Passive sampling and distribution of DDT in air

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I Can Do All Things Through Christ Who Strengthens Me – Philippians 4:13

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"Rume rimwe harikombe churu"

Abstract

Dichloro-diphenyl-trichlorethane (DDT) is a chemical used in malaria control through indoor residual spraying (IRS) and has saved numerous lives in the past six decades. DDT use is restricted/banned under the Stockholm Convention on Persistent Organic Pollutants. Passive air sampling using polyurethane foam was conducted in South Africa to evaluate the presence and trends of DDT and its metabolites. Three sampling sites were used, namely, Barberspan Nature Reserve (rural agricultural), Vanderbijlpark (urban industrial) and Molopo Nature Reserve (isolated nature reserve). Sampling was conducted for a period of one year in 2008. Back trajectories from the three sampling sites were generated using HYSPILT to determine the sources of DDT metabolites to the sampling areas. Forward trajectories were also generated to determine the movement, distribution, and fate of DDT from the areas under Indoor residual spray of DDT for malaria control in South Africa and Swaziland. Chemical analysis was conducted by the RECETOX (Mazaryk University) in the Czech Republic. DDT metabolites (*o,p'*-DDE, *p'p'*-DDE, *o.p'*-DDD, *p,p'*-DDD, *o,p'*-DDT *p,p'*-DDT) were analysed using a GC-ECD (HP 5890). Vanderbijlpark had the highest concentrations of DDT metabolites throughout the year. Barberspan had the second highest concentration and Molopo the least. Seasonal changes in concentration were much the same at the three sites. %*p,p'*-DDT of ΣDDT is consistent with IRS spraying months in South Africa and Swaziland. A combinations of backward and forward trajectories, together with the temporal pattern of change of the %*p,p'*-DDT of ΣDDT support the deduction that DDT sampled from the three study sites (to some degree) came from IRS areas in South Africa and Swaziland. The presence of DDT in Molopo Nature Reserve and Barberspan is evidence of long-range transportation over dry semi-desert areas. Back-trajectories indicate the possible source of DDT were the IRS areas in the provinces of Limpopo, Mpumalanga, and KwaZulu-Natal. Some air masses to the sampling sites came from the sprayed areas. The forward trajectories also revealed that the DDT sprayed during IRS could undergo LRT. The DDT metabolites were able to travel to neighbouring countries such as Mozambique, Namibia, Zimbabwe and Botswana.

Keywords: Key words: DDT; Passive air sampling; long range transportation

Contents

Abbreviations

AMAP	Arctic Monitoring and Assessment Programme
ARL	Air Resources Laboratory
ATSDR	Agency for Toxic Substances and Disease Registry
BNR	Barberspan Nature Reserve
DDD	1-dichloro-2,2-bis(p-chlorophenyl)ethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-Diphenyl-Trichlorethane
GAPS	Global Atmospheric Passive Sampling
GDAS	Global Data Assimilation System
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HLCs	Holocarboxylase synthetase
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IRS	Indoor Residual Spraying
LRT	Long-Range Transport
LRTAP	Long-Range Transport of Air Pollutants
MNR	Molopo Nature Reserve
MONET	Monitoring Network, Africa
NIP	National Implementation Plan
NOAA	National Oceanic Atmospheric Administration
PBTs	Persistent, Bio-accumulative and Toxic substances
PCBs	Polychlorinated Biphenyls
POPs	Persistent Organic Pollutants
PUF	Polyurethane foam
READY	Real-time Environmental Applications and Display System
RECOTOX	Research Centre for Environmental Chemistry and Ecotoxicology
SC	Stockholm Convention

SCPOP	The Stockholm Convention on Persistent Organic Pollutants
SETAC	Society of Environmental Toxicology and Chemistry
UN	United Nations
UN-ECE	United Nations Economic Commission of Europe
UNEP	United Nations Environmental Program
UV	Ultra-violent
VP	Vanderbijlpark
WHO	World Health Organization
WHOPES	World Health Organization Pesticide Evaluation Scheme
WHO-UNICEF WSS	World Health Organization United Nations International Children's Education Fund Water Safety and Sustainability

Chapter 1: INTRODUCTION

1.1 The Stockholm Convention on Persistent Organic Pollutants and DDT

1.1.1 The Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (SCPOPs) is an international treaty that operates under the patronage of the United Nations (UN) to control certain chemicals that are considered persistent organic pollutants (POPs). They are of great concern because of their adverse effects on human health and the environment (Ritter *et al.,* 2005). The SCPOPs aims to protect humanity and the environment from these chemicals through international agreed policies and interventions with the aim to eventually reduce or stop releases of POPs. The convention bans and/or restricts the production and use of the intentionally produced POPs. It also aims at reducing releases of unintentionally produced POPs, which are formed as by-products of combustion and industrial processes (UNEP, 2005). The SCPOPs was adopted at a Conference of Plenipotentiaries on 22 May 2001 in Stockholm, Sweden. The Convention entered into force on 17 May 2004, 90 days after submission of the fiftieth country's ratification of the Convention. Member States to the convention have agreed to take the steps necessary to reduce and eventually eliminate where possible the use of such chemicals. To achieve these goals, nations are expected put in place legislation, monitoring, implementation plans, research programs, and share information on how best to address this problem (Pozo *et al.,* 2008). The treaty is comprised of a number of articles with mandates and expectations each member State (also known as Party) is required to follow or carry out (Stockholm Convention on POPs, 2009).

The main aim of the SCPOPs is to protect human health and the environment from chemicals that are persistent, bio-accumulate, and tend to become geographically widely distributed (Stockholm Convention on POPs, 2009). The SCPOPs, of which South Africa, Botswana, Lesotho, Tanzania, Mauritius, Zambia and Zimbabwe, are Parties, carries a number of obligations and

expectations. Based on the obligation to develop a National Implementation Plan (NIP), member States should have monitoring programmes in place. Developing country Parties are also obliged to reduce or terminate all sources of POPs within the SC provisions, provided that timely and sufficient means have been made available. This therefore implies that the State should know the environmental levels of these POPs whereby priority sources and hotspots can be targeted for interventions. Since much of this information is either old or lacking, research needs to be undertaken (Ross *et al*, 2009). In some countries, due to lack of alternative compounds for industrial use and financial constraints, some POPs compounds like dichloro-diphenyl-trichlorethane (DDT) are still in use. For example, South Africa and Swaziland still uses DDT for malaria control, as do some other developing nations (Hargreaves *et al*., 2000).

The SCPOPs supports the substitution of harmful POPs with safer, cost effective alternatives. However, this process may pose a challenge to developing countries as they lack the financial and technological resources to use and manufacture less harmful chemicals, buy more expensive newer-generation chemicals, or introduce cleaner technologies. The convention calls on developed nations to share their knowledge and lend financial support to developing countries and economies in transition by aiding their transition to more suitable alternatives (UNEP, 2001). The SCPOPs has successfully negotiated the ban or restrictions of 22 POPs.

1.1.2 The Stockholm Convention Guidelines

A number of stipulations have been accepted into the SCPOPs so as to help achieve the goals of the convention. For example, Article 5 stipulates that member States shall take certain measures to ensure that they reduce the total releases derived from anthropogenic sources of each of the unintentionally produced chemicals listed in Annex C, with the goal of their continuing minimization and, where feasible, ultimate elimination (Stockholm Convention on POPs, 2009). Article 7 of the SCPOPs requires member states to develop a NIP in accordance to the state of their respective environments and economies. Research and data on POPs in all

member States is therefore required. This project will inform such documents for South Africa and Swaziland as it will help provide the necessary data.

Article 11 of the SCPOPs states that member States are requested to undertake appropriate research, development, monitoring and co-operation with other nations pertaining to POPs. There is a lack of data and information in relation to POPs in South Africa (Bouwman *et al.,* 2006) and Swaziland. The research presented here will provide a base for further work and generation of more POPs data.

Monitoring of the state of air quality in terms of POPs, DDT in particular, has not had much focus in the past. This project aims to look at the trends in terms of concentration, distribution and fate of DDT is southern African air. The study is in line with the requirement of the SCPOPs Article 16 that requests Parties to establish monitoring programmes. A plan to measure the effectiveness of emission control methods relies on a global monitoring program of key environmental media: initially air and human tissue (Pozo *et al.,* 2008) As part of the SCPOPs, Article 9 highlights the need for sharing information and technology together with technical assistance. The Parties are requested to provide timely and appropriate technical assistance to Developing Country Parties and Parties with Economies in Transition, to assist them, taking into account their particular needs, to develop and strengthen their capacity to implement their obligations under this Convention (Stockholm Convention on POPs, 2009). Through the collaboration with the Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX) in Prague, Czech Republic, knowledge will be exchanged, and information on sample analysis and use of passive air sampling techniques will be shared through this project.

1.1.3 DDT

DDT is arguably the POP that has had the greatest impact on the world (with a possible exception of PCBs), both positive and adverse. Its property as a pest controlling substance was greatly appreciated, with millions of tonnes manufactured between the 1940s and the 1970s. It

helped in reducing malaria mortalities throughout the world. It was a great success for its intended purposes. Things turned around when it was discovered that the chemical was toxic to non-target organisms, had the ability to migrate long distances via air, and water, and to bio-accumulate within the food web (Ritter *et al.,* 2005; Wania and Mackay, 1996). These attributes had adverse effects on environmental stability and human health. The presentation by Rachel Carson in her book "Silent Spring" of possible environmental toxicity from the release of DDT to the environment, triggered global awareness on the dangers of DDT use. As a result the manufacture and use of DDT was greatly reduced and in some cases banned in many countries since 1970.

The SCPOPs is a global treaty with 179 Parties. This convention applies to DDT and 21 other POPs. These include aldrin, dieldrin, endosulfan, endrin, chlordane, heptachlor, hexachlorobenzene (HCB), pentabromodiphenyl, heptabromodiphenyl, hexabromodiphenyl, polychlorinated dibenzifurans and dioxins, tretrabromodiphenyl, mirex, toxaphene, polychlorinated biphenyls (PCBs), and α-, β, and γ-hexachlorocyclohexane (HCH) (Stockholm Convention on POPs, 2009). The SCPOPs aims to eventually stop the usage of all POPs. Due to the lack of alternative to these chemicals, some have remained in use. Most southern African countries such as Mozambique, South Africa, Zimbabwe and Swaziland still use DDT for malaria control (Hargreaves *et al*., 2000; Mpofu, 1987). Under the SCPOPs, DDT is allowed for use in indoor residual spraying (IRS) for disease-vector control. This is a process where the insecticide, DDT, is applied indoors on house walls and under eaves. Concerted large-scale efforts are now underway to reduce both the burden of vector-borne diseases and the use of DDT.

Use and production of DDT is restricted by the SCPOPs. It recognises, however, acceptable uses of the chemical in saving lives in malaria areas. The use of DDT is allowed under the SCPOPs for disease vector control, within the recommendations and guidelines of the World Health Organisation (WHO). DDT use is allowed, provided that no locally safe, effective and affordable alternative is available. It also highlights that Parties prevent or minimise human exposure and the eventual releases of DDT into the environment. The SCPOPs, however, requires Parties that

use or intend to use DDT to notify the Convention Secretariat - this is highlighted under Annex B Part II. Part II requires that notification of the use DDT is required to provide information of the quantities to be used, conditions under which it will be used, and DDT's relevance to their disease management strategy (Stockholm Convention on POPs, 2009).

CHAPTER 2: LITRETURE REVIEW

2.1 Long Range Transport (LRT)

The behaviour and fate of chemicals in the environment is influenced by their chemical and physical properties and by the type of environment they are in. The molecular structure and the elements in the molecule influence the chemical and physical properties of the particular chemical and hence its environmental transportation, distribution, deposition and fate. The compound may be moved via water, air, and animals. Volatilization from contaminated lands brings DDT into the atmosphere. It is then deposited onto land and soil. This cycle may continue numerous times and hence transport the chemicals over a large distance in the atmosphere, called Long Range Transport (LRT) (Ritter *et al.,* 2005; Wania and Mackay, 1996; Gregor *et al.*, 1998). Their physical and chemical properties enable the semi volatile compounds to undergo LRT, allowing the pollutants to become geographically widely distributed, even to regions where they have never been used or produced (Ritter *et al.,* 2005; Stockholm Convention on POPs, 2009). In addition, commercial POPs are also traded over long distances.

2.1.1 Movement and distribution of POPs

POPs are an international concern because they are able to travel across national boundaries; combating POPs is no longer a problem of a single State. The traditionally recognised medium for POPs transportation has always been the atmosphere and such trans-boundary pollution issues are addressed within international conventions such as the protocol on the long-range transport of air pollutants (LRTAP) within UN-ECE. Increasingly, it was realized that other modes of transport can also move pollutants over long distances (water, and migratory animals) and from one jurisdiction to another (AMAP, 1997; Ritter *et al.,* 2005; Berdowski *et al*., 1997).

Their persistence and semi-volatility have led to the spread of POPs to all regions and climates of the world. Ritter *et al.* (2005) and Berdowski *et al*. (1997) report that compounds such as

PCBs have been detected on every continent, at sites representing every major climatic zone and geographic sector. These include remote regions such as the open oceans, the deserts, the Arctic and the Antarctic, where no significant local sources are present. POPs can be transported through a number of media as shown by much positive detection in places such as the Arctic (Hung *et al.,* 2010). Metrological conditions also influence the spread of POPs. For example, Iversen (1996), documents that summer accounts for 20% of the annual south to north air transport (southerlies in the Norwegian Sea (10%), eastern Europe/Siberia (5%), and Bering Sea (5%)). Prevailing winds provide a means to transport contaminants from industrialized North America and Europe to the North Atlantic, but penetration into the Arctic then weakens. The only reasonable explanation for their presence is LRT from other parts of the globe. PCBs have been reported in air, in all areas of the world, at concentrations of up to 15 ng/m^3. In air over industrialized areas, concentrations may be several orders of magnitude greater (Ritter *et al.,* 2005). PCBs have also been reported in rain and snow (Blais *et al.,* 1998). These properties are conferred by the structural makeup of the molecules and are often associated with greater degrees of halogenation (Campbell, 1998).

LRT of POPs is also influenced by factors such as wind speed and direction. At greater wind speed, the chemical will travel further. Hemispheric distribution occurs in a matter of days while inter-hemispheric distribution could take months or even years. Light molecular mass chemicals such as PCBs travel mainly in vapour phase and the heavier chemicals like PBDES are associated with aerosol particles (Chen *et al.,* 2011).

Oceanic currents can transport POPs to other parts of the world where they have never been in use. A number of forces drive oceanic currents namely, mixing of the water currents, wind stress, and tidal forces, of which one force may dominate depending on circumstances. Oceanic currents in the Arctic, where major currents exchange water between the Arctic Ocean and other oceans, are found in Fram Strait. Here, the West Spitsbergen Current flows northward off the west coast of Svalbard, transporting Atlantic water from the Norwegian Sea into the Arctic Ocean (Gregor *et al*., 1998). The mixing of these waters may be a source of POPs into the Arctic.

However, this mode of transportation may take years as the process is slow. Ocean transport is responsible for the movement of POPs such as HCH that are removed from air through precipitation and deposited in water (Li *et al.*, 2002). Rivers and streams also transport POPs. Contaminated water may carry pollutants over a long distance and carry them to the sea. For example, the Russian river, Yenisey, carries pollutants coming from industrial sites to the Arctic Ocean (Gregor *et al.*, 1998).

Migration of animals my spread POPs throughout the world. Some migratory animals and birds travel long distances linking up remote areas, industries, and agricultural regions. According to Wania and Mackay (1996), millions of migrating seabirds bring a gram to kilograms amounts of POPs to the Arctic per year. Seabirds also leave behind guano, which have significant quantities of POPs contaminants that may have accumulated in their systems. As the birds migrate they pass different environments picking up all kinds of chemicals. Evenset *et al*. (2007) found elevated PCBs in fish and sediments from Lake Ellasjøen on Bjørnøya, Svalbard. Animals may later die in remote areas and hence depositing their body burden of pollutants in those areas. This is common in the salmon entering Alaskan rivers to Spawn, most of the fish die after spawning in the upper reaches of freshwaters, releasing the POPs to the environment. Birds are also a source of POPs and a medium of POPs movement.

Animal migration may also spread POPs through food webs. For example, Polar Bears prey on Barents Sea Harp Seals that migrate over long distances picking up pollutants. The seals are exposed to POPs and the chemicals bio-accumulate in the seal. These seals aggregate at the Poles and are a source of food to Polar Bears, Orcas, and other predators, hence contributing to LRT of POPs (Ewald *et al.*, 1998). Many Arctic whales migrate only within the Arctic. However, the Grey Whale migrates as far as between Bering and Chukchi Seas in summer and in winter they are off to the Pacific Coast of Mexico (Baker, 1978). The amount of POPs transported by these whales can be calculated based on the relatively reliable population estimates and recent contaminant concentrations in stranded individuals. It is estimated that 20 to 150 kg of PCBs and 1 to 40 kg of DDT are transported by the Gray Whale (Wania, 1998). The whales at the end

of their lives die in the Arctic, and leave the pollutants there. Dead whales are scavenged upon by Polar Bears and Arctic Fox and thus moving the contaminants up the food web. Considering all migratory whale populations, Wania (1998) concluded that the amount of PCBs and DDTs moved around in the bodies these whales is likely of the order of tens of tons per year. Especially for DDTs, these gross fluxes by whales may be comparable to those in air and ocean currents.

2.1.2 Deposition and fate of POPs

The persistence of organic compounds in the atmosphere is determined by the rates at which they are removed by chemical and/or physical processes. A number of chemical processes can occur. Chemical degradation can occur by the POPs molecules reacting with hydroxyl or nitrate radicals or via reaction with ozone. The chemical can also be degraded by direct photolysis with solar radiation (UV) working on the compounds. Physical removal from the atmosphere can occur by wet or dry deposition of vapour phase or particle-borne species (Campbell, 1998; Blais *et al.,* 1998). An important POPs property is their semi-volatility. The compounds are constantly transferred from one area to the other; they may volatilize from hot regions but will condense and tend to remain in colder regions. Substances with this property are usually highly halogenated, have a molecular mass of 200-500, and a vapour pressure lower than 1000 Pa (Ritter *et al.,* 2005)

Environmental conditions play an important role in the fate of POPs. An example is the net exchange direction for substances in the open ocean. It reflects differences in surface water temperature and the atmospheric concentration of POPs. For example, net movement of certain POPs in the Bay of Bengal in the Indian Ocean is from the ocean to the atmosphere while that in Polar Regions is the reverse (Berdowski *et al*., 1997). Periods of light and darkness also influence POPs concentrations especially in the Arctic. The duration of light or darkness influence the rate of photolytic degradation and chemicals in the air and hence some POPs

concentrations. Lack of photolytic degradation during long periods of darkness may be the reason for high concentrations of POPs in winters (Halsall *et al*., 1998; Blais *et al.,* 1998).

Deposition of POPs from the atmosphere is also an important factor. Its removal is mainly governed by removal through wet and dry deposition. Factors such as the state of the surface, wetness or dryness, and types of vegetation play a role in deposition. The water solubility of the chemical and its particle size are also important. Deposition in other locations may be influenced by temperature. The greater the vapour pressure of the contaminant, up to a maximum, the more freely it will be transported and deposited at higher elevations. The lower the temperatures, the greater partitioning of these compounds from the vapour phase to particles suspended in the atmosphere. This increases the likelihood of their removal and transport to the surface of the earth by rain and snow, variably called scavenging or scrubbing. This is common at high altitudes like mountain areas as the occurrence of snow and rainfall is frequent. Snow is believed to be a very efficient scavenger of both particles and non-polar organic compounds, capable of effectively cleansing the atmosphere (Ritter *et al.,* 2005; Campbell, 1998; Blais *et al.,* 1998).

Mountainous regions have always been considered unspoiled environments with no contamination. Areas with altitudes above 3000 m such as the Himalayas are largely unpopulated by people. There is very little human habitation and agricultural impact at these elevations and because of this it was assumed that this mountain region is largely free of pollution. However, volatile and semi-volatile toxic contaminants such as certain pesticides do not heed the boundaries of human habitation. These contaminants are readily volatilized in regions of use, transported in the air and deposited in colder regions and climates (Blais *et al.,* 1998; Mark *et al.,* 2004). Bahadur, (1993) considers the Himalaya as the third “Pole” and a “distillation tower” or "cold finger" where airborne chemicals are deposited.

Precipitation plays a role in the deposition of POPs from the atmosphere. The kind of precipitation affects the degree of deposition, for example, snow leads to more deposition

compared to rainfall. Snow, because of its greater surface area, scrubs and transports more contaminants to the ground compared with raindrops as the contaminants have a greater area to bind on during precipitation (Franz and Eisenreich, 1998). Rainfall and snow therefore scavenges or scrubs aerosols and vapour phase molecules from the air and deposit them to the earth (Macdonald *et al*., 2000). In dry desert areas, POPs will travel for longer distances as there are fewer precipitation events.

Vegetation also plays a role. Different types of vegetation will adsorb and release different kinds of POPs at varying rates. Recently, Kylin and Bouwman (2012) found significant differences in how moss and lichen in the cold regions of the northern hemisphere treat α- and γ-HCH over dry and wet cycles, and may play a role in determining downwind concentrations in air without actually changing the absolute mass of the compounds in the environment.

2.2 Persistent organic pollutants

By definition, POPs are organic compounds and resistant to degradation. Most of the compounds contain hydrogen and chlorine, some now also bromine and fluorine. The bond between carbon and halogens are stable, and, in general, the greater the halogen substitutions the greater the resistance to degradation. The bond between halogen and an aromatic ring is more stable than an aliphatic structure. As a result, halogenated POPs are typically ring structures with a chain or branched-chain framework. By virtue of their high degree of halogenation, POPs have very low water solubility and high lipid solubility leading to their propensity to pass readily through the phospholipid structure of biological membranes and accumulate in fat deposits (Lukas *et al.,* 2005).

