temperature dependent Henry's law constant) suggest that a high degree of caution must be exercised in interpretation of air – water exchange behaviour.

Snow

- The accumulation profile in snow and ice for the last 50 years reveals that input of endosulfan was higher in the past, although significant post-depositional migration during snow-to-ice metamorphism may obscure this profile.

Biota

- Difficulties with interpretation of biota measurements arise due to former reliance on GC-ECD with associated potential for analytical interference. In particular, differences between the GC-ECD and GC-MS results reported by Kelly (2005) and Stern and Ikonomou (2003) warrant further investigation.
- Concentrations of α-endosulfan were significantly higher in whales from the North Sea, potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species.
- Concentrations of endosulfan in seals around the Arctic Ocean do not correlate with the findings in seawater.

Trophic Magnification, Biomagnification and Bioaccumulation Potential

- It is concluded that α-endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.
- An average fish to mammal biomagnification factor (BMF) of 10.2 (± 16.4) indicates a very high degree of variability and, therefore, uncertainty. On this basis it is not possible to conclude whether there is or isn't a potential for biomagnification occurring at a level of possible concern.
- There is, however, clear evidence that biomagnification from invertebrates to fish and from fish to predatory fish does not occur.
- The implications of very high estimated bioaccumulation factors (BAFs) (ranging from 3.4×10^3 to 2.6×10^7) are unclear. Uncertainties on intermediate micro-organism trophic level and low ambient temperature conditions in the Arctic may lead to an increase in bioaccumulation as a consequence of a lowered rate of metabolism .

Ecotoxicological and Human Dietary Risk Profiles

- There is negligible risk to marine organisms and terrestrial animals associated with exposure to endosulfan in the Arctic

- **Human dietary risk was concluded to be generally negligible except with unrealistic, extreme worst-case assumptions (coincidence of very heavy reliance upon marine mammals and fish characterised by 99th centile endosulfan residue profiles).**

Based on stable concentrations of endosulfan in the environment, the virtual absence of trophic magnification and biomagnification in the food chain, a negligible ecological risk to marine mammals and a negligible human dietary risk, concerns of potential adverse effects on human health and the environment leads to the conclusion that endosulfan does not demonstrate typical POP behaviour that would indicate a requirement to classify it as a POP.

An abstract of the research findings that support these conclusions is provided overleaf for each of the points summarised above.

Temporal trends
Long-term continuous air sampling is available for comparatively few sites of which Alert in the Canadian high Arctic provides by far the most significant and highest value dataset. The long-term trend in endosulfan residues in air in the Arctic appears to be stable. Usage/emission may have peaked during the period 1990-2001 and may now be in decline but establishing the extent of any delay in parallel decline in air residues will require further (and perhaps more extensive) continuous air sampling. The timescales required to assess this cannot be accurately estimated due to a lack of knowledge about the significance of a wide range of potential confounding influences summarised by Hung *et al.* (2005) as well as more up to date and more accurate usage and emission estimates. The available seawater monitoring database does not constitute a robust enough database to allow firm conclusions to be made regarding temporal trends. A survey of glacial firn and ice has revealed the potential for accumulation α- and β-endosulfan. The accumulation profile for the last 50 years reveals that input of endosulfan has declined, although significant post-depositional migration may obscure this profile.

Detailed analysis of temporal trends in biota was not possible due to the absence of long-term, site-specific monitoring campaigns. One noteworthy exception is reported by Stern and Ikonomou (2003), who concluded that endosulfan sulfate residues were increasing in male beluga whales in the Canadian Arctic. However, a 10-20 fold differences between the GC-ECD and GC-MS results reported by Kelly (2005) needs to be investigated further before reaching firm conclusions. The timescales considered, relative to recent trends in emission and air and seawater are probably insufficient to allow firm conclusions to be reached regarding whether endosulfan residues would continue to apparently plateau or decline in the near future.