The physical and chemical properties of POPs vary greatly depending on the structure of the particular compound. The compounds vary in levels of persistence, chemical toxicity, movement, transportation, and distribution. Compounds with low persistence and toxicity may not have a huge impact on the environment and human health, but POPs on the other end of

the scale pose a greater risk. Environmental behaviour of chemicals and exposure are strongly related. Therefore, the risk of exposure to a substance will be much lower if the substance is not persistent and the risk, if any, will be localized unless the substance has properties that allow its movement to distant locations (Ritter *et al.,* 2005). These contaminants are continually deposited and re-volatilised and fractionate according to their volatilities. The result is relatively rapid transport and deposition of POPs having intermediate volatility, such as HCB, and slower migration of less volatile substances such as DDT.

An example of the danger posed POPs is the extensive use of organochlorine pesticides and industrial applications of compounds such as PCBs and polybrominated diphenyl ethers (PBDEs) resulted in negative effects on terrestrial and aquatic ecosystems (Sakellarides *et al*., 2006). According to the SCPOPs, a chemical is considered persistent, from an atmospheric point of view, if it has been detected or found at locations distant from potential sources. In general, POPs are chemicals in vapour-phase reaction half-lives greater than two days, and POPs absorbed onto fine particulate matter are capable of undergoing long-range atmospheric transport. Under typical wind speeds, a chemical can travel 150-800 km in two days and result in contamination of remote locations (Scheringer, 2009; Ritter *et al.,* 2005).

POPs have to ability to bio-accumulate. Wahlström (1987) defines bioaccumulation as “the ability of a chemical to accumulate in living tissues to levels higher than those in the surrounding environment, expressed as the quotient between the concentration in the target tissue and the environmental concentration”. POPs work themselves up the food web by accumulating in the fatty part of living organisms and increase in concentration as they move up the food web. The affected organism therefore has a greater concentration of the chemical than that of the surrounding environment. POPs normally have a high lipid affinity and hence accumulate in the fatty tissues of the exposed organism (Wahlström, 1987; Schecter *et al*., 2006). This therefore puts animals high up the food web in greater danger. Because of their lipophilic nature, these pollutants can also accumulate in matrices rich in organic matter, such as some soils, and sediment (Schecter *et al*., 2006).

People are exposed to POPs through diet, occupation, the environment such as air, water, and the soil. Occupational exposure is common in industrial workers, farm workers, and miners. This is because many of these chemicals are used or have been used by industry and agriculture. Stober (2008), reports that according to recent data from different parts of the world, cases of organochlorine pesticide poisoning are still occurring, and are mainly due to aldrin, dieldrin, HCB, and chlordane. Endosulfan has recently been added to the SCPOPs and should also be considered as a cause of many poisonings. Food contamination mainly occurs through environmental pollution of air, water or the soil. Infants are also exposed to POPs through breast milk and this can have adverse impacts on the child's development (Bouwman *et al.,* 2006, 2012). Human exposure to POPs can lead to health problems such as dermal effects, liver, and kidney illnesses, defects of the immune, reproductive, nervous and endocrine system modulation, and even cancer.

2.3 Dichloro-diphenyl-trichlorethane (DDT)

2.3.1 The history of DDT

DDT, was first synthesised in 1873 (Zeidler, 1874), but its useful properties as an insecticide were only noted by Paul Muller in 1939 (Nobelprize.org, 2012a). DDT as was used in Europe to successfully eradicate malaria in the 1940s. In Italy during World War II, 1 300 000 people were treated for typhus. It was also used as a contact insecticide against several arthropod pests because it does not wash off easily with water. DDT was the active ingredient in many aerosol fly sprays. It was incorporated in plastic kitchen shelf linings to keep weevils out of food and applied to home carpets to prevent flea infestation. By the end of World War II, DDT was used extensively for insect vector control and in agriculture as insecticide, and demand increased (Batterman *et al.*, 2008; WHO, 1979).

Controversy came in 1962 when Rachel Carson published the book Silent Spring (Bernes, 1998). The book highlighted the potential environmental implications of the arbitrary spraying of DDT

and other insecticides in the United States and elsewhere. The book condemned the release of large amounts of chemicals into the environment without full knowledge of their effects on ecology or human health. Carson suggested that DDT and other pesticides may cause cancer and that their agricultural use was a threat to wildlife, particularly birds. The book had such a great impact that the Government of Sweden gave the Stockholm University special funds to analyse DDT (Bernes, 1998). Experiments began in 1964 and less than a year after the book was published it led, *inter alia*, to the identification of polychlorinated biphenyls (PCB) as environmental contaminants in 1966 (Jensen, 1966). Silent Spring gave rise to environmental movements and resulted in a large public outcry that eventually led to DDT being banned in the United States in 1972 (Lear, 1998; Bouwman *et al*., 2012). Another reason was probably that the negative effects first reported were on birds as many people were (and remain) interested in birds, and declines in the populations of birds of prey were observed in many places of the world and tied to eggshell thinning after bioaccumulation of DDT (Bernes, 1998; Bernes and Lundgren 2009).

It is estimated that about 1.8 million tonnes of DDT have be produced globally since the 1940s. Huge quantities of DDT were applied directly to the soil for agricultural purposes. DDD was used as a pesticide for a limited period in the past. The general use of DDT against pests like the stalk borer and snout beetles in maize crops, or cutworms and army worms in groundnuts and soya beans, was banned in Zimbabwe in 1982 (Mpofu, 1987). The presence on DDT is the environment is mainly due to its continued use today, and from legacy sources. DDT's major current use is for malaria control as it is used for indoor residual spray (IRS). Despite its ban in agriculture therefore, DDT is currently used in countries like Zimbabwe, Swaziland, Uganda and South Africa for malaria control (Mpofu, 1987; Hecht, 2004; Bouwman *et al*., 2006).

2.3.2 DDT use in Africa

Based on the United Nations Environment Program, the global production of DDT for vector control was estimated to be 6269 metric tonnes in 2005. DDT is produced in China and India, and South Africa and Ethiopia can also formulate DDT from ingredients imported from China. South African further exports DDT to other African countries (Klanova *et al.,* 2009). DDT was the primary tool used in the first global malaria eradication programme during the 1950s and 1960s. The insecticide was used to spray the walls and ceilings of houses and animal sheds with coverage of the dwellings of entire populations (MacDonald, 1956). Malaria has been successfully eliminated from many regions, but remains endemic in large parts of the world (Mendis *et al.,* 2009). Malaria is a serious problem in Africa. Some 90% of the world's malaria infections and deaths occur in sub-Saharan Africa, and the disease now accounts for 30% of African childhood mortality. This has promoted the use of DDT in malaria control. Mozambique, Zambia, Malawi, South Africa, and Zimbabwe are reported to have increased their DDT usage for IRS since 2005 (Klanova *et al.,* 2009; van den Berg, 2009).

For the year 2008, the WHO estimated 243 million cases of malaria and 863 000 deaths, 90% of these deaths occurring in Africa, mostly infants under the age of five (Weir, 2007). DDT used for malaria control was effective in reducing malaria deaths in Europe (Thomas, 1981). The campaign by the WHO to control malaria was successful in Asian countries such as Sri Lanka where it reduced malaria cases from about three million to only 29 in 1964. The program was a huge success initially and was replicated in other countries such as Zimbabwe. The campaign in Sri Lanka was not sustained and malaria returned. DDT, applied as IRS, continuously exposes all members of a household, including infants, children, pregnant mothers, and the elderly. At applications of about 64–128 g/year per dwelling, DDT is continuously bio-available within the homestead because it has to remain effective against mosquitoes (Sereda *et al.,* 2009).

Based on work by De Meillon (1936), IRS with DDT to interrupt malaria transmission was introduced in South Africa in 1946, achieving complete coverage of malaria areas by 1958

(Sharp and le Sueur, 1996). DDT is still used in specific areas of South Africa for IRS to control malaria vectors. For example in the Limpopo Province, DDT spraying has not stopped since 1945 (Bornman *et al.,* 2012). In many parts of the world, campaigns to treat dwellings with DDT and IRS to control malaria transmission remain the only viable option, thereby unintentionally but inevitably also causing exposure to inhabitants (Bouwman and Kylin, 2009). DDT remains effective in a number of countries and continues to be used for malaria control today (van den Berg *et al.,* 2012). Residents could be exposed to residues of DDT through various pathways including indoor air, dust, soil, food, and water (van Dyk *et al*., 2010). Eskenazi *et al.* (2009) provides evidence that DDT and DDE may pose a risk to human health; they also highlight the lack of knowledge about human exposure and health effects in communities where DDT is currently being sprayed for malaria control. WHO recommends DDT as an insecticide of IRS for malaria control (WHO, 2006). The walls are sprayed because most mosquito species rest on the wall before or after feeding (Yakob and Yan 2010). DDT use is recommended in areas of episodic transmissions or seasonal transmissions of malaria. People living in areas where DDT is used for IRS have high levels of the chemical and its breakdown products in their bodies (Wahlström, 1987; Schecter *et al*., 2006). The WHO has reaffirmed its commitment to eventually phasing out DDT, aiming "to achieve a 30% cut in the application of DDT world-wide by 2014 and its total phase-out by the early 2020s if not sooner", while simultaneously combating malaria. The WHO plans to implement alternatives to DDT to achieve this goal (WHO, 2008).

In 1996, South Africa substituted a synthetic pyrethroid insecticide for DDT, under pressure from environmentalists. However, pyrethroid-resistant mosquitoes returned to South Africa. As a result, between 1996 and 2000, the number of malaria cases in South Africa increased by more than 450%, with an increased mortality rate of nearly 1000% (Hecht, 2004) However, DDT has until recently been used as a vector control agent in the tsetse fly control programs in the Kariba Basin of Zimbabwe (Nhachi *et al.,* 2002).

2.3.3 DDT and its metabolites

Note 1: The term DDT is used in a general sense as including DDT, DDE and DDD, as well as the *p,p'*- and *o,p'*- isomers. When all six compounds are implied, the terms DDTs (for general discussion) or ΣDDT (meaning the sum of the concentrations of the DDT compounds measured) are used.

Note 2: In general discussion, when referring to "DDT" or "DDE" or "DDD" without isomer identification, the *p,p*'- isomer is usually implied.

DDT is a very controversial pesticide. In a pure state, DDT is a cream-white to pale-yellow waxy solid with a fruity, almond-like odour. The technical chemical name for the compound is Dichlorodiphenyltrichloroethane. The commercial DDT is a mixture of closely related compounds. Commercial mixtures, often called technical-grade DDT, contain two major isomers, the active ingredient, *p,p´*-DDT, and an unintentional by-product, *o,p´*-DDT which is less toxic. *p,p'*-DDT and its primary breakdown product, dichlorodiphenyldichloroethylene (*p,p'*-DDE) have long half-lives of six years and possibly up to 10 years, respectively (Longnecker 2005; Wolff *et al*. 2000). The different DDT isomers (*p-p'* isomers and *o-p'* isomers), make up 77% and 15% of commercial DDT of the sprayed mixture, respectively. The remainder is DDE and 1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD), both also with *p-p'*- and *o-p'*- isomers. DDD and DDE are major metabolites of DDT.

DDT is insoluble in water, but is soluble in most organic solvents. It is semi-volatile and can therefore move (volatilisation into vapour phase) into the atmosphere. Its presence is ubiquitous in the environment and residues have even been detected in the Arctic and Antarctic. It is lipophilic and partitions readily into the fat of all living organisms. It can bio-accumulate and bio-magnify in food webs. The breakdown products of DDT, DDD and DDE, are also present virtually everywhere in the environment and DDE is more persistent than the parent compound (ATSAR, 2002).

DDE forms from DDT after application, because of environmental and biological processes that degrade the original chemical form. DDT can also be transformed into 1–dichloro-2,2-bis(p-chlorophenyl)ethane (DDD) (WHO, 1979).Under anaerobic conditions, DDT is degraded mainly to DDD due to biotic and abiotic processes. DDD can be further broken down by aerobic bacteria. Soil microorganisms such as the bacteria *Aerobacter aerogenes* and *Escherichia coli* have been reported to degrade DDT to DDD (Chacko *et al.,* 1966). DDT can also break down to DDE under aerobic conditions. DDE is a highly persistent compound and has a high potential to harm the environment (Boul *et al.,* 1997; Kveseth *et al.,* 1979).

DDT, DDE, and DDD may occur in the atmosphere in vapour phase or attached to solids or aerosols in air. The different isomers have different levels of volatility. Spencer and Cliath (1972), report that the vapour pressure of of *o,p'*-DDT is 7.5 times that of *p,p'*-DDT. At 30°C, the atmosphere above a surface deposit of technical grade DDT contains approximately 62% *o,p'*-DDT, 16% *o,p'*-DDE, 14% *p,p'*-DDE, and only 8% *p,p'*-DDT. DDT is hydrophobic and absorbed by soil. These qualities allow DDT, DDE and DDD to last in soils for long periods. Their half-lives in soil range between as little as 22 days to as much as 30 years. The length of time the chemical remains in the soil is dependent on the type of soil, temperature, and moisture. DDT remains in soil for a much shorter time in the tropics where the chemical volatilise faster and where microorganisms degrade it faster. DDT is degraded faster when the soil is flooded or wet than when it is dry. It is lost from the soil through processes such as runoff, volatilisation, photolysis, and aerobic, and anaerobic biodegradation. DDT in soil can also be absorbed by some plants and by the animals or people who eat those crops (ATSDR, 2002).

2.4 Adverse effects of DDT

2.4.1 Impacts on the environment

In aquatic ecosystems, DDT is absorbed quickly by organisms and by soil. A very small quantity of the compound remains in the water. It binds to suspended particles or deposited in the

sediment. Plants and plankton may absorb the compound and it is then taken up by fish as it bio accumulates to levels thousands of times greater than the water, for example in whales (Ewald *et al.*, 1998). This allows DDT to bio-accumulate and magnify up food webs, especially in birds. DDT is acutely toxic to birds at oral LD50 values in the range of 595 mg/kg body mass in quail to 1334 mg/kg in pheasant. However it is best known for its adverse effects on reproduction, especially by DDE, which causes eggshell thinning in birds with associated significant adverse impact on reproductive success (ATSDR, 2002). DDT reduces the reproductive rate of most birds by affecting the eggshells. DDT causes eggshell thinning and hence egg breakage and embryo death through dehydration. Sensitivity to DDT differs amongst birds. According to the Pesticides News 2003, predatory birds are the most sensitive. The bald eagle in the United States almost went extinct because of DDT. Signs of exposure can be noted on albatross in the Midway Islands of the mid-Pacific Ocean. The signs include deformed embryos, eggshell thinning, and a 3% reduction in nest productivity. DDT is known to have caused the decline in populations of the bald eagle and birds of prey (Jones *et al.,* 2008). Jones *et al*. (2008) found levels of DDT in bald eagle adults, chicks, and eggs nearly as high as levels found in bald eagles from the North American Great Lakes. DDT related deformities in birds include clubbed feet and crossed bills.

2.4.2 Impacts on humans

The world is aware of health concerns, especially in developing countries, resulting from exposure to POPs, in particular impacts upon women and, through them, upon future generations (Stockholm Convention on POPs, 2009).

DDT and DDE mainly affect the nervous system when ingested in large amounts. Early signs in of poisoning are tingling on the face, hands and feet. Headaches, dizziness, vomiting, and nausea are also common. The Agency for Toxic Substances and Disease Registry (ATSDR, 2002) report on DDT discuss in detail the acute exposure effects on the nervous system, the effects of chronic exposure to small amounts of DDT being mostly limited to changes in liver enzymes.

People that have been exposed to DDT for a long time had changes in liver enzymes (ATSDR, 2003). Studies on mice by Craig and Ogilvie (1974), exposure to DDT timed to sensitive periods of prenatal nervous system development has been shown to cause behavioural and neuro chemical changes into adulthood.

The International Agency for Research on Cancer (IARC) classified DDT as a possibly cause of cancer in humans. Women seem particularly vulnerable to environmentally-induced carcinogenesis (such as breast cancer) during several critical periods such as *in utero* and before puberty (Eskenazi *et al.,* 2009). Evidence that adult DDT exposure is associated with breast cancer was equivocal until Cohn *et al.* (2007) reported DDT levels in archived serum samples collected between 1959 and 1967 (peak years of DDT use) in the USA from pregnant women participating in the Child Health and Development Studies (CHDS), and found a strong association between early exposure to DDT and cancer development in later life. The length of exposure is also important. In Cohn's studies, for the subset of women born more than 14 years before agricultural use, no association between DDT and breast cancer was found. However, for younger women exposed earlier in life, the third that were exposed most to DDT had a fivefold increase in breast cancer incidence over the least exposed third.

DDT is also known to accumulate in mothers and passed on to infants through breast milk. First-born infants receive much higher levels of DDT in breast milk than their siblings (Bouwman *et al.,* 2006; 2012; Gyalpo *et al.,* 2012; Harris *et al.,* 2001). Gender may also play a role in the differences in pollutant levels between female and male infants (Bouwman *et al*., 2012; Gascon *et al*., 2011; Grimalt *et al.,* 2010). In regions were DDT is sprayed for malaria control, the concentrations of DDT greatly exceed the acceptable levels and standards for cow's milk consumption (Bouwman *et al.,* 2006; 2012). Studies in the 1960s by Longnecker, when DDT was widely used, highlighted that the high concentrations of DDE blood raised the risk of premature birth or low weight. Premature babies account for a large proportions of infant deaths (Young, 2001). DDE is therefore a major concern.

DDT and DDE, like other organochlorines, are known to have xenoestrogenic activity, meaning they are chemically similar enough to estrogens to trigger hormonal responses in animals and humans (Colburn *et al.,* 1996). The endocrine disrupting quality of the chemical has been noted in mice and rats in laboratory experiments. The Environmental Protection Agency (EPA) reports that DDT can have adverse impacts on the reproductive system. Rogan (2005) suggests that exposure to DDT at amounts that could be needed for malaria control have the potential to lead to preterm birth and early weaning. He also states that toxicological evidence indicates signs of endocrine-disruption. In humans, possible disruption has been seen in semen quality, menstruation duration, lactation, and gestational length. In a study by de Jager *et al.* (2006) the percentage of motile sperm was negatively correlated with plasma DDE concentrations, whereas the percentage of sperm with morphologic tail defects and insufficient sperm chromatin condensation was positively correlated with these levels.

DDE is believed to be genotoxic and a cause of endocrine disruption to the infant. A study at the University of California revealed that foetuses exposed to DDT while still in the womb are at risk of developing health problems. In addition, other studies have found that even low levels of DDT or DDE in umbilical cord serum at birth are associated with decreased attention at infancy and decreased cognitive skills at four years of age (Sagiv *et al.,* 2008). There have also been suggestions that DDT may be a cause of cancer. Studies by Rogan *et al.* (2005) indicate that DDT causes cancers of the liver, pancreas, as well as breast cancer.

2.5 Malaria and indoor residual spraying (IRS)

Malaria remains a major concern in poor nations, though it has been successfully contained in large economies. In Africa, malaria is a major life threatening diseases. It is ranked as the second major killer after Human Immunodeficiency Virus/Acquired Immuno Deficiency Syndrome (HIV/AIDS) (Lopez *et al.,* 2001). Malaria has an impact on most African economies in terms of healthcare costs, reduced economic production, and weak foreign investments (Sachs and Malaney, 2002). These impacts of malaria on poor nations are of a serious concern as it

fuels poverty and mortality. Although the SC targeted DDT as one of the POPs for phase-out and eventual elimination, it allowed a provision for DDT's continued indoor use for disease vector control. DDT is highly effective and is a cheap option (WHO, 2003).

Primary prevention of malaria is achieved through two main vector control interventions, indoor (house) IRS and insecticide-treated mosquito nets. IRS has a long and distinguished history in malaria control. WHO has recommended a number of insecticides for IRS. These insecticides include DDT, malathion, fenitrothion, pirimiphos-methyl, bendiocarb propoxur, alpha-cypermethrin, cyfluthrin, deltamethrin, etofenprox, and lambda-cyhalothrin (WHOPES, 2007). The insecticides are applied over a large area to capitalise on the mass effect of the chemical. Through mainly using DDT, IRS has been able to eliminate or greatly reduce malaria cases in Asia, Russia, Europe, and Latin America (Lengeler and Sharp, 2003). WHO has directly been promoting the use of IRS using DDT. It recommends implementation in essentially all epidemiologic settings, including unstable, epidemic-prone areas, stable-endemic areas with seasonal transmission, and stable-hyperendemic areas with seasonal or perennial transmission (WHO, 2006). Mabasa (2004), reports that IRS protects more than 13 million people in Southern Africa from malaria. South Africa, Swaziland, Namibia, Zimbabwe, and Mozambique all use IRS for malaria control.

During IRS, DDT is sprayed on the walls and any other surface where the female *Anopheles* mosquitoes land inside dwellings. The recommended spraying concentrations by WHO is 1-2 g active ingredient per m^2 every six months (WHO, 2006). Once the mosquito has had sufficient contact with the insecticide, it is killed. More importantly, DDT has an excitorepellent effect, deterring entry into and promoting exit from sprayed dwellings (Roberts and Andre, 1994). It is argued that the combined mosquito toxicity and effects as a mosquito-repelling chemical, DDT may maintain its continued efficacy even in areas where mosquitoes are physiologically resistant against it (Roberts and Andre, 1994). A recent study from India assessing the impact of IRS with DDT on malaria transmission corroborated the results of earlier Indian studies

reporting marked reductions in vector densities and malaria incidences although the targeted malaria vector had a reduced susceptibility to DDT (Sharma *et al.,* 2005).

Application of IRS for malaria control in South Africa goes back to 1932 following a trial test that was carried out in 1931 in KwaZulu-Natal using pyrethrum (Park Ross 1936; De Meillon 1936; Mabaso *et al.,* 2004). Pyrethrum was later replaced by DDT in 1946 (Sharp et al., 1988; le Sueur *et al.,* 1993). In 1958, the areas at risk of malaria transmission where all sprayed, and in 1970 a comprehensive malaria control program was launched (Sharp & Le Sueur 1996). The use of DDT was carried out until 1996 and then the country moved to pyrethriods (mainly deltamethrin). The pyrethriods were only applied for four years until high malaria transmission of epidemic proportion was reported due to the emergence of the pyrethroid resistant *An. funestus* (Hargreaves *et al.,* 2000). According to a report by the WHO, IRS is the cornerstone for malaria control programmes in South Africa and southern Africa, with great success. Therefore, to achieve success in malaria control, collaborations with South Africa's neighbouring countries Zimbabwe, Swaziland, Namibia, and Mozambique, in IRS programs is vital.

Of the 45 000 000 residents of South Africa, 4 500 000 are at risk of contracting the disease. Malaria occurs in three provinces of the country, namely, Limpopo, KwaZulu-Natal and Mpumalanga. The transmission of malaria in these provinces is described as unstable and seasonal. In the Limpopo Province, DDT is mainly used because of its effectiveness and low cost but it is does have environmental and health consequences (van Dyk *et al.,* 2010). In South Africa *An. arabiensis* is the only vector. Other *Anopheles* species are also present. These include *An. merus,* but this species has not yet been implicated in transmission despite the fact that it plays a significant role in other countries. *An. funestus* used to be a very important vector before it was eliminated through years of IRS with DDT. This vector re-appeared following the replacement of DDT by pyrethroids in 1996, to which *An. funestus* was resistant (Hargreaves *et al.,* 2000). Because of this, the reintroduction of DDT in 2000 became vital. After reintroducing DDT, the vector disappeared. No record of its presence was made since the reintroduction of

DDT. Later on, DDT resistance was identified in a population of *An. arabiensis* in two localities in KwaZulu-Natal (Hargreaves *et al.,* 2003).

South Africa has different climates ranging from Mediterranean in the south-western corner, to temperate in the interior plateau, and subtropical in the northeast. A small area in the northwest has a desert climate. South Africa is considered a relatively dry area with an average rainfall of 464 mm. however different regions of the country have a huge difference in climate. The Limpopo Province is to the north of the country. It is at the boundary of South Africa and Zimbabwe and parts are a malaria region. The province has a savannah climate with grassland and indigenous trees widely spread. The region experiences dry winters and wet summers. Some rivers and streams dry up. Most of the animals migrate to find food. The region has an average summer temperature of 32^{o}C. Its winter nights are described as very cold. Heavy storms are common and account for most of the annual rainfall in the country (van Zyl 2003).

The Vhembe and Mopani districts in the Limpopo Province have been under IRS for malaria control (Moonasar *et al*., 2011). It is estimated that a population of about 1 800 000 people are at risk to contracting malaria in these areas. The amount of DDT that has been used in the two Limpopo districts between 2005 and 2010 is about 307 781 kg (Moonasar *et al.,* 2011). IRS was done between September and December for all the years sprayed.

The Drakensberg Mountains is the border that separates KwaZulu-Natal from the Mpumalanga Province. Mpumalanga Province is partially in the Highveld and is composed of grasslands. The eastern half of the province is in low subtropical Lowveld. Most of the province is a mountainous area. In the east the Lebombo Mountains form the range at the border with Mozambique. The weather in the province is influenced by the Indian Ocean. The Highveld is comparatively colder because of the differences in altitude; 2300 m compared to 1700 m above sea level in the Lowveld. The province has an average summer temperature of 27°C and a mean annual rainfall of 800 mm. The Ehlanzeni district is a malaria controlled area, with 66 000 people at risk. The area has been sprayed with 140 089 kg of DDT between 2005 and 2010 using

IRS (Moonasar *et al.,* 2011). Spraying was conducted between the months of September and December with percentage coverage above 80% of all the dwellings.

Towards the east of South Africa, there is the province of KwaZulu-Natal. It covers an area of 92 100 km^2. The area has a varied climate due to the diverse, complex topography. The inland regions of the coast are generally colder. The annual rainfall at the coast is 1000 mm and a day time peak temperature of 28°C between January and March, and it drops in winter. At the Drakensberg Mountains, heavy winter snow is often experienced. The hottest place is the Zululand north coast where sugar cane is grown. The area is quite humid (Zyl, 2003). KwaZulu-Natal has not had that much DDT sprayed in the area. Only 31 463 kg of DDT were sprayed till 2010 (Moonasar *et al.,* 2011). The percentage household coverage for DDT spray was above 85% throughout. Spraying was conducted between the months of September and December.

The WHO (2010) reports that about 7000 tonnes of DDT is sprayed in Swaziland for malaria control every year, on a similar schedule as South Africa.

Zimbabwe has an estimated population of 12 000 000 with almost half of the population, 5 500 000, at risk of malaria. Transmission is seasonal and there are risks of an epidemic. Perennial malaria transmission exists in lowland areas, especially in major river basins. *An. arabiensis* is also the main vector of malaria in Zimbabwe. *An. gambiae* has been recorded in recent times from the Zambezi Valley (Masendu *et al.,* 2004). However, there is little information on its role in malaria transmission in this locality. *An. merus* is commonly found in some parts of the country particularly, but, as for South Africa, no information is available on its role in malaria transmission (Masendu *et al.,* 2005). *An. arabiensis* is resistant to dieldrin but susceptible to pyrethroids and DDT.

IRS for malaria control in Zimbabwe began in 1947 and a large-scale spraying program was launched in 1949 using DDT (Alves & Blair, 1953). Indoor residual spraying continued expanding as a strategy of “barrier spraying” to prevent epidemics and the spread of the disease to the

malaria free Highveld parts of the country. Spraying continued until 1970 and then interrupted due to the war of liberation. Spraying was re-introduced in 1981, covering all malaria areas known as a blanket coverage approach. In the 1990s, the blanket coverage system was replaced by selective spraying (Mabaso *et al.,* 2004). This method targeted only areas with a high risk of malaria. However, over the past few years, geographical size and population coverage of the IRS program has been fluctuating due to inconsistent availability of resources.

Indoor residual spraying remains the main method of malaria control in Zimbabwe. The country's management of quality and effectiveness in IRS is highly regarded by the WHO. However, in recent years, resource constraints and scarcity of technical capacity has crippled the IRS program. In 2003, spraying was conducted only in a few localities as a result of inadequate financial resources to secure insecticides. This has impacted on the quality and extent of the intervention. Improvements have however been noted in IRS management and coverage is increasing as more resources are available (WHO, 2006). A strategic plan to eliminate malaria in the southern province of the country was developed in 2006. This is linked to the malaria elimination plan in South Africa and Swaziland, which includes cross-border collaboration in order to curtail the chance of reintroduction of the disease (WHO, 2006). Nevertheless, coverage has increased in the past two years due to support from the Global Fund for HIV/Aids, Tuberculosis and Malaria. In the 2005-2006 malaria season, 44 districts in the eight provinces of Zimbabwe were sprayed and 40% of the 5 500 000 at risk population was protected (Unpublished documents of Ministry of Health, Zimbabwe).

2.6 Passive Air Sampling

With industrialisation and development, environmental pollution has become an increasing concern, particularly of the air, increasing the need to monitor air pollution. Due to financial and other constraints associated with active sampling methods, passive sampling has been encouraged. Passive sampling can be defined as any sampling technique based on free flow of analytes from the environmental medium to a collection medium because of the difference in

chemical potential of the analytes between the two media (Gorecki and Namiesnik, 2002). In simpler terms, it is a sampler that can collect analytes passively without using electric power. The process is dependent on the diffusion of the sampled compound to collection surfaces or sorbents. The pre-determined effective flow is slightly affected by temperature, but unaffected by pressure or altitude. Flow of the analytes from the atmosphere goes on until a level of equilibrium is reached or until sampling stopped.

Measuring pesticides in the atmosphere allows for a better understanding of their sources, fate, and LRT (Pozo *et al.,* 2006; 2009). A number of studies to determine pesticide concentrations in air have been carried out using passive air samplers. Passive air sampling has been successfully carried out by The Global Atmospheric Passive Sampling (GAPS) study. GAPS demonstrated that it is feasible to used passive samplers to assess the spatial distribution of persistent organic pollutants on a worldwide basis. The GAPS network included more than 40 sites on seven continents, mainly at background locations, with some representation of urban and agricultural areas (Shunthirasingham *et al.,* 2010; Pozo *et al.,* 2006). In South Africa, Batterman *et al.* (2008) used passive air sampling to monitor organochlorine pesticides in ambient air in Durban. Passive air sampling by GAPS showed that DDT and its metabolites and chordane-related compounds tend to be more prevalent in developing countries (Shunthirasingham *et al.,* 2010)

2.6.1 Merits and demerits of passive air sampling

Passive air sampling is fast becoming popular as it has a number of merits. The process is generally cheaper than active sampling as no energy source is required. In addition, many passive samplers are capable of providing comparable performances to active samplers in terms of sensitivity and reproducibility (Fan, 2011). An advantage of using passive air samplers is that they can be used in any area, even in remote places with no power (Shoeib and Harner, 2002). Maintenance is generally easy since the sampler does not really need any monitoring

after deployment. They can also be deployed for a long period as for example by the Monitoring Network, Africa (MONET), which deployed samplers on a monthly basis in 2008.

Passive air samplers however have their problems. The samplers may require long exposure times, between 8 hours to one month. This implies a long study period. They measure average concentrations and hence emission events can be missed. The method also generates few data points and the sampling volume is not known (Shoeib and Harner, 2002). One of the goals of the SCPOPs is to monitor POPs movement, transportation, and distribution. The sampling of air to study LRT of POPs is of vital importance.

2.6.2 Polyurethane foam (PUF) passive air samplers

There are different types of passive air samplers, based on the intended chemicals to be sampled and the length of deployment. Polyurethane foam (PUF) is used in passive air sampling of POPs. This is because they have a high retention capacity for these types of compounds. PUFs are easy to handle and can be deployed for long periods. The large deployment time, ranging from a day to months, make it possible for them to collect quantifiable levels of a wide range of compounds in large-scale ambient sampling campaigns. It also makes it possible to deploy them in remote areas. For outdoor use, the PUFs is covered by two stainless steel bowls, which serve to protect the sampling disk from light and rain and any other harsh weather conditions (Figure 2). A metal rod that runs through both bowls is held by metal clamps that supports the disk.

To calculate and accurately estimate of chemical concentration, uptake rate, and data on calibration are required (Chaemfa *et al.,* 2008). The sampling rate is derived from carrying out calibration experiments using gas generation systems. It can also be determined by a field-based sampling next to a high volume air sampler. The sampling rate is an important parameter in POPs. In this study, only the amounts of DDT on the filter were used. The principles of passive air sampling are explained in detail by Shoieib and Harner (2002). The uptake of the sampling

air is determined by what is known as the air mass transfer coefficient. It is wind dependant. PUFs trap DDT as both the vapour phase and as particulates. According to Klanova *et al.* (2008) the particle-phase sampling rate is approximately 10% of the vapour phase.

Passive air samplers have been used in monitoring programs from air quality. Monitoring has been viewed as a very important tool for the evaluation of persistence and LRT of POPs. Monitoring is defined as the long-term and standardised measurement, observation, evaluation, and reporting of physical, chemical, or biological parameters in order to define status, trends, and mass-flow (MONET, 2008). Monitoring programs have played a key role in the discovery, and understanding of the behaviour of POPs. Systematic air monitoring studies, such as by RECETOX, have shown that a range of chemicals are subject to long-range transport, while monitoring of biological samples has demonstrated a range of compounds that are persistent and prone to bioaccumulation. In addition to identifying chemicals of concern, multi-media monitoring programs also have demonstrated the effectiveness of various emission reductions, phase outs, and elimination measures in reducing the environmental levels of pollutants (RECETOX, 2009). The ability of POPs to travel long distances is part of the explanation for why countries that banned the use of specific POPs are no longer experiencing a further decline in their concentrations; the wind may carry chemicals into the country from other regions that still use them. The monitoring of these compounds in air becomes critical to determine the effectiveness of their ban.

Passive air sampling has been used in a number of studies throughout the world. Article 16 of the SCPOPs highlights the importance of monitoring the concentrations POPs in the environment. Its intent is to evaluate the effectiveness of the Convention through a global monitoring program. Such programs for air monitoring have been carried out, for example the MONET Africa program, carried out in 2008, in which 15 African countries participated by providing and servicing sites. Passive air sampling was carried out using PUFs. PUFs were used as long term sites were required for the program and because they are cheap. This study considered the South African participation to MONET-Africa.

Background data from such monitoring programs is important as it provides a backbone for further research and innovations. The SCPOPs, of which South Africa is a Party, carries a number of obligations and expectations. Based on the obligation to develop a NIP, the State is obliged to reduce or terminate all sources of POPs within the SC provisions. This therefore implies that a state should know the environmental levels of these POPs whereby priority sources and hotspots can be targeted for interventions. Since much of this information is either old or completely lacking, research needs to be undertaken (Ross, 2004). The use of passive sampling methods has made it possible for such programs to be carried out on such a large scale.

2.7 HYSPLIT trajectories

The HYSPLIT has a number of advantages and restrictions. The model is a complete system for computing simple air parcel trajectories to more complex dispersion and deposition simulations. The model is able to simplify complex air data and produce simple output to be interpreted. The advantage of the software is that computation is relatively simple and using it does not require intensive training. The simplification of the products allows it to be used by a various organisations or individuals across different displines. Another advantage of using HYSPLIT is that it is readily available on the internet and therefore accessible. The software is suitable for small number of sources or receptors and therefore suitable for this particular study. HYSPLIT allows the user to pinpoint source areas using different tools in the software. Through the dispersion model and given the necessary data sets, HYSPLIT is able to determine pollutant spread. It also allows the user to set up his/her own parameter to use in prediction studies. HYSPLIT also makes it easy to determine trans-boundary transport through air.

The use of HYSPLIT however does have restrictions. The model is highly depended on meteorological data, such as temperature, wind speed and wind directions, and therefore it may not be useful in areas where there is a gap in this data. The online version of the software

has a limited run time and therefore cannot produce results for a large run-time (450 hours). The software cannot is unable to process multiple pollutant transport runs at a time. Each run has to be done one by one. Another restriction is that if many sources or receptors are considered, computational effort approaches are not possible. This limits the number of source and receptor areas that can be studied at a time.

Air movement can be predicted or backtracked to determine direction of the origin it comes from. Pollutants can be carried by winds over a long distance and reach remote areas. The movement of air can be tracked by studying air mass trajectories. The trajectories show the movement of air over a selected period (Saso, 2011). There are two types of trajectories, forward trajectories and backward trajectories. Forward trajectories are able to show the movement of an air mass or pollutant from a particular point of origin. Forward trajectories are typically used in connection with the calculation of pollutant distribution from accidental releases where the emission source is single and strong. Backward trajectories show the pathway of air that reaches a particular site. The backward trajectories are typically used for modelling air pollution from multiple distributed emission sources (Saso, 2011). The procedure for calculating trajectories is to choose a receiving or starting point and then calculate back or forward in time according to the direction and speed of the wind. The software developed by the Air Resources Laboratory (ARL) HYSPLIT, is used to run the trajectories under the National Oceanic Atmospheric Administration (NOAA). The model is able to show air mass movements as trajectory and associated height. The software indicates the height of the air mass at every particular point of the trajectory. In this study, the height was not considered as the focus of the research was more included to the horizontal movement of the air masses and surface areas covered, as deposition via rain and dust is not covered by HYSPLIT.

2.8 Monitoring Network in Africa (MONET-Africa)

There is a data gap on ambient air pollution in Africa. There was also no regular, uniform, or consistent monitoring system. The Monitoring Network in Africa (MONET-Africa) project by the

United Nations Environmental Program (UNEP) was conducted throughout Africa during 2008. Project design was based on the experience from pilot studies done by RECETOX in the Czech Republic and western Balkans in 2003. The MONET-CZ was a monitoring programme that used passive air sampling to sample for POPs in air within the Czech Republic (Klanova *et al.,* 2009). The use of passive air sampling using PUFs is ideal for Africa, as it is generally cheap and requires very little maintenance compared to other methods. The sampling survey of MONET-Africa was done at 26 sites across Africa with the goal to establish baseline information on POPs contamination in ambient air (Klanova *et al.,* 2009). Countries that took part were Kenya, DRC, Ethiopia, Ghana, Mali, Mauritius, Nigeria, Senegal, South Africa, Sudan, Togo and Zambia.

LRT of POPs may affect the African continent, making it an important issue to understand. Knowledge of LRT of POPs in Africa would help identify and assess areas at risk, and knowledge about source areas would help in developing better management methods. MONET-Africa's goal was to establish a long-term monitoring system of background sites, to detect and evaluate integrated trends and LRT of airborne POPs. This would help in determining the extent of pollution and inform about potential effects of POPs in Africa.

2.9 Aims

The aims of this study:

- Passive sampling and analysis of airborne DDT at three sites; Vanderbijlpark, Barberspan Nature Reserve, and Molopo Nature Reserve
- Determine the distribution of DDT by air movements from DDT-sprayed areas on a monthly basis from 54 sites using HYSPLIT.
- Compare model data with passive air sampling data
- Determine the populations and ecosystems that may be exposed to airborne DDT.
- Establish the spraying period with the longest and shortest air transportation distances.
- Determine any trans-boundary LRT via air.
- Identify potential airborne DDT sampling sites as a result of long range transport of DDT.

CHAPTER 3: METHODS AND MATERIALS

This chapter is divided into two sections. Section One focuses on passive air sampling of DDT and metabolites in ambient air at three sites in South Africa. Section Two looks at the generation of backward and forward trajectories to determine the potential movement of DDT from malaria sprayed areas, and towards the sampling sites.

Section One

3.1. Passive sampling sites

South Africa, through the NWU, operated three sampling sites. The sites included a background site, an agricultural site, and an industrial site. The sites spanned a 520 km east-west transect from Vanderbijlpark (urban industrial), Barberspan Nature Reserve (rural agricultural), to Molopo Nature Reserve (nature reserve). Considerations for sighting the stations apart from general location were accessibility, safety, and low risk of theft.

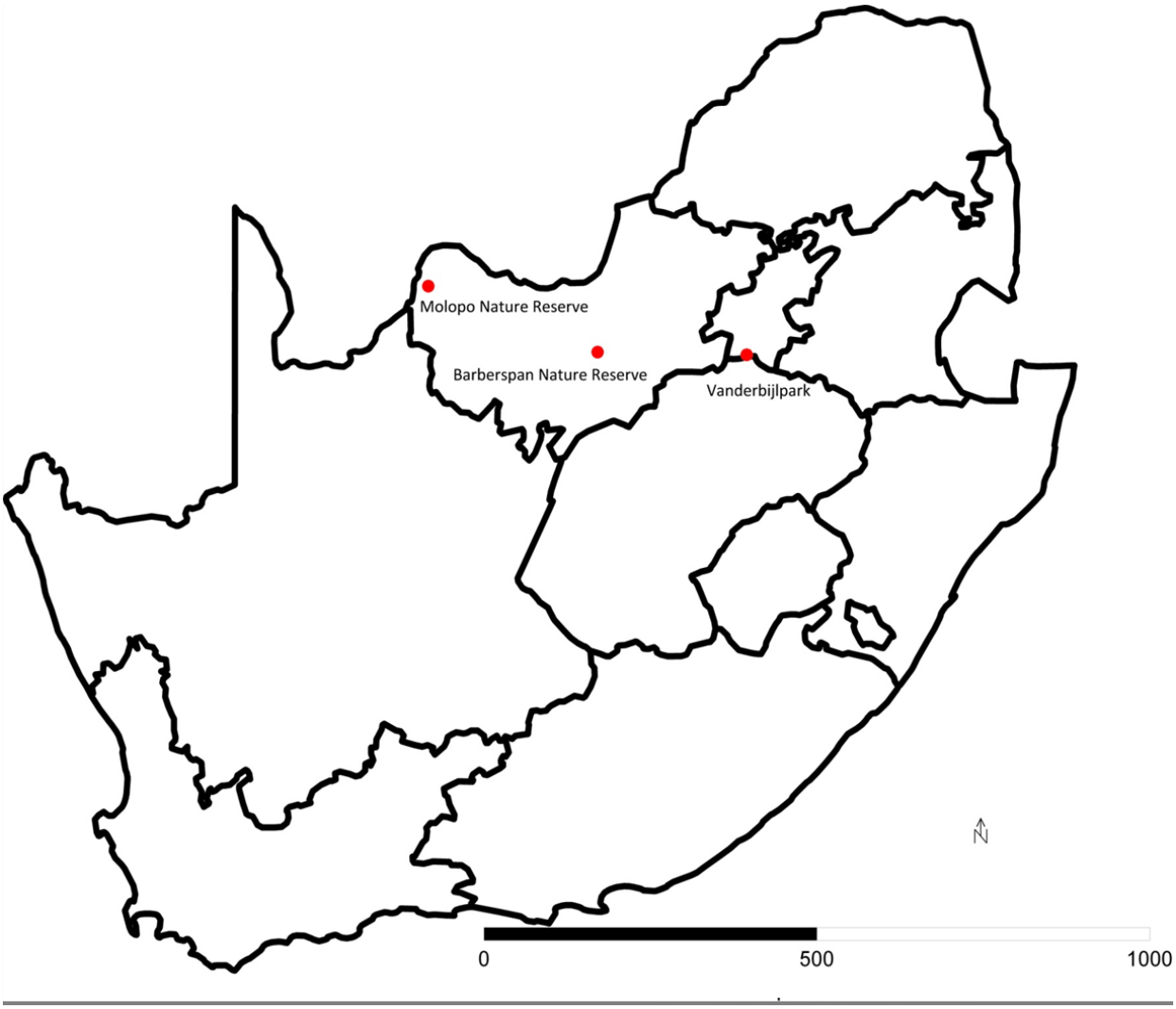

Figure 1: Passive air sampling sites on a country basis.