Spatial trends
As summarised earlier, the NCP (Northern Contaminants Programme) air monitoring station in Alert in the Canadian high Arctic is the most most robust dataset available. Additional monitoring has been conducted at sites in the Canadian sub-Arctic, western Siberia, the Bering Sea and in Norway. Nonetheless, it has been possible to exploit certain databases with the aim of identifying source regions that contribute most significantly to airborne residues at specific locations. Spatial variation in endosulfan concentrations is not pronounced across the Arctic region as a whole, with yearly averages varying by less than a factor of 2. The assembled database of seawater monitoring suggests that most sectors of the Arctic Ocean are included with the Bering Sea, Beaufort Sea, Canadian Archipelago particularly well-represented. However, the Central Asian Arctic is poorly represented. This may have implications when considering the potential of Asian rivers as routes of entry for

endosulfan into the Arctic. Concentrations of both α- and β-endosulfan east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this are uncertain. There is, nonetheless, a relatively high degree on analytical consistency in seawater monitoring results. Analysis of snow has been conducted at a range of sites in Canada and Norway. However, spatial trends in snow and ice are difficult to determine due to the high variability in snow concentrations. In the Canadian Arctic the two most northerly sample sites, with the coldest air temperatures displayed the widest range in concentrations with higher average concentrations than sites located further south. However, higher rates of precipitation experienced at the more southerly stations result in similar depositional fluxes across the Canadian Archipelago.

Spatial variation in residues of α-endosulfan in biota was specifically considered for ringed seal blubber and minke whales. Further, region-specific data was available in the form of the Greenland diet study (Johansen et al., 2004a). In ringed seals, the highest concentrations of α-endosulfan were found in the Beaufort Sea. Concentrations in the eastern Canadian Arctic, Greenland and Russian Arctic are much lower although in general α-endosulfan was detectable at sub-ng/g in all blubber samples. However, there appears to be no relationship to endosulfan concentrations in seawater. Residues of α-endosulfan were significantly higher in whales from the North Sea than those from all other locations. Minke whales from the Barents Sea had higher α-endosulfan than those from Jan Mayen and west Greenland - potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species.

Transport mechanisms and environmental fate

Key studies conducted in the Canadian sub-Arctic (Tagish, Yukon) have been interpreted with air mass back trajectories to assess potential sources of contaminants into the western Canadian Arctic and other Canadian monitoring locations. This research indicates that continental/southerly air masses in North America are likely to be more significant contributors to Arctic contamination than Asian sources. Attribution of source regions for endosulfan arriving in Arctic regions of eastern North America, Europe and Asia remains uncharacterised.

Although both α- and β-endosulfan concentrations east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain and it has not been possible to attribute oceanic transport sources. Air-water exchange is one of the most important environmental fate processes that will define behaviour in the Arctic. There appears to be significant regional differences in air-sea gas exchange behaviour for α-endosulfan. The use of fugacity ratios to estimate the net transfer air-sea gas exchange behaviour relies very heavily on an estimated temperature dependent Henry's law constant. This is considered to be the single greatest uncertainty in evaluating air-sea gas exchange behaviour (and perhaps behaviour of endosulfan in the Arctic as a whole). Nonetheless, the calculations suggest that in some regions there is a net seawater → air transfer mechanism occurring or that air and seawater are at close to equilibrium (e.g. Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea). In other areas (notably the Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) there appears to be a net air → seawater transfer mechanism occurring. It is likely that seasonal changes in the ice pack will have a very significant influence on behaviour. There is insufficient data available to accurately estimate net air-sea gas exchange behaviour for β-endosulfan. The lack of clear consistent air-sea gas exchange behaviour is in contrast to γ-HCH where recent results suggest a clear air → seawater transfer mechanism in operation.

When taken together, the compounded uncertainties associated with issues such as low level analysis in seawater, reliance on a very limited set of air sampling campaigns, the lack of availability of a temperature dependent Henry's law constant, suggest that a high degree of caution must be exercised in interpretation and attribution of behaviour as evidence of POP characteristics. It can be argued that the high degree of variability observed would, in fact, favour the combined influence of a far more complex set of processes than is implied in typically simplistic POP profiles where there is a degree of spatial consistency.

Trophic magnification potential

Trophic magnification profiles from three of the four sites for which sufficient data was available to allow analysis (Barrow, Lake Superior, and White Sea) suggest that there is no significant relationship between measured concentration and trophic level for either α-endosulfan or lindane. The evidence for the remaining site (Holman) is ambiguous. At this site, there appears to be a significant relationship between measured concentration and trophic level for all three investigated compounds (α-endosulfan, lindane and PCB 153). However, it is well recognised that lindane does not biomagnify in aquatic food webs (Moisey *et al.* 2001; Hoekstra *et al.* 2003) giving rise to concerns surrounding the interpretation and significance of the dataset for this site. Taking this into account it is concluded that α-endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.