3.1.1 Vanderbijlpark

Vanderbijlpark (26.7S, 27.8E) is highly industrial with a population of about 220 000. It lies next to the Vaal River and is in the south of the Gauteng Province. The major activities in the area include an iron and steel manufacturing plant, petrochemical plant, power plant, and a coal mine. A major steel company, Vanderbijlpark Steel is located in the town. The town is also surrounded by other industrial towns such as Vereeniging and Sasolburg. Major organisations such as VECOR, the largest comprehensive heavy engineering works in the Southern

Hemisphere was located in Vanderbijlpark. The town also houses Cape Gate (Pty) Ltd, a major market share holder in the wire and cable industry. The first steel factories in Vanderbijlpark began operating in 1947. Since then, it has grown to become an industrial giant in South Africa. 60% of the town's residences are employed by the town's factories. The town experiences hot and wet summers from November to March and a cold dry winter through June to August. Average summer temperature is 27^0C and in winter it is as low as 4^0C. The town is also known for its recreational facilities, mostly water sports. Activities like cruises on the river are popular.

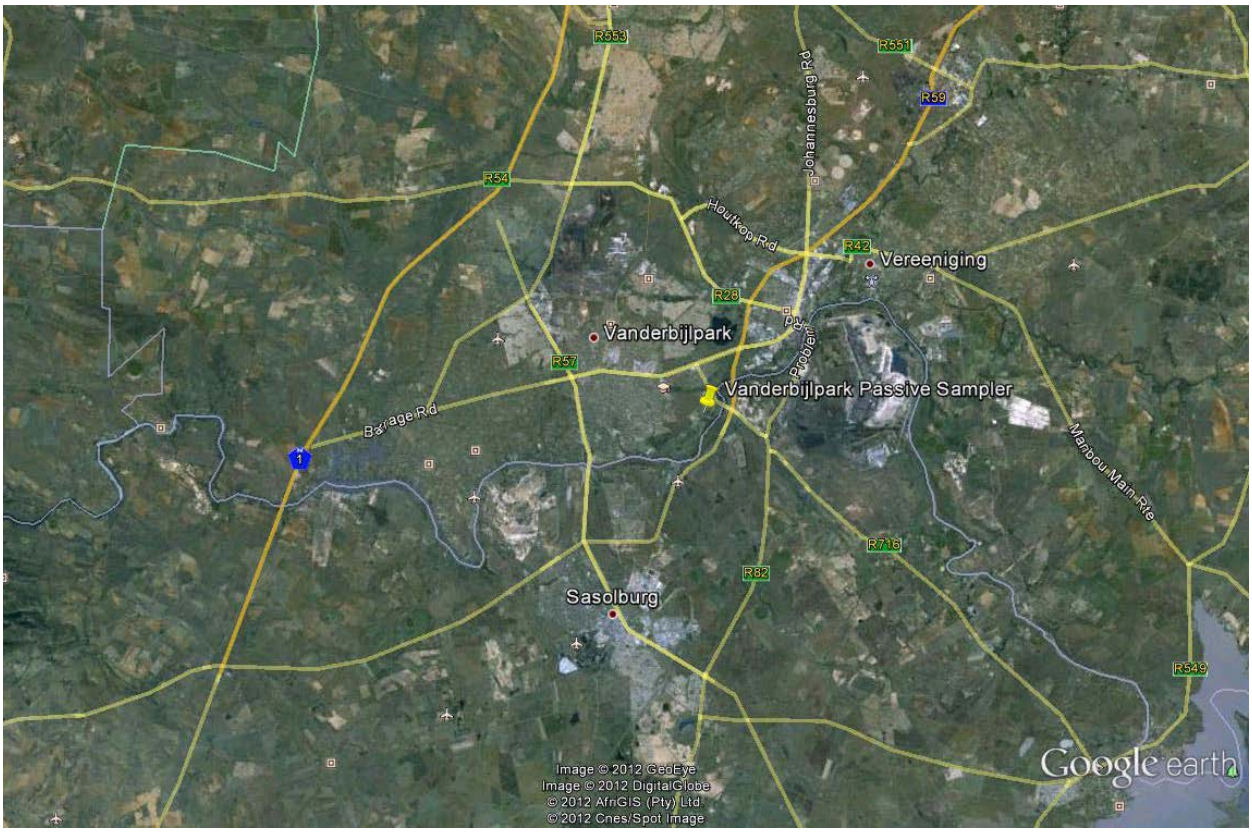

Figure 2: Map of Vanderbijlpark. The location of the sampling station is located by a yellow marker.

Figure 3: Vanderbijlpark passive PUF sampling station.

3.1.2 Barberspan Nature Reserve

Barberspan Nature Reserve (26.6S, 25.5E) was the second site. It is located in the North West Province, 17 km north-east of Delareyville at an altitude of between 1345 m and 1360 m above mean sea level. The sanctuary has a 3118 ha wetland. The vegetation is mainly flat grassy plains and a few scattered trees. The reserve qualified as a wetland of international importance according to the Ramsar Convention, and was listed in 1975. 2000 ha of the sanctuary is water. Barberspan is the largest in a series of pans in the fossil bed of the Harts River (Barberspan, South Africa, 2009). The alkaline pan is connected to the Harts River being the largest of a number of depressions along the channel. The area has different wetland types including permanent rivers, streams, and creek, permanent fresh water pools, and perennial freshwater and alkaline pans (Acocks, 1953). The Harts River pushes water into Barberspan during the

wetter summers, which is enough to last throughout the dry winters. The water channel is of ecological importance since the pan now became a large perennial water body in an area of otherwise seasonal pans and vleis. A large number of birds, especially water fowl, now rely on the pan for feeding, drinking, roosting, moulting and breeding (Barberspan Reserve, 2003). The area is semi-arid and records an average temperature of 18^{o}C and a mean temperature range between 9^{o}C to 27^{o}C. The area's catchments receive summer rainfall during the hot summer months. The winters are however cool, dry, and windy. There is very occasional snow in the south and eastern areas of the Province. Wind direction in the North West Province is predominant from a northerly direction. There is a trend for the windy conditions between August and November (Milstein, 1975). The pan is protected as a Provincial Nature Reserve proclaimed in 1954. The nearest town to the reserve is 16 km northeast and is known as Delareyville. The area surrounding the sanctuary is predominately agricultural land. The main activates or form of agriculture is cattle ranching and maize farming.

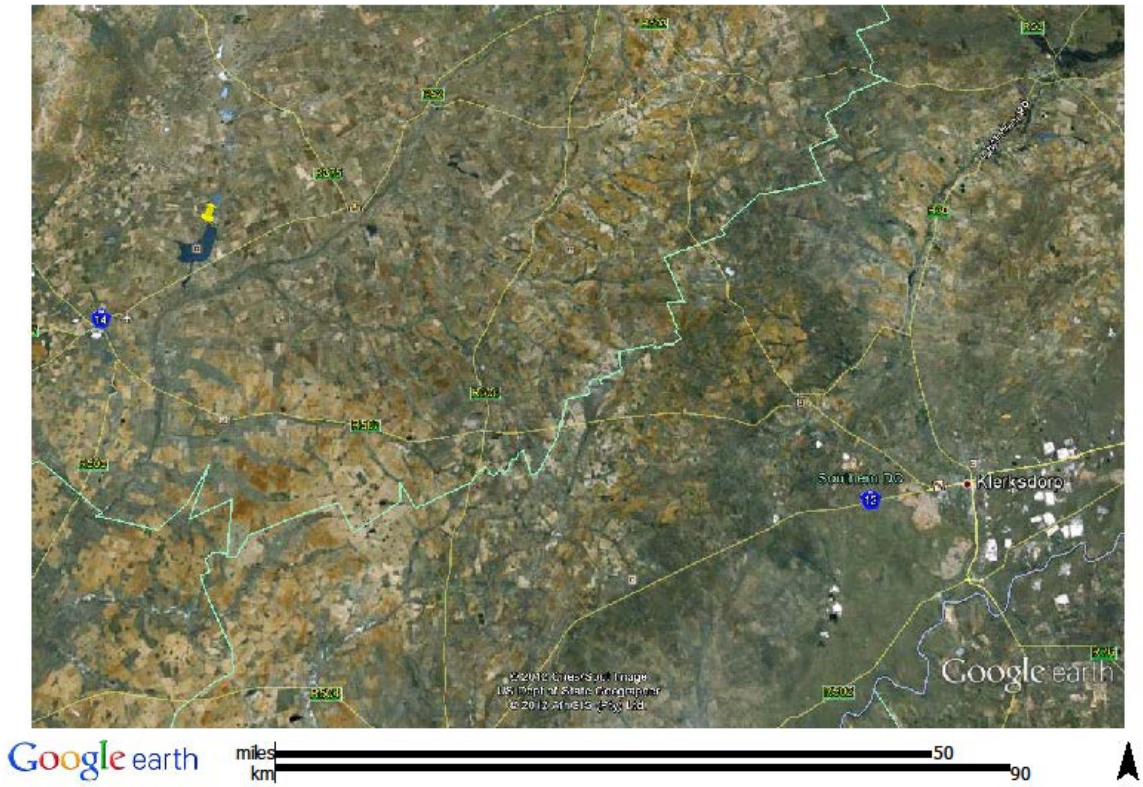

Figure 4: Map of Barberspan Nature Reserve. The location of the sampling station is indicated by the yellow marker.

Figure 5: Barberspan passive sampling station.

3.1.3 Molopo Nature Reserve

Molopo Nature Reserve (25.8S, 22.9E) was chosen as a remote background site. The reserve is located on 24 000 ha of conserved land. It lies on the Botswana border in the far west of the North West Province, 250 km north of Vryburg, and 7 km west of the village of Vostershoop. The vegetation is Kalahari grassland. The area is arid and receives very little rain. A large number of bird species and wildlife are found at the reserve, including eland, blue wildebeest, gemsbok, red hartebeest, kudu, zebra impala waterbuck, and springbok. The reserve has recorded over 129 species of birds and this includes breeding pairs of bateleur, tawny eagle and martial eagle. White-backed vultures and lappet faced vultures are also common. The reserve's climate is greatly influenced by the Kalahari Desert. The temperatures can rise up to 40^{o}C.

Rainfall is experienced during the hot summer. This is between December and April. The rainfall is rarely more than 100 mm/annum. The area may experience heavy rains for a short period, changing the vegetation to a much greener site. The winters are between June and August. They generally have dry air with an average temperature of 25^{o}C during the day. The evenings however get very cold.

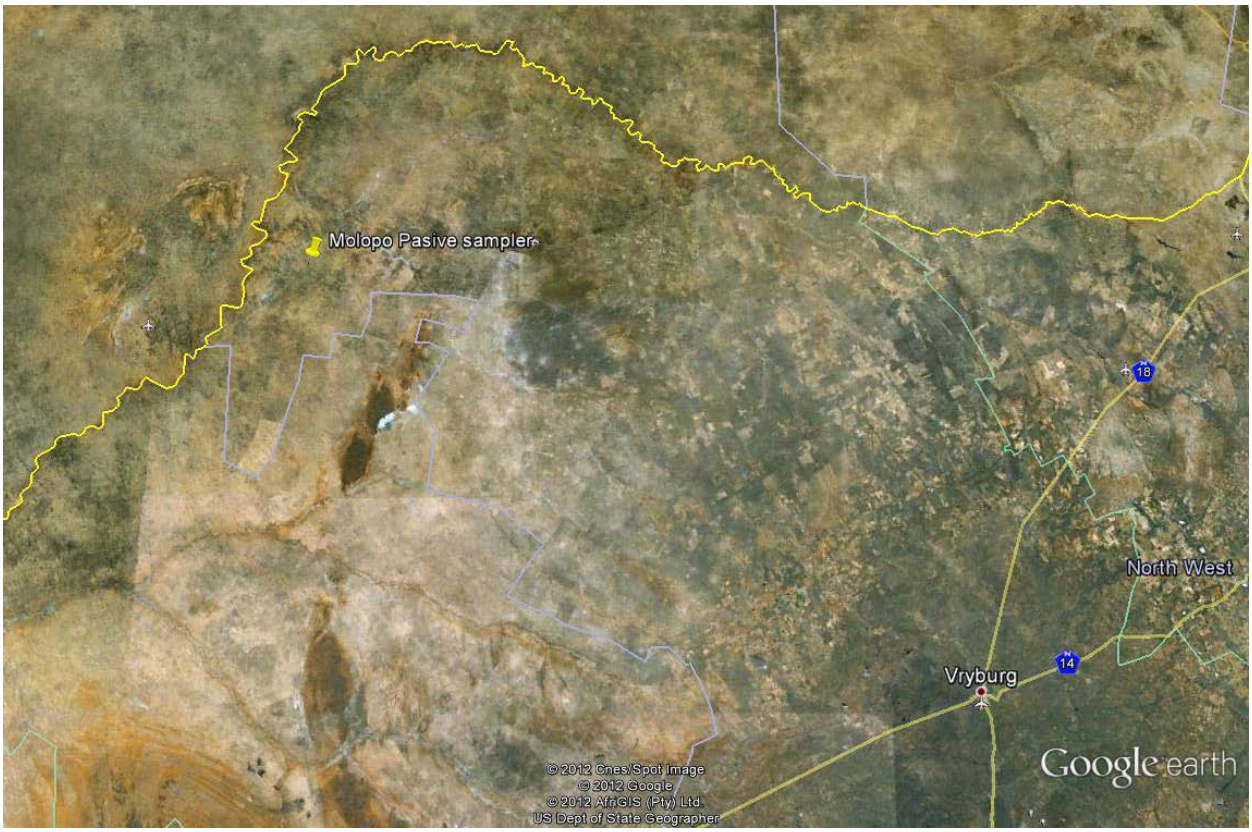

Figure 6: Map of Molopo Nature Reserve. The location of the sampling station is indicated by the yellow marker.

Figure 7: Molopo passive sampling station.

These three sites were used as sites for passive air sampling. Passive air samples were collected at the sites for a year at monthly intervals.

3.2 Passive air sampling

3.2.1 Principles of passive air sampling

Passive air sampling is viewed as a cheaper method for comparative studies on various sites or for verification of information obtained from active samplers. Passive air sampling implies that the air is not forced through sorbent, but instead is allowed to passively flow through the sorbent. A basic characteristic of passive samplers is a low sensitivity to accidental short-time changes in the concentration of pollutants. They only provide information on the integrated

long-term contamination of the studied environmental compartment, in this case air. The air is allowed to move freely around the filter, membrane or other medium known as the sorbent. This captures the pollutant during the period of sampling. However, the association between the amounts of POPs captured on the polyurethane filter (PUF) and their concentrations in the sampled air is yet to be fully explained mathematically. Multiple compounds can be extracted and measured from each filter, but only one data point per compound per filter is obtained.

3.2.2 Filters

Passive air sampling filters were made of white non-coloured polyurethane with a density of 0.030 g/cm^3. The type of polyurethane is known as N3038 and is produced by Gumotex Breclav, Czech Republic. All PUFs were Soxhlet extracted with acetone for eight hours and then a further eight hours in dichloromethane. The filter was dried, wrapped individually in clean foil, and then individually placed in a plastic 'Ziplock' bag.

3.3.1 Sampling procedure

Samples were collected from three sites. The passive air sampling device consists of two stainless steel bowls attached to the common axle and formed a protective chamber for the PUF. The chambers were washed and rinsed with acetone before installation. The sampler was hanging vertically at a height of 1.0-2.0 m above the ground. Placement of the sampler is best when the terrain was open without any significant obstacles for free airflow. Figures 4, 5, and 6 show the deployment situation for each sampler. The sites were all reasonably well secured against theft and tampering.

The average air sampling rate is estimated at between 3.5 and 7 m^3/day (RECETOX, 2006). This translates into between 100-200 m^3 of air sampled over the four-week sampling period. Because this is a passive sampling method, the air concentrations cannot be calculated. Instead, the amounts per PUF were used. The assumption here is that the between-month and between-site variation is less than the variations in air concentrations, and therefore comparable within and between sites. When collecting samples, gloves were used to handle

PUFs during collection. On collection, the exposed filters were wrapped in two aluminium foils, labelled, and kept at a temperature of 5°C during transportation. The samples were stored at -18°C before analysis. Samples were collected over a period of one year at one-month intervals from January 2008 to December 2008. A single filter was collected from each sampling site after each sampling interval.

3.3.2 Sample Analysis

Extractions and analyses were done at RECETOX, Czech Republic. All standards (calibration sets, natives, and mass labelled compounds) were purchased from Wellington Laboratories (Canada). PUFs were extracted using the automated Buchi System B-811 (Büchi, Switzerland) warm Soxhlet extractor (60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing) with toluene. The concentrated extracts were cleaned-up on a H_2SO_4 modified (30% w/w) silica column, eluted with 40 ml DCM/*n*-hexane mixture (1:1). Fractionation was achieved in a micro column (6 mm i.d.) containing from bottom to top: 50 mg silica, 70 mg charcoal/silica (1:40) and 50 mg of silica. The column was prewashed with 5 ml of toluene, followed by 5 ml of dichloromethane/cyclohexane mixture (30%). The sample was added on top and eluted with 9 ml dichloromethane/cyclohexane mixture (30%).

HRGC/HRMS instrumental analysis was performed on a 7890A gas-chromatograph (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 um DB5-MS column (Agilent J&W, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at a resolution of >10 000.

3.3.3 Quality assurance and quality control

Recoveries were determined for all samples by spiking with the surrogate standards prior to extraction. For BDEs, recoveries ranged between 60-110%. All data were recovery corrected. Laboratory blanks were under the quantification limits for all compounds. Field blanks consisted of pre-extracted PUF disks and were taken once at each sampling site for the whole campaign. These were extracted and analyzed in the same way as the samples, and the levels in

field blanks never exceeded 3% of the quantities detected, indicating minimal contamination during the transport, storage and analysis.

3.2 Section two

3.2.1 Starting Points for forward trajectories

Tables 1 and 2 show the starting points for the forward trajectories from 54 sites. Each point is coded and the coordinates given. The code is based on the grid of the grid map generated with Map Viewer.

Table 1: Coordinates for the 1st 27 starting points.

Site code	X-coordinates	Y-coordinates
A5	29.4	-22.37
A6	28.89	-22.37
A7	29.95	-22.37
A8	30.47	-22.37
A9	31.01	-22.37
B7	29.95	-22.9
B8	30.47	-22.9
B9	31.01	-22.9
B10	31.55	-22.9
C7	29.95	-23.49
C8	30.47	-23.49
C9	31.01	-23.49
C10	31.55	-23.49
D8	30.47	-24.04
D9	31.01	-24.04
D10	31.55	-24.04
E8	30.47	-24.58
E9	31.01	-24.58
E10	31.55	-24.58
E11	31.92	-24.58
F8	30.47	-25.11
F9	31.01	-25.11
F10	31.55	-25.11
F11	31.92	-25.11
G8	30.47	-25.68
G9	31.01	-25.68
G10	31.55	-25.68

Table 2: Coordinates for the 2nd 27 starting points.

Site code	X-coordinates	Y-coordinates
G11	31.92	-25.68
H8	30.47	-26.2
H9	31.01	-26.2
H10	31.55	-26.2
H11	32.07	-26.2
J8	30.47	-26.7
J9	31.01	-26.7
J10	31.55	-26.7
J11	32.1	-26.7
J12	32.62	-26.7
L8	30.47	-27.25
L9	31.01	-27.25
L10	31.55	-27.25
L11	32.1	-27.25
L12	32.05	-27.25
M8	30.47	-27.77
M9	31.01	-27.77
M10	31.55	-27.77
M11	32.05	-27.77
M12	32.46	-27.77
N9	31.01	-28.32
N10	31.55	-28.32
N11	32.05	-28.32
N12	32.41	-28.32
P9	31.01	-28.89
P10	31.55	-28.89
P11	32	-28.89

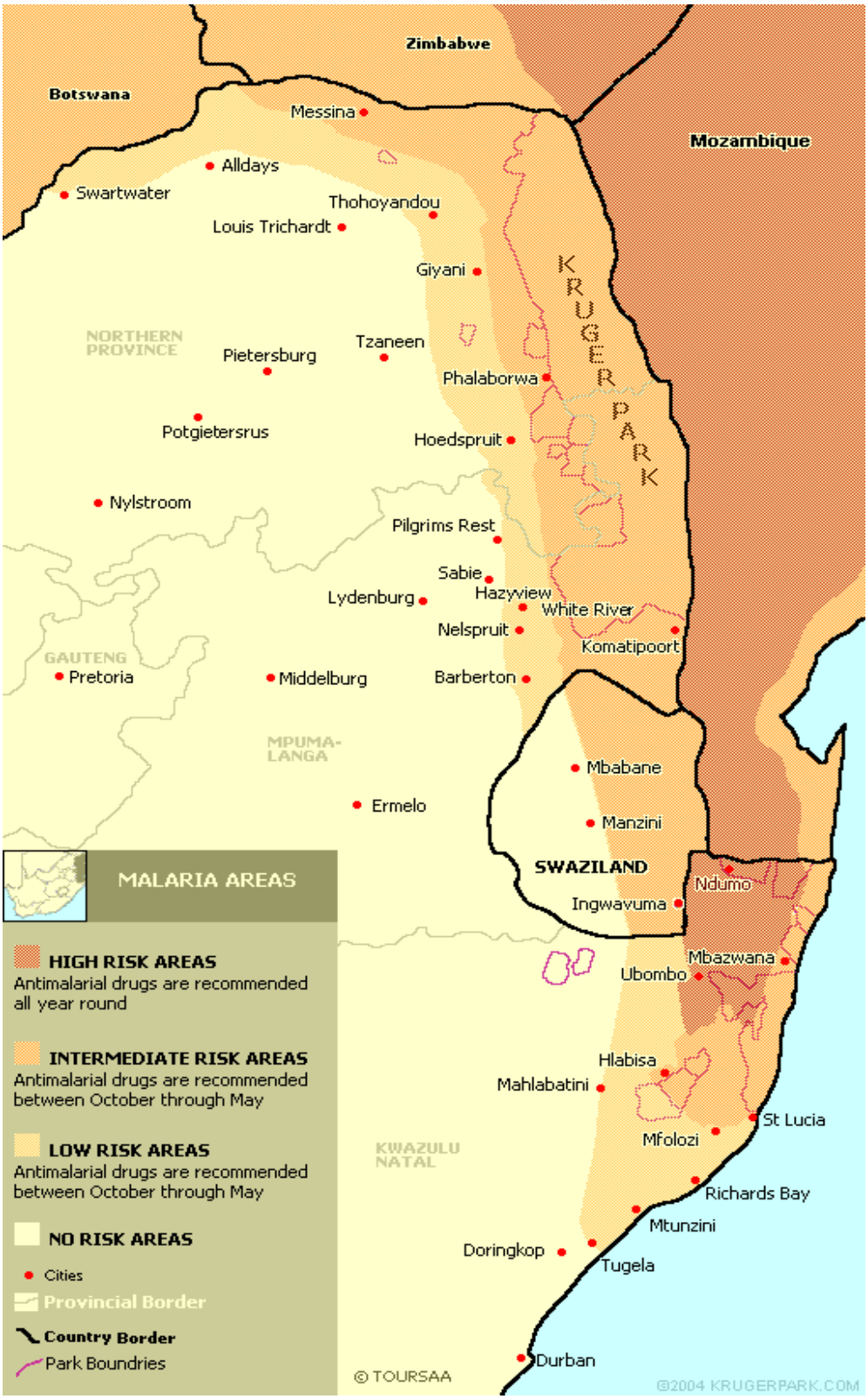

Figure 8a: Malaria risk areas in South Africa, Swaziland, and Mozambique (Moonasar *et al*., 2011).

Figure 8a shows the areas at risk of malaria in South Africa. The degree of malaria risk is shown by the different shades of orange. The selection of the starting points for forward trajectories included sprayed and potentially sprayed areas. Swaziland was also included as DDT is also being used here for IRS. However, Mozambique has been excluded, as IRS is only sporadic and mostly not using DDT. The starting points are indicated in Figure 8b. 54 points were used as starting points on a 60 X 60 km grid basis, as smaller distances would not add more information to the trajectories. To maintain the integrity of the grid and to cover the peripheral areas where DDT may be applied, some of the points fell in Mozambique (J11 and J12) but considered part of the SA and Swaziland contiguous area of IRS. The map was developed using MapViewer 7 (www.goldensoftware.com).

Limpopo Province had 16 starting points with five close to the Zimbabwean boarder. Most points are to the east of the province, with some points close to Mozambique. Some points were inside the Kruger National Park where malaria control is also done. Mpumalanga Province had 17 points with three on the border with Limpopo. Like Limpopo Province, the points were mostly to the east. Six starting points fell within Swaziland. KwaZulu-Natal provided 15 of the starting points.

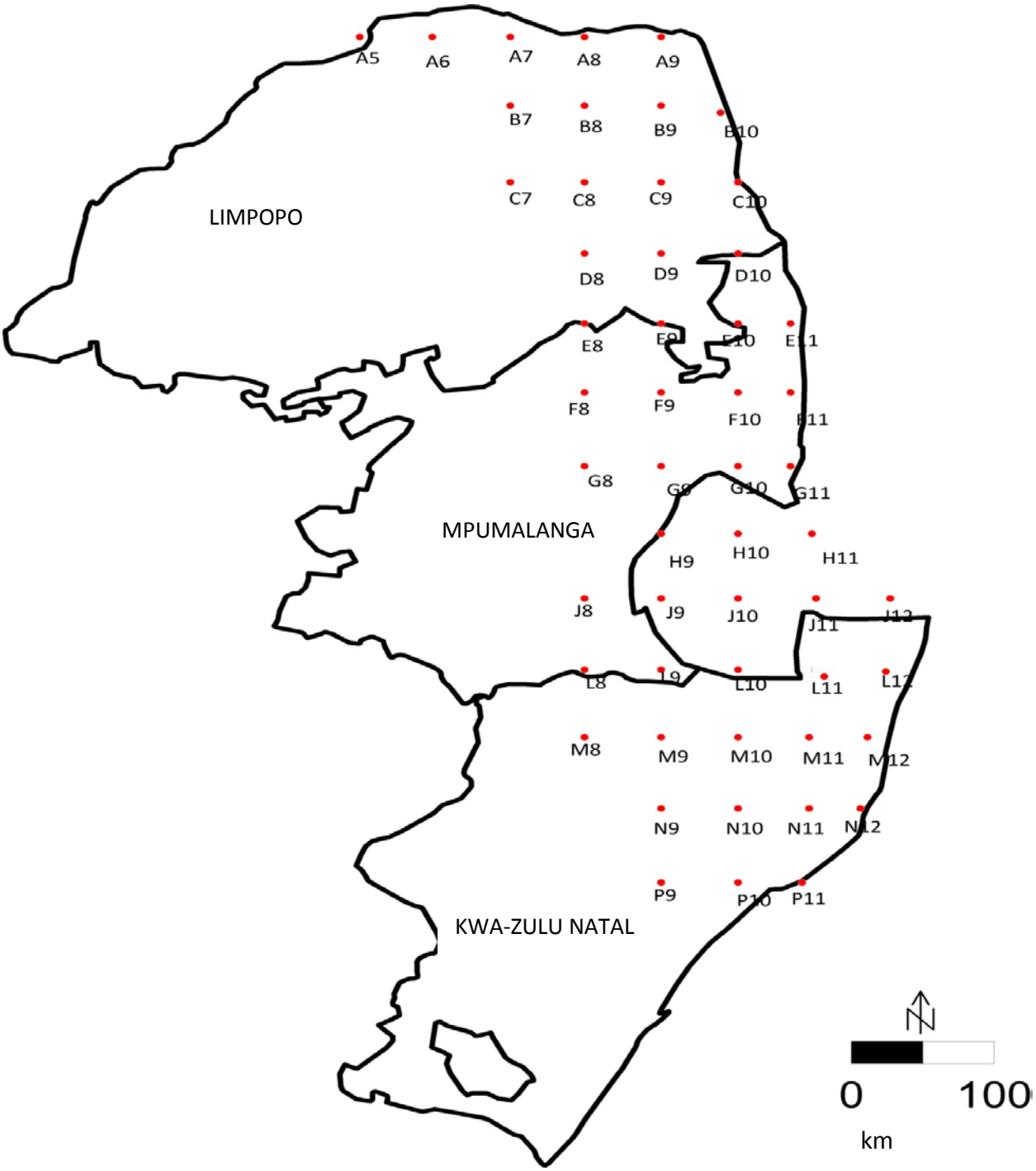

Figure 8b: Map of the starting points for forward trajectories.

3.2.2 How HYSPLIT Works

The unintentional or planned discharge of chemical, biological or nuclear agents can have considerable adverse health, safety, security, economic, and ecological results. The Air Resources Laboratory's (ARL's) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model is a tool to assist in explaining how, when, and where chemicals and materials are atmospherically transported, dispersed, and deposited. Such knowledge is critical for responding appropriately and preventing or predicting disasters and threats. The technology has been use in predictions of volcanic ash plume locations allowing aircraft to avoid dangerous areas. Understanding the sources of hazardous air pollutants allows air quality managers to develop targeted policies and plans to mitigate the problem.

The HYSPLIT model is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations. The model was first developed as a result of a joint effort between National Oceanic and Atmospheric Administration (NOAA) and Australia's Bureau of Meteorology. Over the years, the model has been improved with enhancements provided by a number of different contributors. Some newer features include improved advection algorithms, updated stability and dispersion equations, continued improvements to the graphical user interface, and the option to include modules for chemical transformations. Without the additional dispersion modules, HYSPLIT computes the advection of a single pollutant particle, or simply its trajectory, as was done here.

3.2.3 Generation of trajectory maps

Forward and backward trajectory maps were generated using the HYSPLIT model of the American NOAA. Coordinates for starting points, the run time, direction of trajectory and height were fed in the HYSPLIT data sheet (Figure 9). The Global Data Assimilation System (GDAS) archive of meteorological data was used. The trajectories were all generated at a starting height of 10 m. The run time for each trajectory was 168 hours (7 days). Trajectories were produced on a monthly basis for the whole year (2008) and for each sprayed DDT area. The text files for each week were then converted into excel format. Using MapViewer7, point coordinates were

plotted for every hour (dots) of the one week run time. For forward trajectories, the plotted points were overlain to make one map for all 54 sites and for every month. Plotted points for backward trajectories were plotted for the three sites together, on a monthly basis, for 2008.

HYSPLIT Trajectory Model

Model Run Details

Meteorology: GDAS1

Source Location: Lat: -24.58 Lon: 22.37

The GDAS1 archive file contains data beginning at 0000 UTC 10/22/08.

Change Default Model Parameters and Display Options

Trajectory direction:	Help	● Forward			
		● Backward			
Vertical Motion:	Help	● Model vertical velocity			
		● Isobaric			
		● Isentropic			
Start time (UTC):	Help	year 08	month 10	day 22	hour 00
Total run time (hours):	Help	168			

Start a new trajectory every:	Help	24 hrs	Maximum number of trajectories: 24	
Start 1 latitude (degrees):	Help	-24.58		
Start 1 longitude (degrees):	Help	22.37		
Start 2 latitude (degrees):				
Start 2 longitude (degrees):				
Start 3 latitude (degrees):				
Start 3 longitude (degrees):				
Level 1 height:	Help	10	● meters AGL	● meters AMSL
Level 2 height:		0		
Level 3 height:		0		

Display Options

Plot resolution (dpi):	Help	96			
Zoom factor:	Help	70			
Plot projection:	Help	● Default	● Polar	● Lambert	● Mercator
Vertical plot height units:	Help	● Pressure	● Meters AGL	● Theta	
Label Interval:	Help	● No labels	● 6 hours	● 12 hours	● 24 hours
Plot colour trajectories?		● Yes	● No		
Plot source location symbol?		● Yes	● No		
Distance circle overlay:	Help	● None	● Auto		
U.S. county borders?	Help	● Yes	● No		
GIS output?	Help	● None	● GIS Shape file	● Google Earth (kmz)	
Postscript file?	Help	● Yes	● No		
PDF file?	Help	● Yes	● No		

Plot meteorological field along trajectory?	Help	● Yes	● No	Note: Only choose one meteorological variable from below to plot
Dump meteorological data along trajectory:	Help	☐ Terrain Height (m) ☐ Potential Temperature (K) ☐ Ambient Temperature (K) ☐ Rainfall (mm per hr)		

Figure 9: Data entry sheet for a forward trajectory run (http://ready.arl.noaa.gov/HYSPLIT.php)

CHAPTER 4: RESULTS

The results chapter is divided into three sections. Section A shows the trends and levels of DDT and its metabolites in the deployed PUF samples. Each graph shows the trend of a particular metabolite over a period of one year for the three passive air-sampling sites. Section B shows monthly maps of forward trajectories from the 54 sites under IRS treatment for the complete sampling year of 2008. Section C shows backward trajectory maps from the three passive air sampling sites. It shows areas where the air masses carrying the DDT and its metabolites originated.

4.1 SECTION A: The trends and levels of DDT and its metabolite at the sampling sites.

Figures 10-15 show monthly concerntration graphs in ng/fliter on a single filter for six DDT compounds, namely *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE and *p,p'*-DDE at the three passive monitoring sites throughout 2008. Figure 16, shows the trend of the sum total of DDT (ΣDDT) metabolites throughout the year.

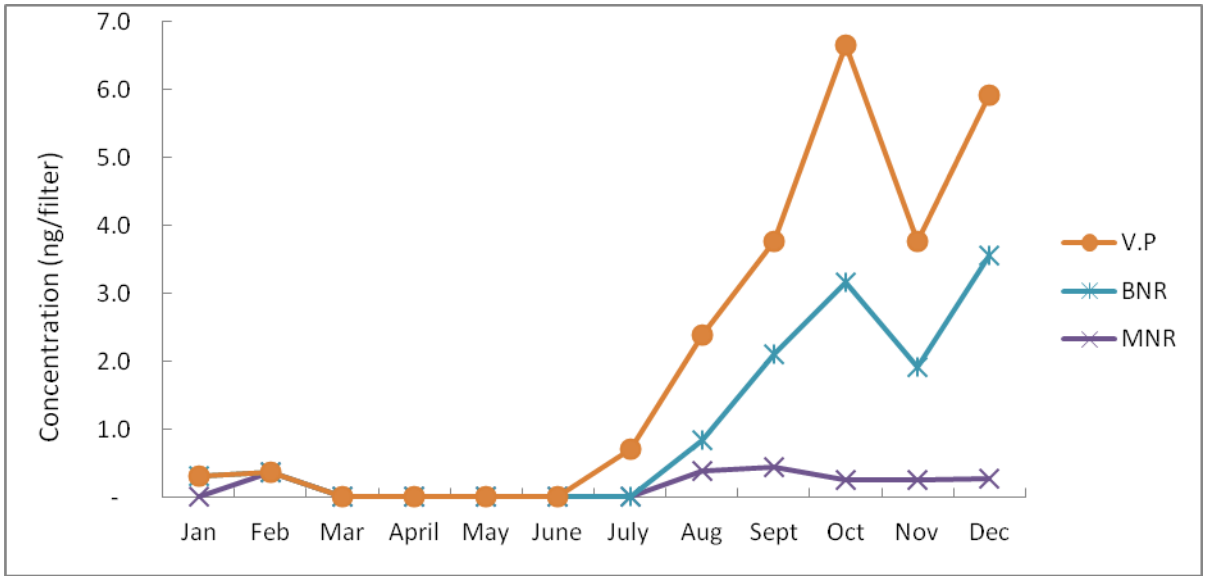

Figure 10: *o,p'*-DDT trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

Figure 10 shows that *o,p'*-DDT concentration started very low at the beginning of the year and increased as the year progressed. Molopo and Vanderbijlpark detected *o,p'*-DDT in January and February, with Barberspan having its first quantifiable detection of the compound in February. Relatively low concentrations were, however, recorded between January and February. All sites did not record quantifiable *o,p'*-DDT between March and June. Concentrations increased at all three sites in July till year end. In October, Molopo Nature Reserve had the lowest concentrations in general and Vanderbijlpark recorded the highest concentration. From July to October, there was a steady decrease in concentrations at Barberspan and Vanderbijlpark, with a dip from October to November at both sites. *o,p'*-DDT in Molopo was below 1 ng/filter throughout the year. Vanderbijlpark recorded concentrations above 6 ng/filter and had, when detectable, the highest concentrations.

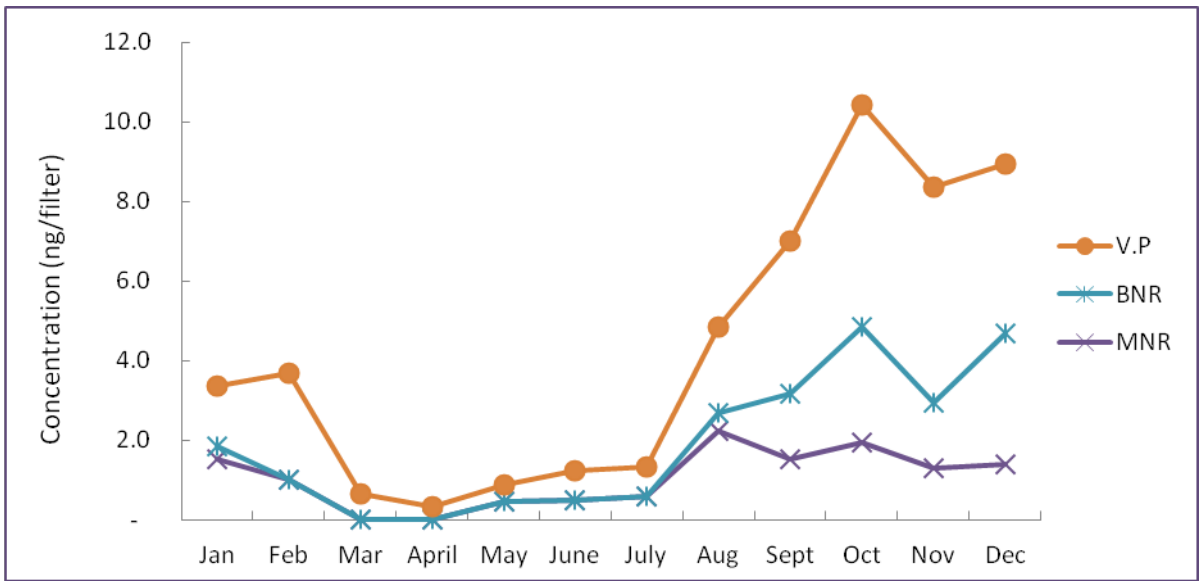

Figure 11: *p,p'*-DDT trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

Figure 11 shows changes in concentrations of *p,p'*-DDT. Vanderbijlpark again dominated with the highest concentrations, going up to 10 ng/filter. The graph looks similar to Figure 10. *p,p'*-DDT was detected at the beginning of the year at all sites. Concentrations then took a dip at all

three sites between January and March. Molopo and Barberspan had the lowest concentrations compared with the other two sites, with non-detects recorded for March and April. A steady decrease was then experienced at all three sites till July. July to October saw a steep decrease at all three sites. *p,p'*-DDT generally had higher concentration compared to *o,p'*-DDT. Barberspan and Molopo had almost the same concentrations between April and August when its concentrations increased. October to November had a dip in concentrations at all sites, much the same as for *o,p'*-DDT in Figure 10.

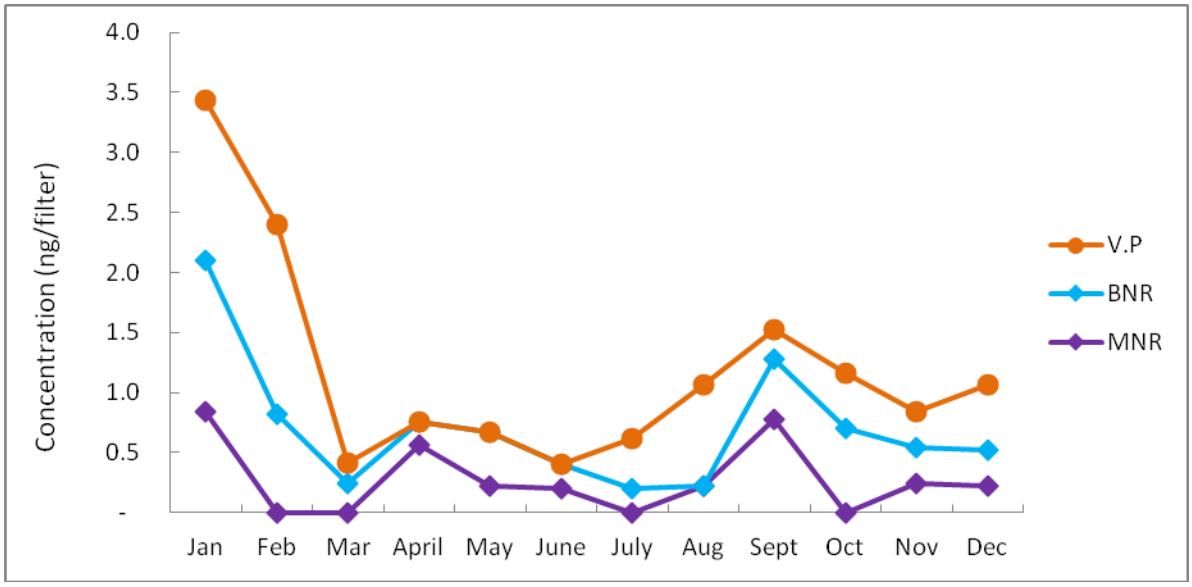

Figure 12: *p,p'*-DDD trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

Figure 12 shows the changes in concentrations of *p,p'*-DDD. Generally the concentrations were somewhat lower compared to *o,p'*-DDT and *p,p'*-DDT (Figures 10 and 11), ranging between non-detect-3.5 ng/filter at all three sampling sites. The highest concentrations per site were recorded at the beginning of the year. All three sites followed a similar pattern with concentration dips from January to March but increasing March to April. All three sites decreased between April and June, followed by an increase in concentration from July to

September at all sites. Molopo recorded the lowest overall concentration, with non-detects on four occasions. Vanderbijlpark had the highest concentrations in most months.

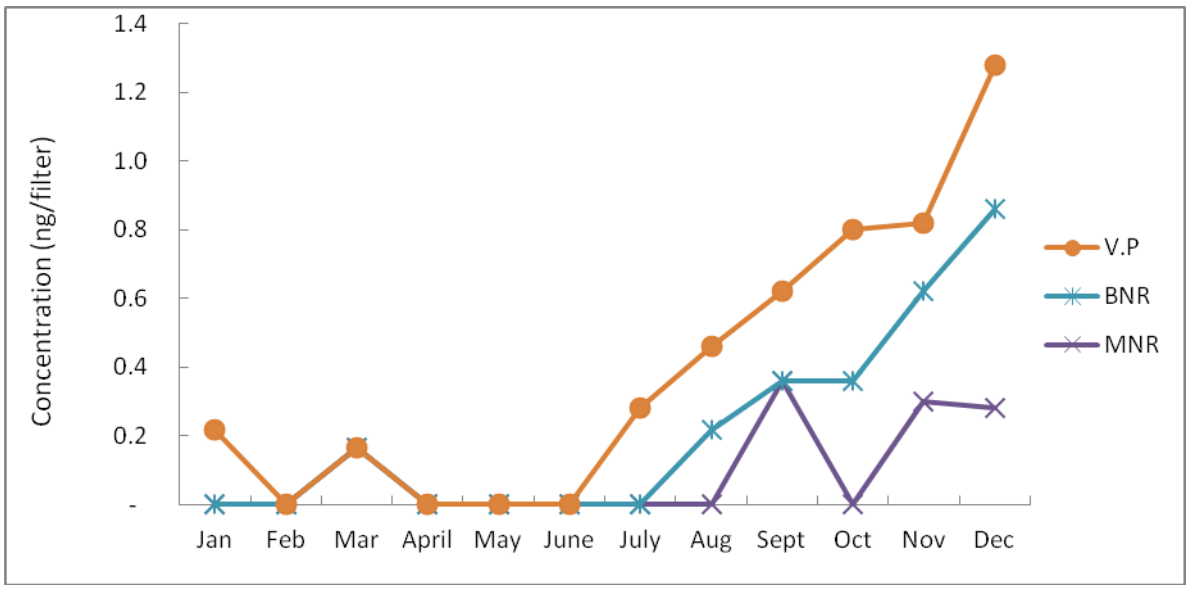

Figure 13: *o,p'*-DDD trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

o,p'-DDD concentrations were generally low at all the sites, ranging between non-detect-1.3 ng/filter. During the beginning of the year, concentrations were low with many non-detects at all sites. In Vanderbijlpark, the concentration rose steadily from June to December which had the highest concentration of *o,p'*-DDD. Molopo had a recording of eight non-detects at different stages of the sampling year. Comparatively low concentrations were recorded in Molopo and Barberspan.