Biomagnification potential

Although there are no biomagnification factor (BMF) triggers within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs, there are criteria applied to bioconcentration or bioaccumulation in aquatic species (BCF (bioconcentration factors) or BAF (bioaccumulation factors) > 5000). BMF values found to be statistically greater than unity are considered to accumulate from prey to predator. Based upon the triggers established for BCF it would be possible to conclude that BMF values of > 10 may also be of consistent concern (Default BCF and BMF values within the EU Technical Guidance Document (ECB, 2003) imply that where BCF of >5000 occurs, BMF values of *ca* 10 may be expected, although caveats are noted regarding assumed relationships between BCF, BMF and K_{ow}). Calculated biomagnification factors based on residue measurements for a range of Arctic species ranged from 0.056 to 64.7. These ranges both reflect calculations for fish to marine mammal food chain links. The high degree of variability within this food chain links is particularly noteworthy. Further analysis revealed that average invertebrate to fish and fish to predatory fish BMF values were very low (0.38 and 0.60, respectively). The average fish to mammal BMF value was 10.2, lying at a possible threshold of concern. However, this estimate needs to be interpreted recognising a very high degree of variability (±16.4) and therefore, uncertainty. High fish to mammal BMFs may be due to contribution from interference in α-endosulfan analysis by GC-ECD that biomagnified e.g. a chlordane or toxaphene component, thus artificially raising the BMF. The exact contribution is difficult to assess (because both fish and marine mammals have interferences by GC-ECD) but based on paired GC-ECD and GC-NIMS analysis could result in overestimation by up to 4x. In summary, there is no clear evidence of biomagnification for invertebrates to fish and fish to predatory fish. There is a high degree of uncertainty surrounding fish to marine mammal food chain links – on this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern.

Bioaccumulation potential

Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000. Measured bioaccumulation factors (BAF values) for a range of Arctic species ranged from 3.4 x 10^3 to 2.6 x 10^7. The implications of very high BAF values are unclear. The potential for other uptake/retention mechanisms remains a possibility. General consistency is noted despite studies and analysis having been conducted by a number of researchers in different institutes based on monitoring in a range of differing locations. The transfer to zooplankton has been assumed to be mainly *via* water but recent studies suggest that the microbial food web could be important (Wallberg *et al.* 2001) and may unexpectedly influence such calculations. The influence of low temperature on increasing bioaccumulation under Arctic conditions by reducing metabolism potential has been postulated. Such an influence could account for differences between bioconcentration profiles observed under laboratory conditions (BCF: 200-3700, typically measured at 20-25°C) and ambient Arctic conditions (typically <5°C). There is, however, insufficient data to confirm this for endosulfan, although the possibility is considered in studies for other compounds (Buckman *et al.*, 2004).

Ecotoxicological risk

A relatively robust evaluation of ecotoxicological risks has been facilitated through access to a very large database of effects studies. Risks to freshwater or marine animals are minimal. The toxicity value from laboratory studies for the most sensitive animal was about three orders of magnitude greater than the highest measured concentration for Arctic marine waters. This applies to both the acute and the chronic toxicity values. These data clearly show that there is essentially negligible risk to aquatic animals from acute and chronic exposures to endosulfan residues in Arctic marine systems.

Risks to terrestrial animals were assessed by direct comparison of mammalian toxicity data with measured residues in relevant organisms. The results of this assessment support the same conclusion of negligible risks to marine mammals and terrestrial wildlife from endosulfan exposures via the environment and the food chain.

Human dietary risk

The most common criterion for judging human exposure for the purposes of risk assessment is the Reference Dose (RfD) or the Acceptable Daily Intake (ADI). This is determined from the results of laboratory animal studies in which the highest dose that does not cause an adverse acute or chronic response in the most sensitive test species is divided by an uncertainty factor (100) to account for differences between humans and laboratory animals and within humans, such as the elderly or very young. Critical dietary residue profiles were obtained from valuable research conducted in Greenland by Johansen *et al.* (2004a). Probabilistic analysis of exposures, based on residue data for various food items were then used to estimate 90^{th}, 95^{th}, and 99^{th} centiles of intake potential based on limited dietary component analyses carried out in the Arctic (Greenland and Russia).

With the exception of a hypothetical individual in Greenland that consumes all food items with the 99^{th} centile concentration of endosulfan, all other consumption scenarios suggest negligible risk. Similar results were obtained when the concentrations of endosulfan in imported food items were assumed to be the same as those for the US population. Human dietary risk is concluded to be generally negligible except in extreme worst-case situations where there is a coincidence of very heavy reliance upon locally sourced food items drawing heavily upon marine mammals and fish characterised by 99th centile endosulfan residue profiles. It should be noted that even if this unrealistically high uptake profile is compared to the lowest available chronic NOEL from the most sensitive mammalian species tested a safety factor of 21 can be demonstrated.