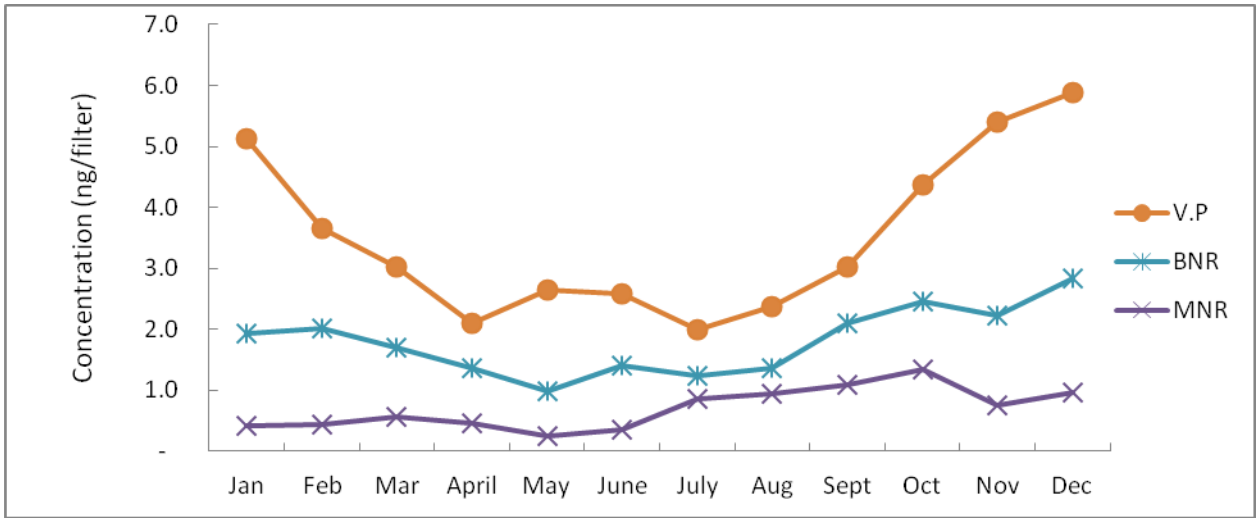

Figure 14: *p,p'*-DDE trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

Figure 14 shows the concentration trends of *p,p'*-DDE at the three sites. Concentrations ranged between 0.2-6 ng/filter. At Molopo and Barberspan, concentrations remained generally constant. Vanderbijlpark recorded the highest concentrations every month. Concentrations decreased from the beginning of the year at all the sites. The concentrations in Barberspan and Vanderbijlpark started the year relatively high and decreased as the year progressed. Between April and June, Vanderbijlpark had a steady increase in concentration. Concentrations then increased at both Barberspan and Vanderbijlpark from July till yearend. Molopo had relatively steady concentrations compared to the other two sites and the lowest concentrations out of all sites throughout the sampling period.

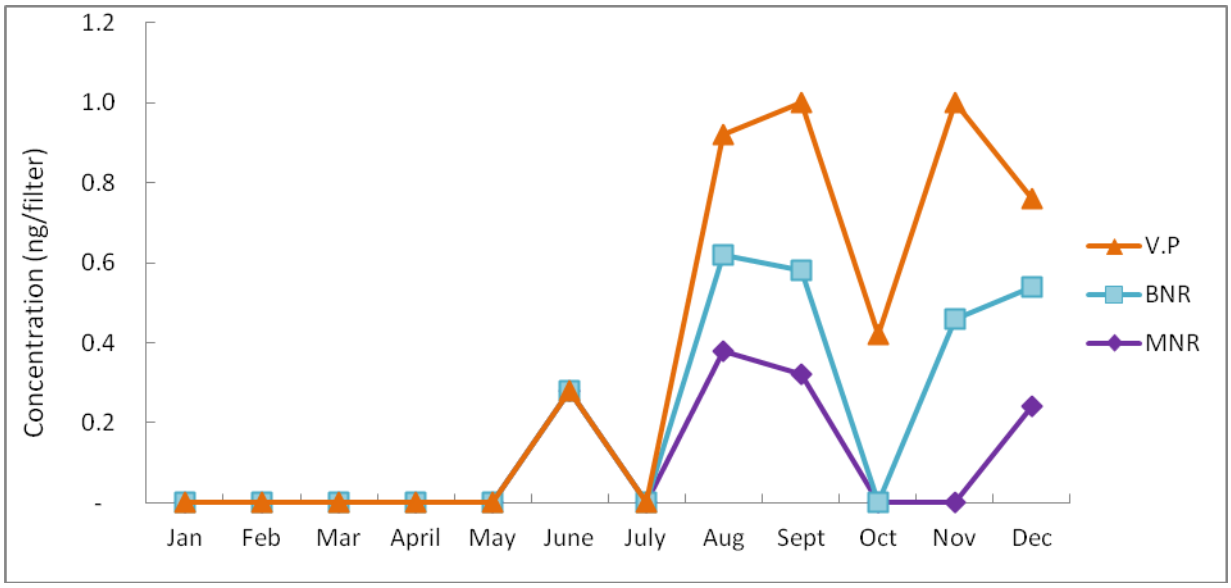

Figure 15: *o,p'*-DDE trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

Figure 15 shows *o,p'*-DDE concentrations. No quantifiable concentrations of the chemical were recorded in the first five months of the sampling year at all three sites. June had the first detection of *o,p'*-DDE at all three sites. Concentrations rose in July for all sites with a sharp uniform reduction in October. Molopo and Barberspan concentrations were below quantification levels in October. Vanderbijlpark had the highest concentrations, followed by Barberspan, then Molopo. The levels of concentration were generally low compared to the other DDTs, with nothing above 1 ng/filter.

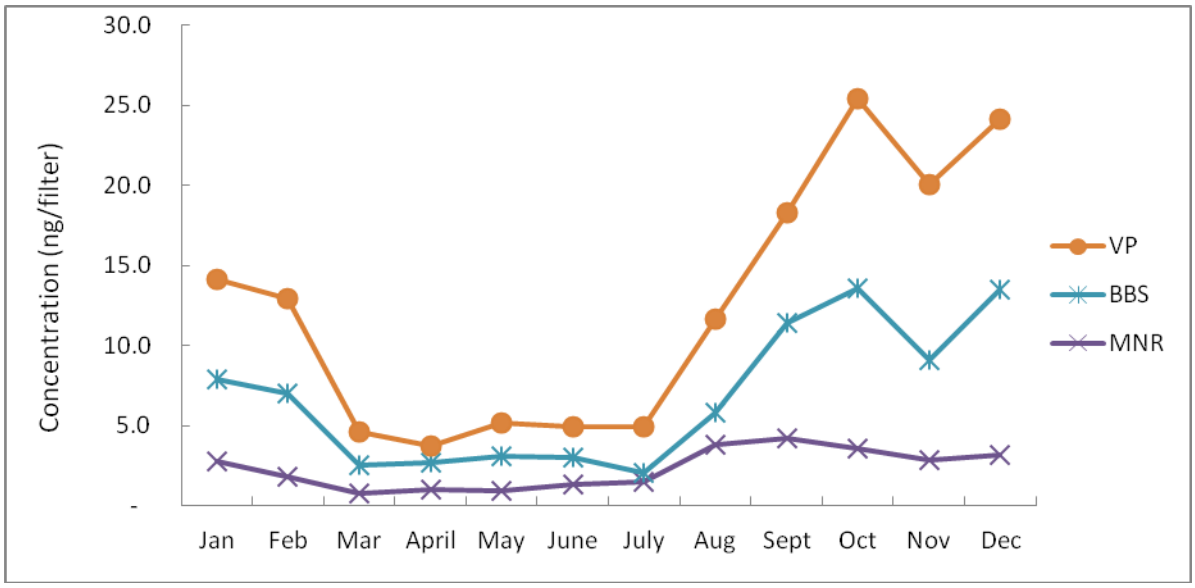

Figure 16a: ΣDDT trends over a period of one year (2008) at three sites in ng/filter on a single sample. V.P = Vanderbijlpark, BNR = Barberspan Nature Reserve, MNR = Molopo Nature Reserve.

Figure 16 shows the sum total of DDT compounds as ΣDDT. ΣDDT was evident at all three sites. Trends were fairly similar at all sites, with a general dip in concentrations between March and July. Concentrations of ΣDDT increased sharply from July till year end. Vanderbijlpark recorded the highest concentration, which was above 20 ng/filter. There was a dip in concentrations found in the November filters. Molopo had the lowest concentrations with nothing above 5 ng/filter.

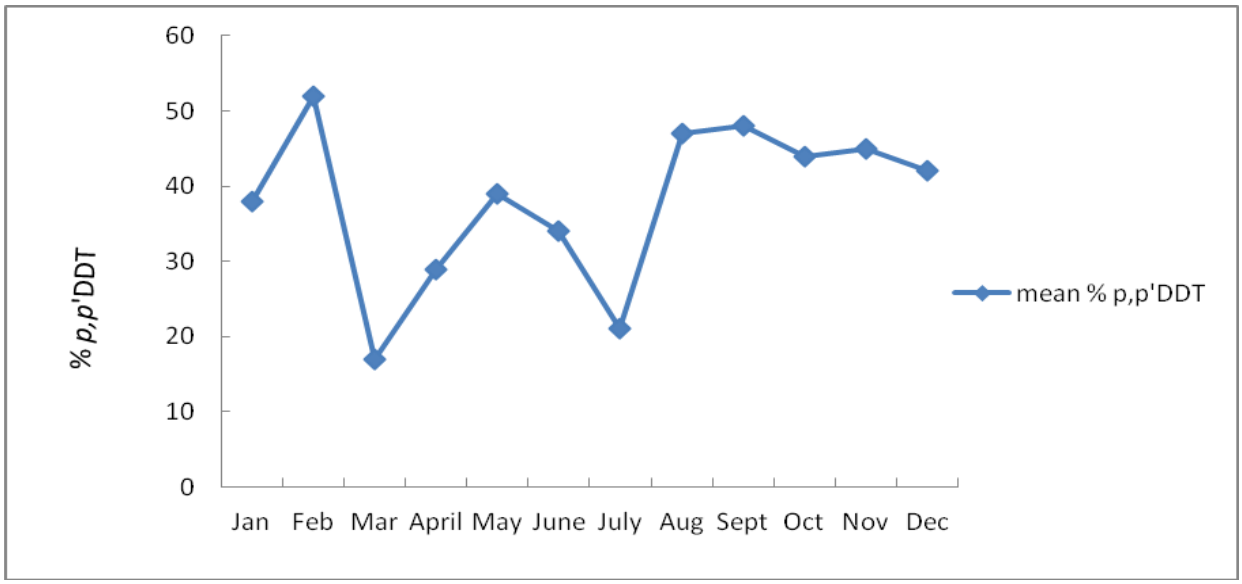

Figure 16b: Mean % *p,p'*-DDT of the three sampling sites over a period of one year.

Figure 16b shows the mean percentage of *p,p'*-DDT of ΣDDT all three sites. The graph shows that the percentage declined from February to March. The percentages increase again between March and May. This is the followed by another decline till July. There was an increase from August and a slight drop in November and December.

4.2 Section B: Forward trajectory maps for 2008

The Guidance document for the Global Monitoring Program for POPs under the Stockholm Convention states that a better description of POP concentrations and trends at particular sites can be achieved through the evaluation of regional and global atmospheric transport pathways. Figures 17-28 shows the calculated forward air mass trajectories from 54 sites in current and potential malaria control areas. The run time for each trajectory was 168 hours (7 days), generated for every day for every starting point, for 1620 trajectories per month. Each map shows the combined air mass trajectories for each respective month. The air mass trajectories show the path and areas over which the air masses passed.

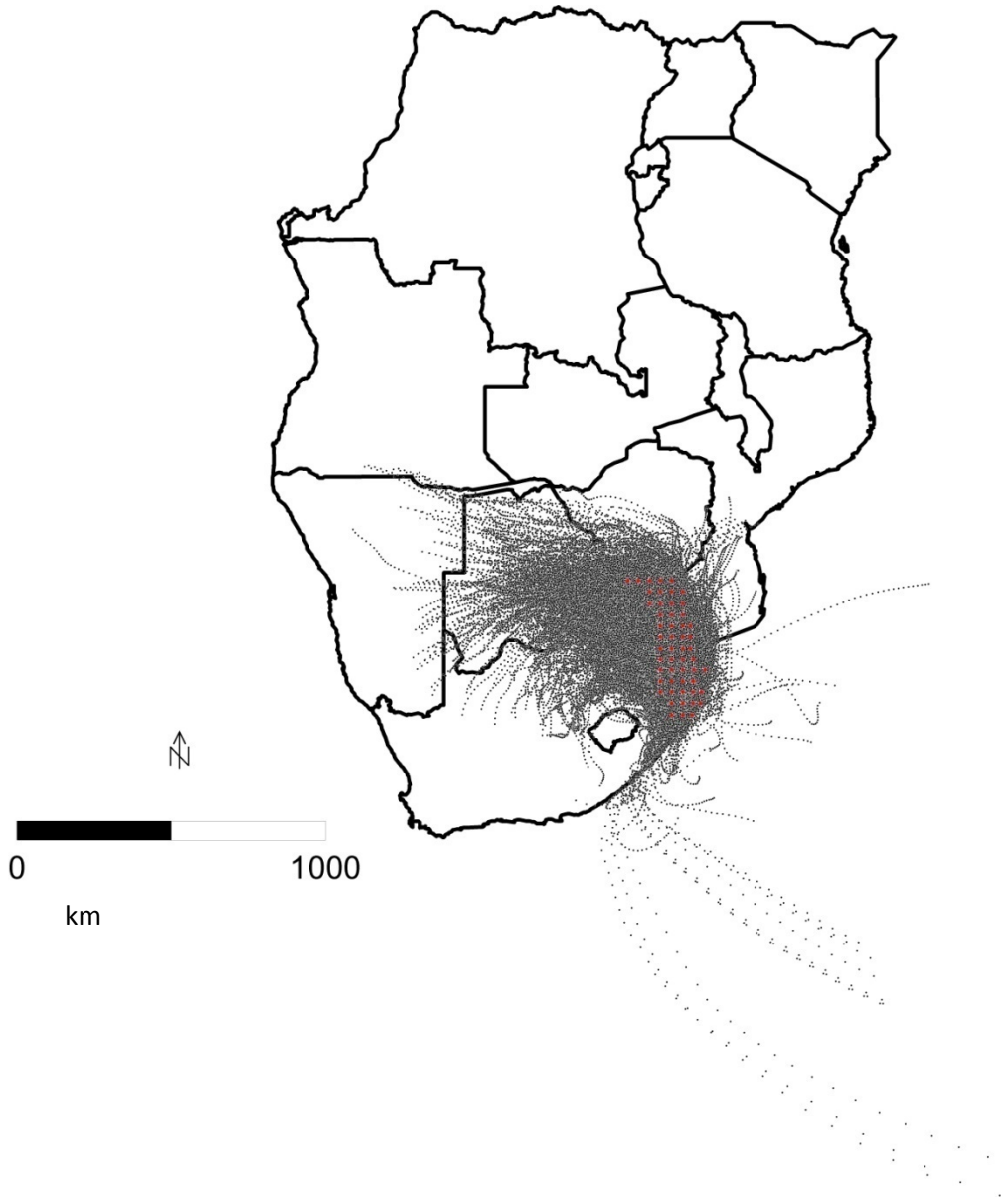

Figure 17: Forward air mass trajectory map for January, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

In Figure 17, the prevailing winds in January appeared to be favouring a north-western movement. Compared with the following months, forward trajectories were relatively short, covering a smaller area in seven days. Major air mass movement covered the north-western end of South Africa, with a trajectory stream towards the south. The whole of Swaziland was covered by the trajectories and also the southern part of Mozambique. Some air masses moved

into the eastern part of Botswana and the southern part of Zimbabwe. Very few air mass movements were towards the east. South-easterly movement was limited, with few air masses moving into the Indian Ocean. It seems as if the Drakensberg Mountains shielded Lesotho and the Eastern Cape. It is also obvious that the three active sampling points were covered less the further west they were located from the source area (Figure 7). Molopo had almost no trajectories covering it, while Vanderbijlpark seemed to be the most densely covered.

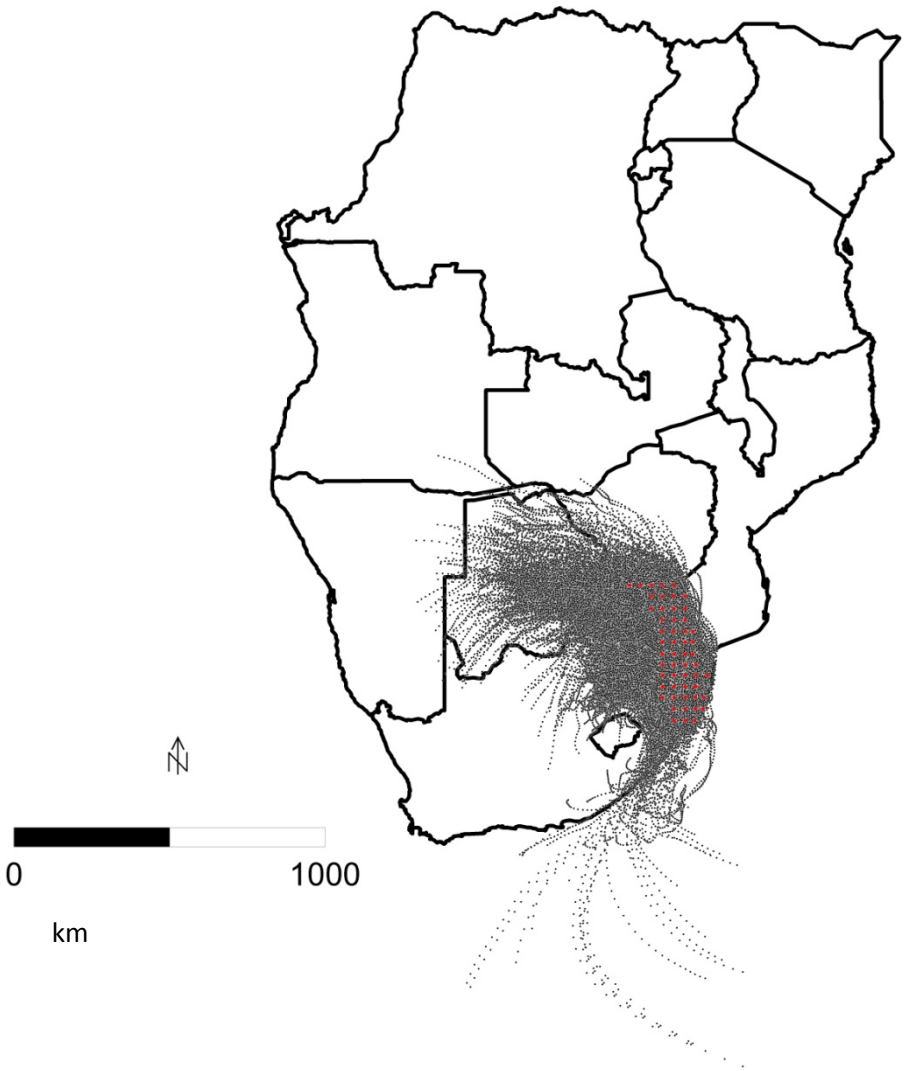

Figure 18: Forward air mass trajectory map for February, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

Figure 18 shows the forward trajectories for February, 2008. The prevailing wind moved air masses towards the north-west. The February map (Figure 18) looks much the same as for January (Figure 17), with perhaps a smaller component towards the east. The area covered was more to the north of the South African border crossing into the southern part of Zimbabwe and

covering most of Botswana. There was little movement toward the centre of South Africa. There were other trajectory streams, that moved along the eastern coast of South Africa with some air masses ending up over the Indian Ocean. Again, the possible shielding effect of the Drakensberg Mountains seems to be in effect. Although southern Botswana received air masses from the spayed areas, the Molopo received very little.

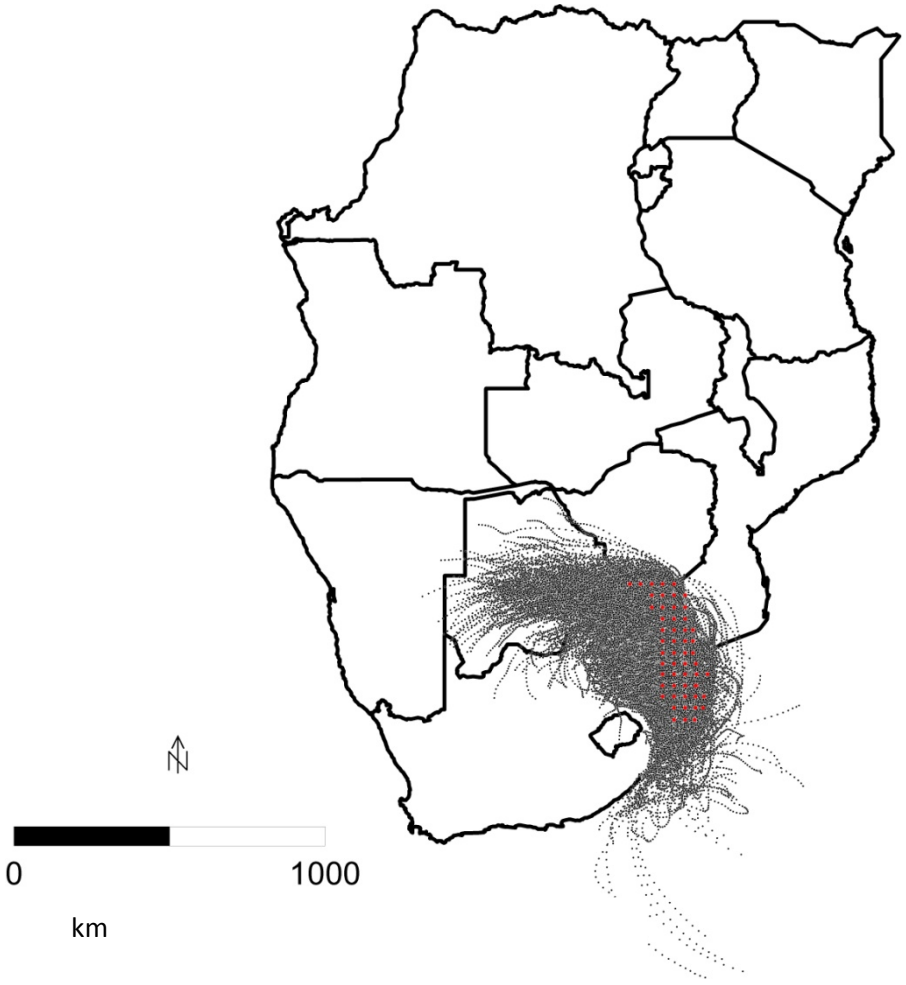

Figure 19: Forward air mass trajectory map for March, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

The March map (Figure 19) had a similar pattern as the ones in January and February (Figures 17 and 18). Air masses moved from the sprayed areas towards parts of Botswana and a small

part of southern Zimbabwe and Mozambique. Air masses also moved southwards from the sprayed areas towards the Indian Ocean. The reach of the air masses was smaller than that noted in figure 17 and 18.

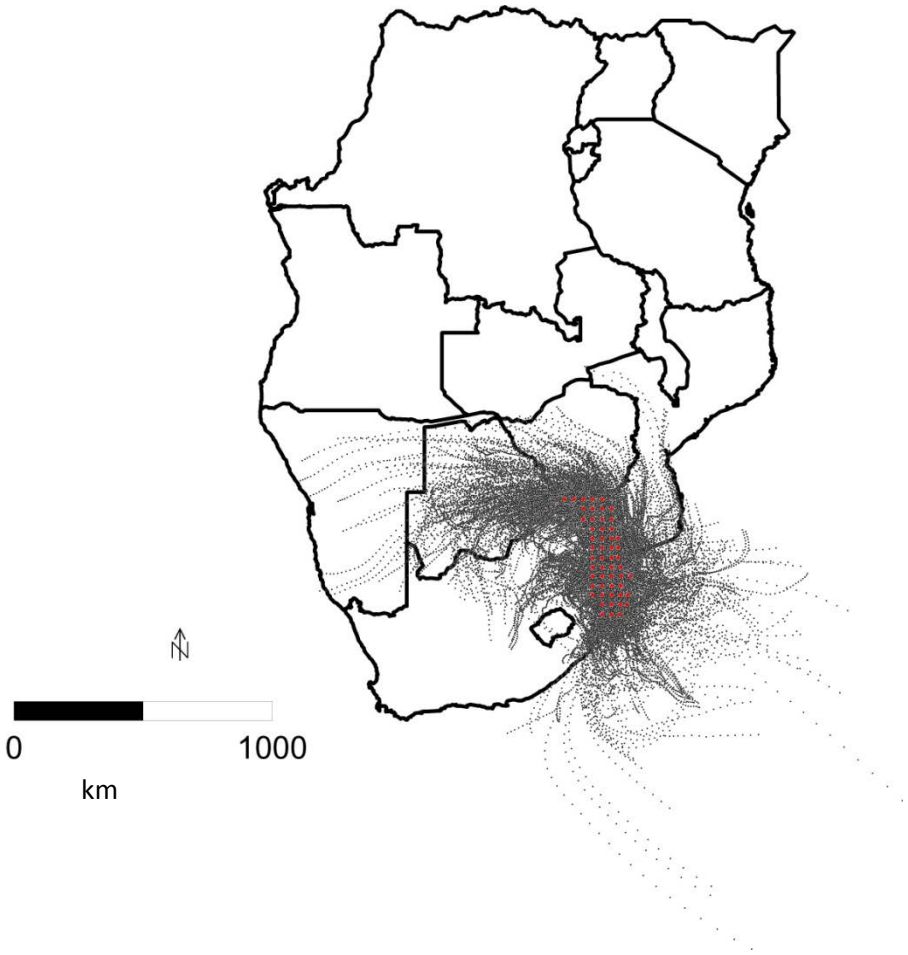

Figure 20: Forward air mass trajectory map for April, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

The distribution of air mass movements was more diffuse in April (Figure 20) compared with previous months. The air masses distributed more to the east than earlier. There was a stronger southern component away from the sprayed areas towards and over the Indian Ocean. More air moved into central South Africa (Free State) as well, circling around Lesotho, in a distinct

trajectory stream. The air masses spread further to the northwest into most of the eastern parts of Botswana. Some air masses also reached as far as Namibia via Botswana. However, very few air mass trajectories made it as far as Namibia. Air masses also moved further up into Zimbabwe. In Zimbabwe, the whole southern part was covered by the air mass trajectories. In Mozambique, some southern and central parts were also covered.

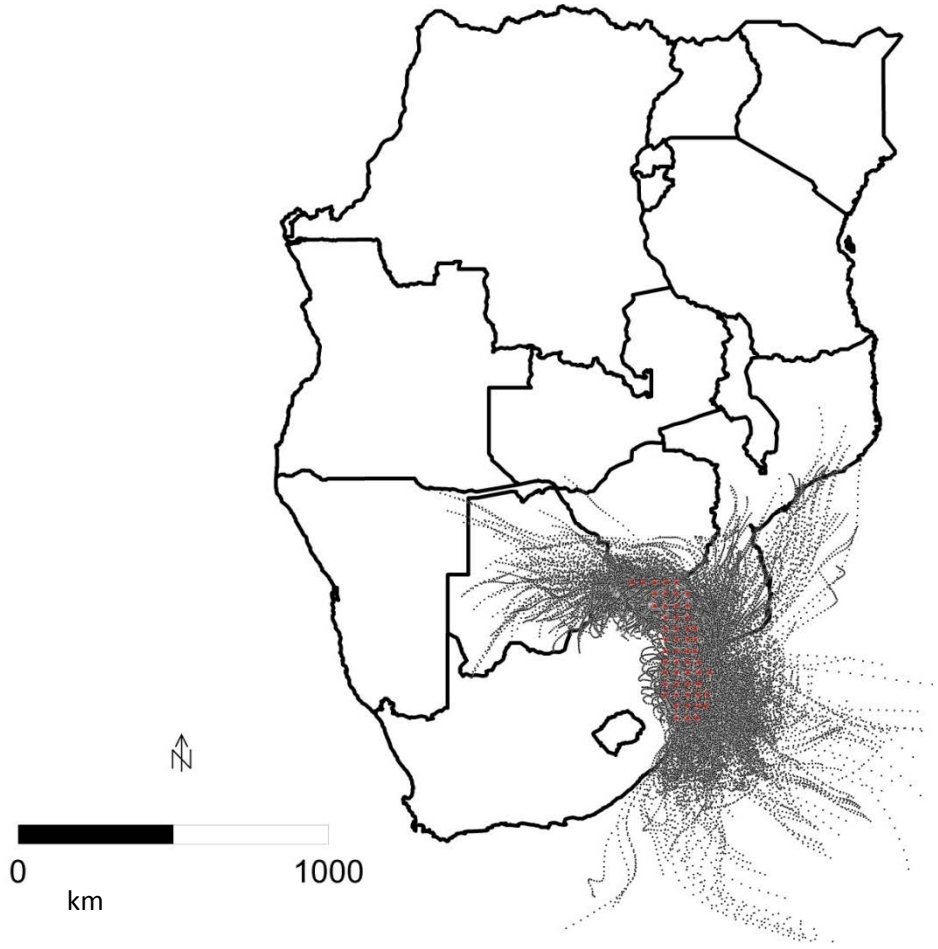

Figure 21: Forward air mass trajectory map for May, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

In May (Figure 21) the trajectory pattern had a much stronger southern and eastern component, much of the air masses moved across the coast into the Indian Ocean. Mozambique received more air mass trajectories than the previous months (Figures 17-20). There is also movement away from the sprayed areas into Botswana and Zimbabwe. The diffusion into these countries was much less when compared to April (Figure 20). The north-eastern part of South Africa received quite a number of air masses, but the central and southern parts received no air from the sprayed areas.

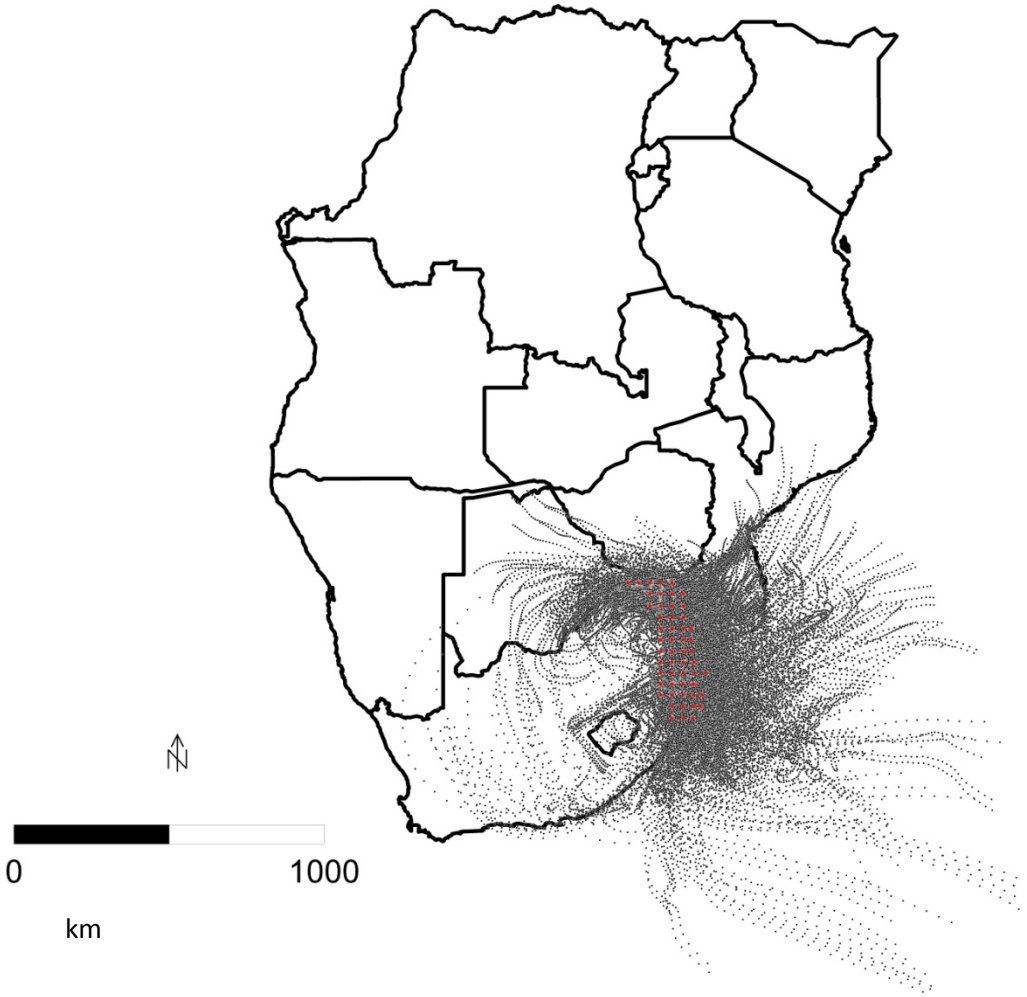

Figure 22: Forward air mass trajectory map for June, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

June (Figure 22) experienced a general movement of air in almost all directions. Air masses moved further out into the Indian Ocean compared with previous months (Figures 17-21). The spread to the east was also much wider than before, covering large parts of Mozambique. A few days in June saw movements towards the northwest, with the air masses spreading throughout the country. Areas at the border with Zimbabwe were densely covered by trajectories. Movement of air was also noted towards and through Botswana, but with a lesser spread than previous months. For the first time, air reached the Western and Northern Cape, while the Drakensberg Mountains was crossed into the Eastern Cape. A large proportion of the air masses reached the Indian Ocean by eastern, south-eastern and southern movements, some more than a 1000 km into the Indian Ocean.

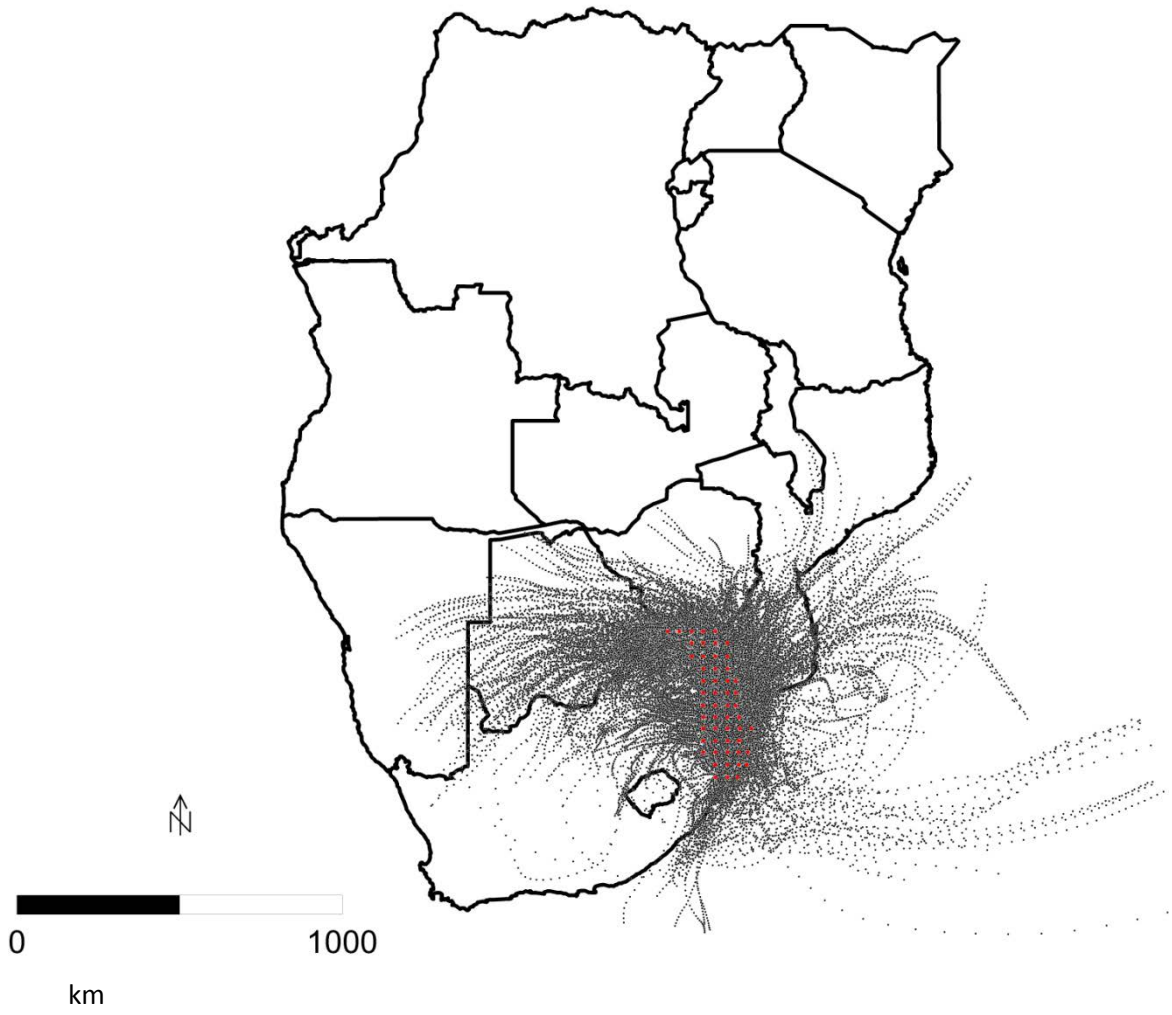

Figure 23: Forward air mass trajectory map for July, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

July (Figure 23) also had a great spread of air mass trajectories. Air masses moved predominantly west and northwest, with some long trajectories south and eastwards into the Indian Ocean. There was a great movement of air masses into Botswana, reaching as far as

Namibia. To the north, Zimbabwe and Mozambique received air masses coming from the sprayed areas. One air mass went as far as the northern end of Zambia.

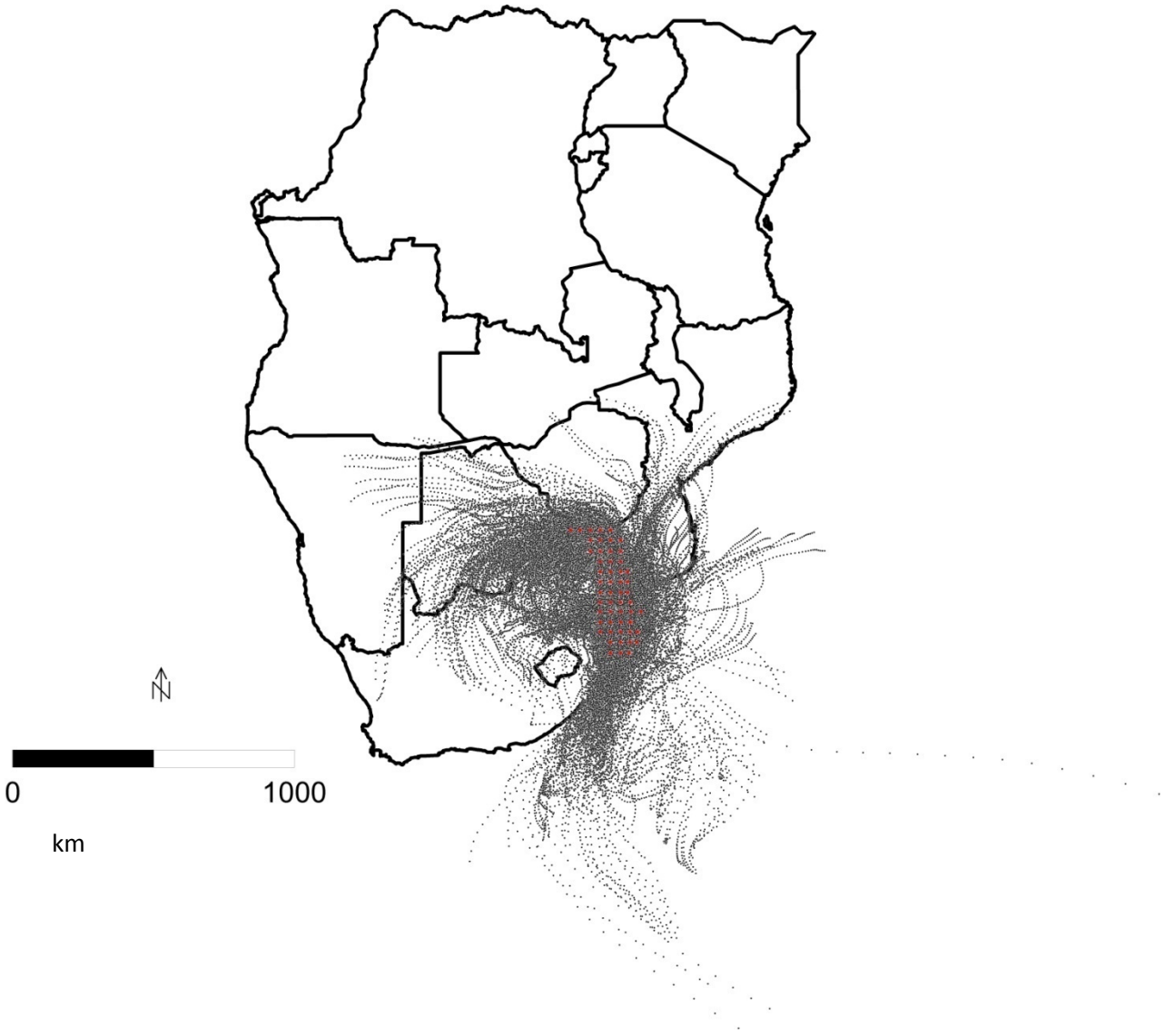

Figure 24: Forward air mass trajectory map for August, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

In August (Figure 24), a number of air mass trajectories moved south of the sprayed area and then into the Indian Ocean - one air mass travelling about 2500 km. The east coast and

southern Mozambique received many air masses. Some air masses moved up to the north east into Botswana, nearly reaching all parts of the country. The eastern part of Botswana had winds moving towards it. The southern part of Zimbabwe received air from the sprayed areas as well. A few air masses went as far as Namibia, Zambia, and the Northern Cape. Some air masses also crossed the Drakensberg into Lesotho.