Research recommendations

A review of strengths and weaknesses in the available datasets was conducted with the aim of identify and characterising uncertainties. Many of the uncertainties highlighted in this review are discussed in this summary and studies that are considered to provide critical, high quality datasets have similarly been identified. This also provided an opportunity to consider how monitoring and risk assessment research in this field might be improved through changes in analytical strategy, monitoring design or other data gathering exercises. A summary of the key recommendations is provided overleaf.

Air
• *Additional quality control procedures should be put in place to periodically confirm the presence of analytes reported by GC-ECD. Further controls such as inter-laboratory round-robins and analysis of quality assurance standards could be regularly implemented.* • *The long-term air monitoring programme based at Alert in the Canadian high Arctic has provided vital data in understanding the behaviour and trends in many chemicals. It is recommended that this programme be continued to assist in better understanding trends in chemicals with current usage such as endosulfan.* • *It is further recommended that such monitoring programmes be potentially extended to consider other locations to assist in the development of a more complete understanding of potential source regions for chemicals. The expense and logistical difficulties associated with running such a study are recognised.*
Seawater
• *Additional quality control procedures should be put in place to periodically confirm the presence of analytes reported by GC-ECD. Further controls such as inter-laboratory round-robins and analysis of quality assurance standards could be regularly implemented.* • *Coupled air /seawater measurements to assess localised air-water exchange during periods of melt and freeze. The work could also be conducted in the vicinity of an ice-lead to quantify the role of polynyas/leads in contributing to air-water exchange during the winter and spring.* • *Deep water sampling to establish the vertical extent of endosulfan occurrence in the water column. The hypothesis here is that endosulfan residues are unlikely to be detected (unlike HCHs) due to removal via hydrolysis.* • *Potential for widening seawater monitoring campaigns to include an assessment of the Central Asian Arctic.* • *Increased accessability of monitoring databases for large Asian rivers (Ob, Yenisey and Lena Rivers) in order to assess scale of riverine sources into the Arctic* • *Potential for establishing seawater monitoring designs (seasonal or monthly sampling) for selected sites that would provide a more robust basis for establishing temporal trends.* • *Further investigation into the role of meltwater as a local source of residues into seawater.* • *More extensive seawater monitoring from below the ice pack to assist in further understanding seasonal variation in water residues and air-water exchange behaviour.* • *Of specific relevance to endosulfan, the determination of a temperature dependent Henry's law constant*
Snow
• *Process-based studies are required to examine the fate of endosulfan following snow ageing and melt. Percolation and transport of chemical residues both within and out of the snowpack during periods of thaw are poorly understood and both laboratory simulations and controlled field studies are required to address these areas.* • *Combined air and snow sampling is required to determine field-based scavenging ratios and relate these to temperature, the physical properties of the snow and theoretically derived values.* • *Snow-air partitioning studies are required to determine the suitability of Henry's Law (at sub-zero temperatures) in describing the chemical composition in aged snow.* • *Studies are required to investigate the role of the sea-ice-snowpack in contributing endosulfan to surface seawater.* • *Photochemcial studies are required in photic snow layers to understand chemical degradation/transformation following polar sunrise and 24 h daylight.*

Biota
• *Analytical methodology employed in biota monitoring programmes be upgraded to GC-MS.* • *Differences between the GC-ECD and GC-MS results reported by Kelly (2005) and Stern and Ikonomou (2003) warrant further investigation to assist in understanding temporal trends.* • *The influence of low ambient temperature conditions on bioaccumulation and metabolism potential should be investigated with species of relevance to such conditions.* • *Widening the range of sites considered to include the Asian Arctic could strengthen further understanding of spatial variation in biota residues.*
Risk Assessment
• *A more thorough dietary residue analysis for endosulfan would facilitate more robust human dietary risk assessments* • *A more extensive (population level) and higher resolution (dietary component) dietary profile for a range of Arctic diets should be developed - similar to that employed in conventional human dietary risk assessments for pesticides. This is currently underway in the United States for Alaska but may not be representative of diets in other regions in Canada (Nunavut, Nunavik), Greenland, Scandinavia and Russia.*