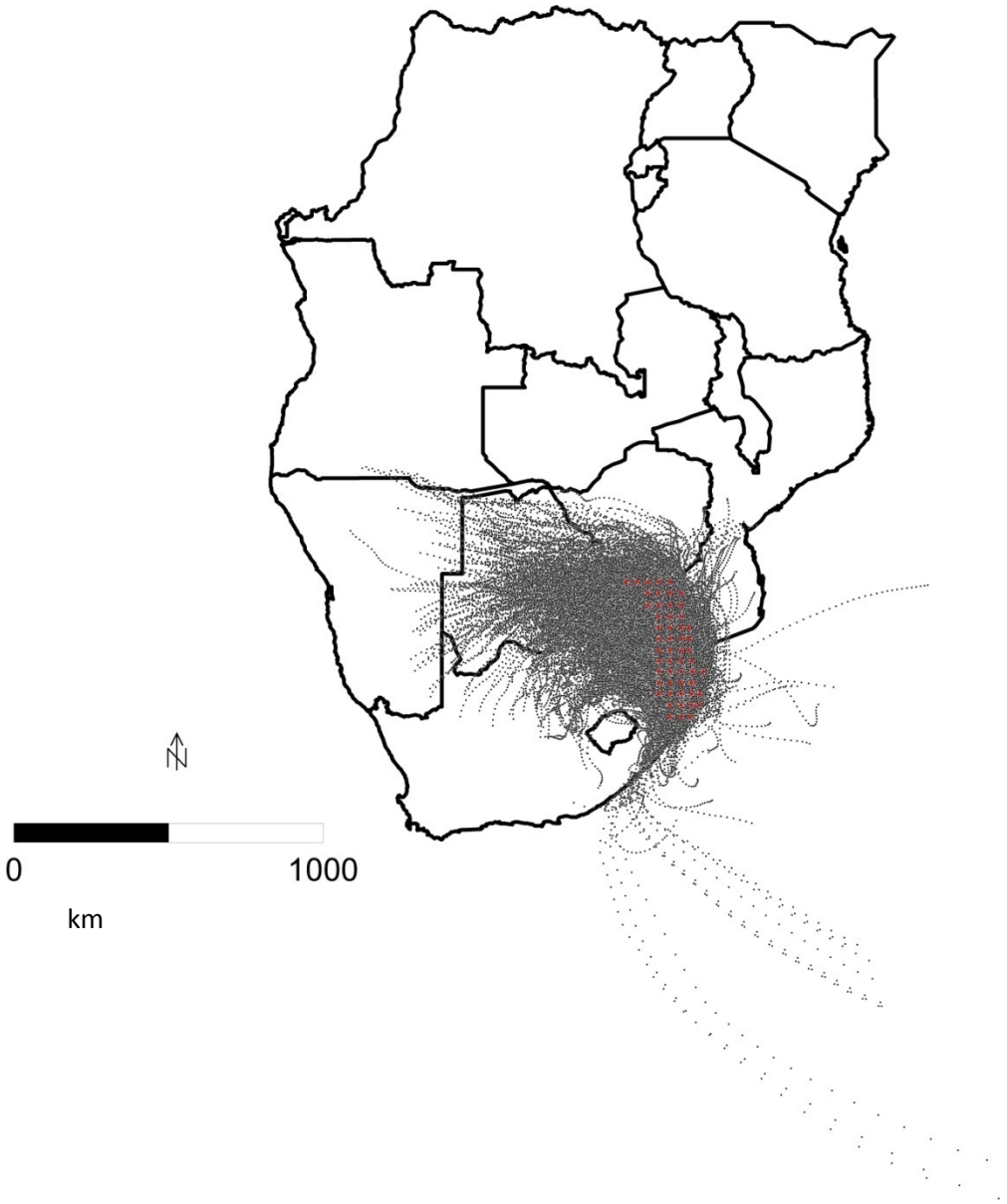

Figure 25: Forward air mass trajectory map for September, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

September (Figure 24) had a very compact distribution of air masses, densely covering southern Zimbabwe and most of Botswana, central South Africa, and the south coast of KwaZulu-Natal. Some air masses reached the southern Indian Ocean. Fewer trajectories moved off-land compared to August (Figure 24). The effect of the Drakensberg is clearly seen.

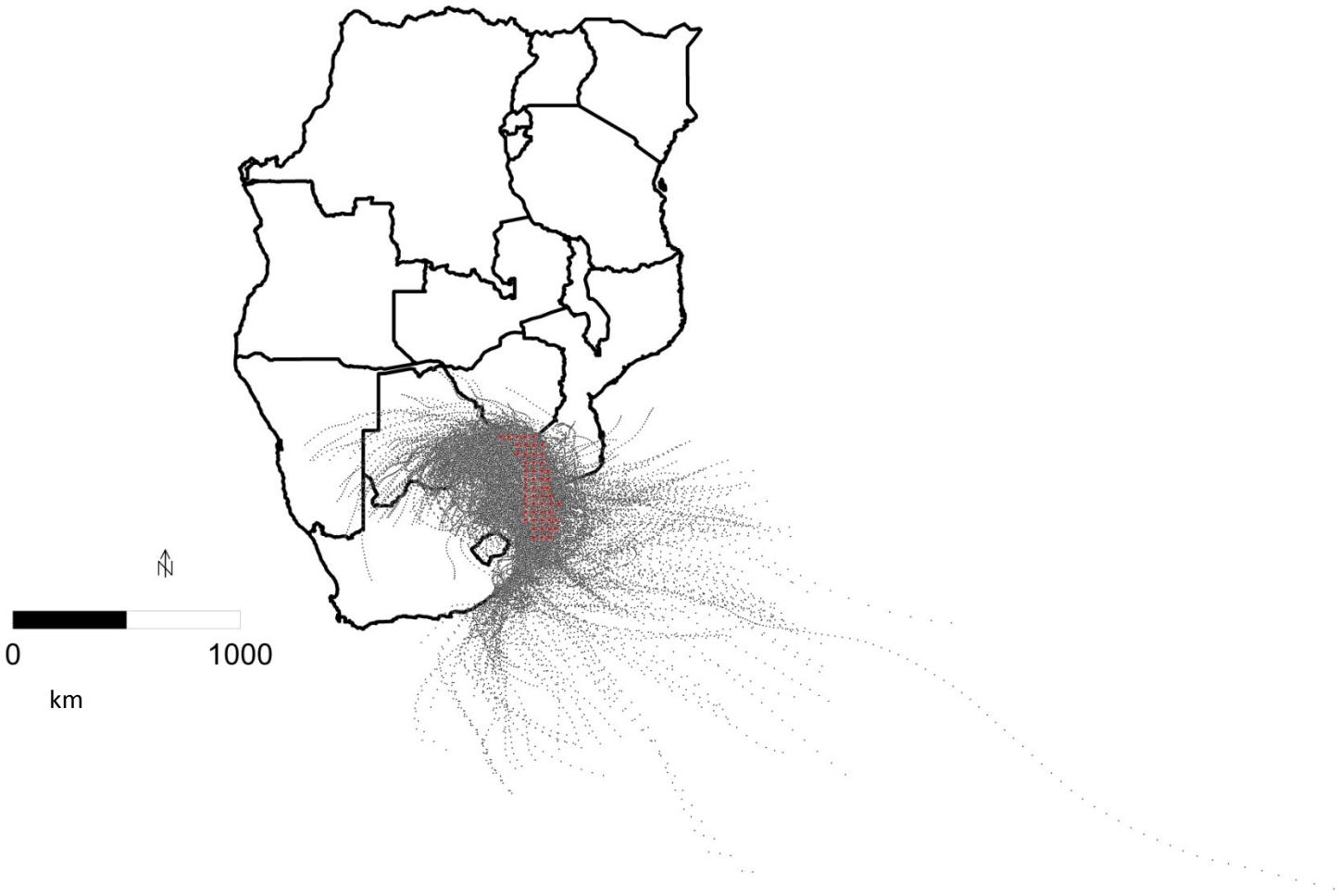

Figure 26: Forward air mass trajectory map for October, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

October (Figure 26) looked much like September (Figure 25), with a stronger eastern and southern component. One trajectory reached very far into the Indian Ocean. A number of

trajectories reached Namibia and the Northern Cape. The southern trajectory stream followed the coast to near Port Elizabeth.

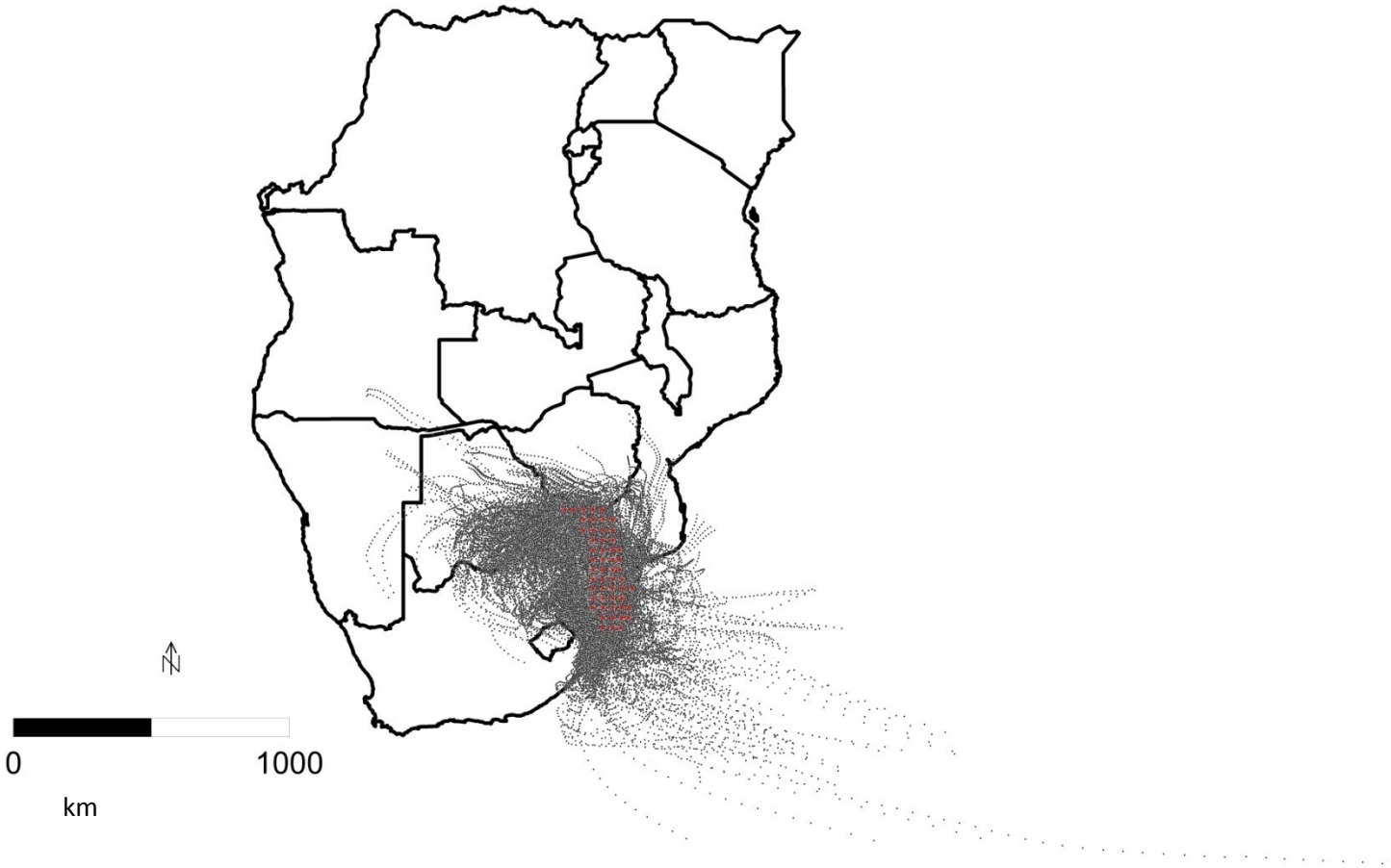

Figure 27: Forward air mass trajectory map for November, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

November (Figure 27) also had a wide spread of air mass trajectories. The eastern part had air masses reaching far into the southern Indian Ocean. The whole northern part of South Africa and southern Zimbabwe had air masses moving over it. The air masses moved into the east of Botswana and a few reached as far as Namibia and Angola.

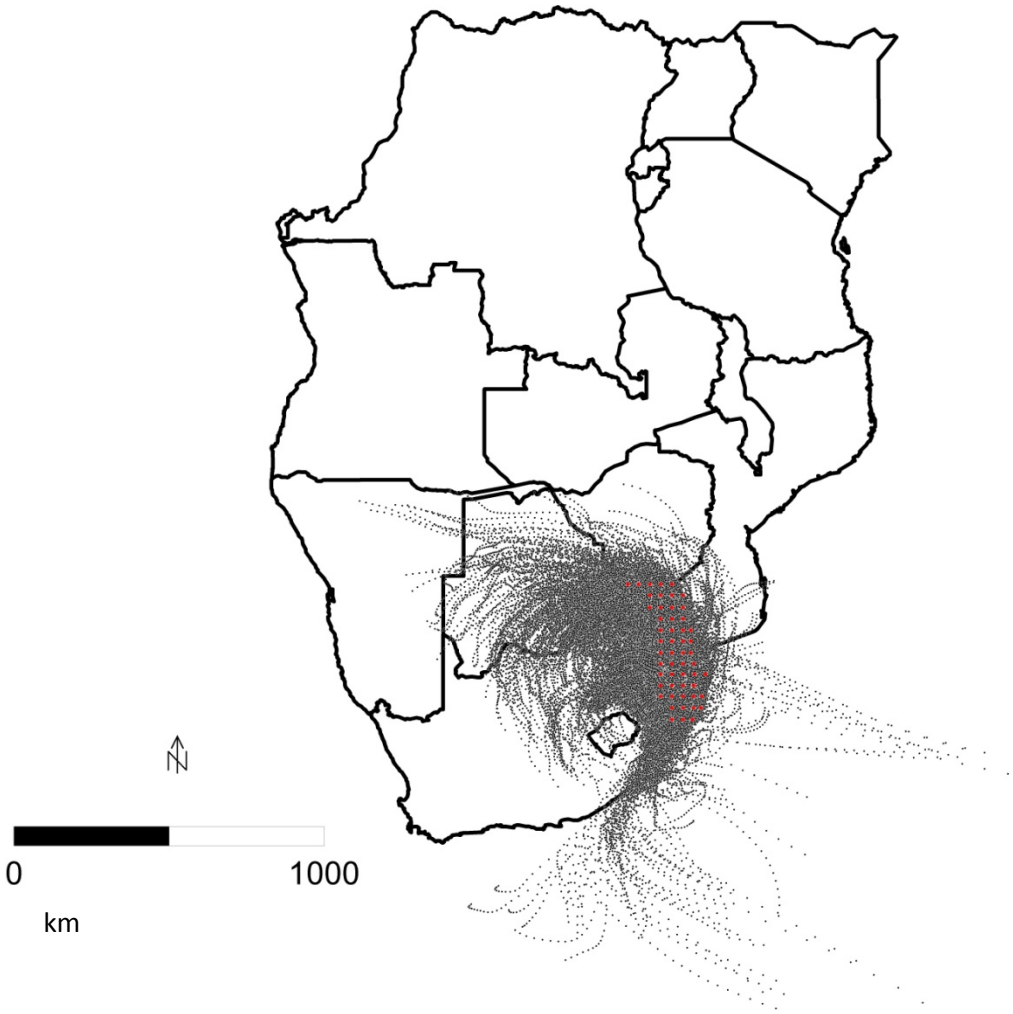

Figure 28: Forward air mass trajectory map for December, 2008, from 54 sites. Each trajectory is a 24-hour forward trajectory from one site for each day of the month.

In December (Figure 28), the distribution and wind patterns shifted more towards the west of the sprayed areas. The northwest part of South Africa was covered with trajectories that also crossed into Zimbabwe, Botswana, and parts of Namibia. There was also a distinct trajectory stream around Lesotho, both north and south. Two trajectory streams reached the Indian Ocean, one towards the east, and another towards the south.

4.3 Section C: Backward trajectory maps for 2008

The maps (figure 29-40) show backward trajectories from three passive air sampling sites. Each map shows air mass movements for each month at all three sites. Each trajectory shows air movement for a period of 24 hours before it reached the sampling area.

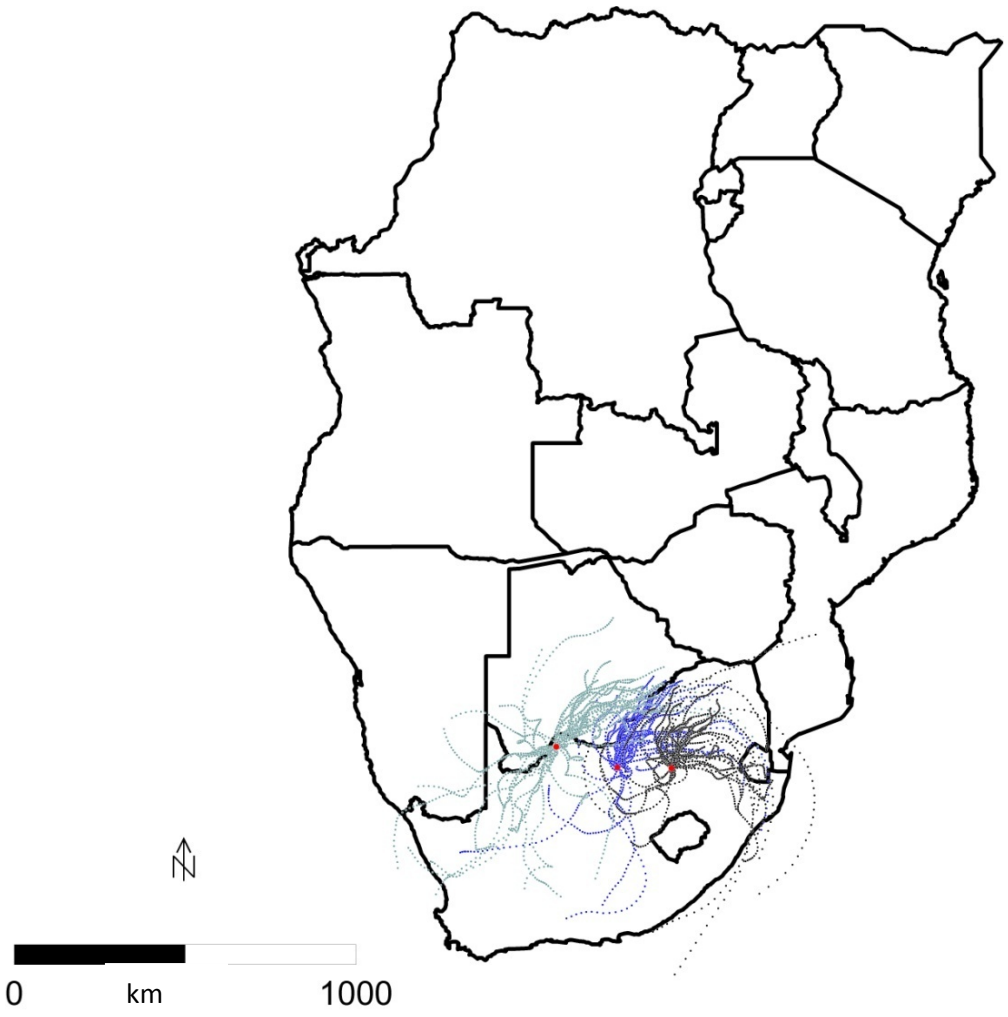

Figure 29: Backward air mass trajectory map for January, 2008, from three sampling sites. Each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

Figure 29 shows that most of the air masses in January originated from the northern part of South Africa. Vanderbijlpark received air directly from IRS areas. Barberspan also received air masses from Limpopo, but not as much as Vanderbijlpark. Molopo, which is further away from the IRS areas, had less influence from the sprayed areas. Molopo also received air masses from the arid south-western parts of South Africa.

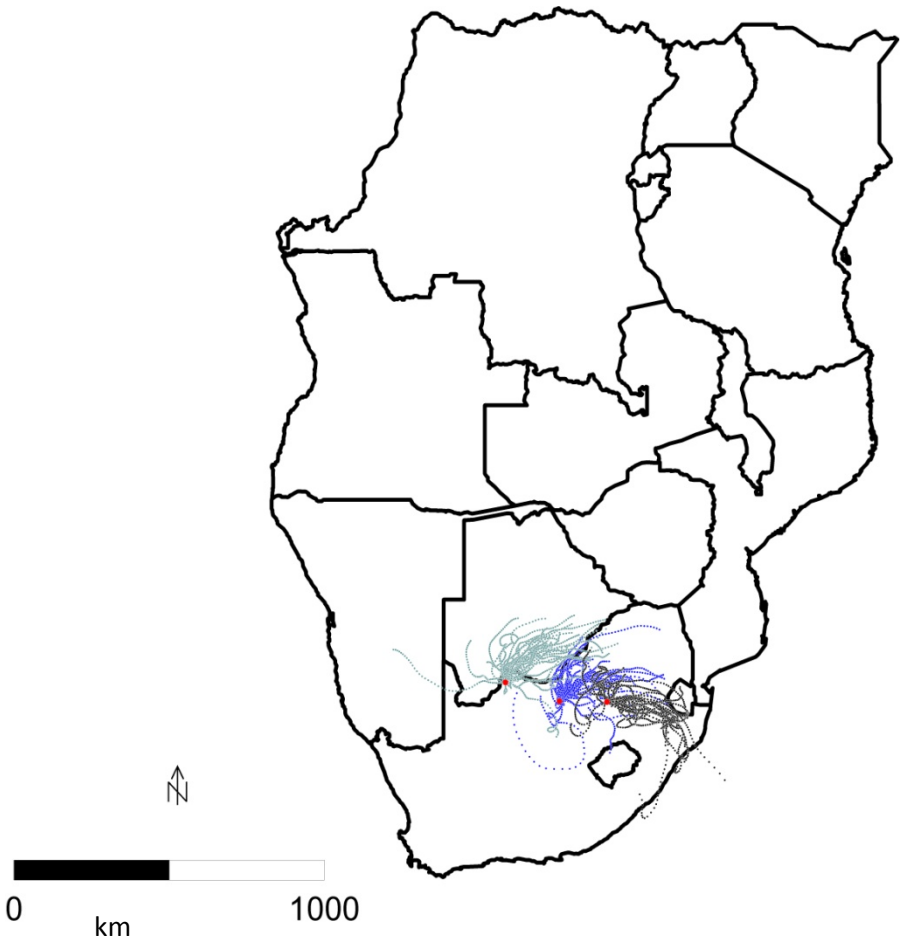

Figure 30: Backward air mass trajectory map for the month of February, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

The month of February (Figure 30) shows that air mass movements to the sampling areas originated closer when compared to January. Vanderbijlpark received air masses from Mpumalanga and KwaZulu-Natal provinces. Some air from the sprayed areas reached Barberspan. Most of the air masses to Molopo came from the northern border between South Africa and Botswana.

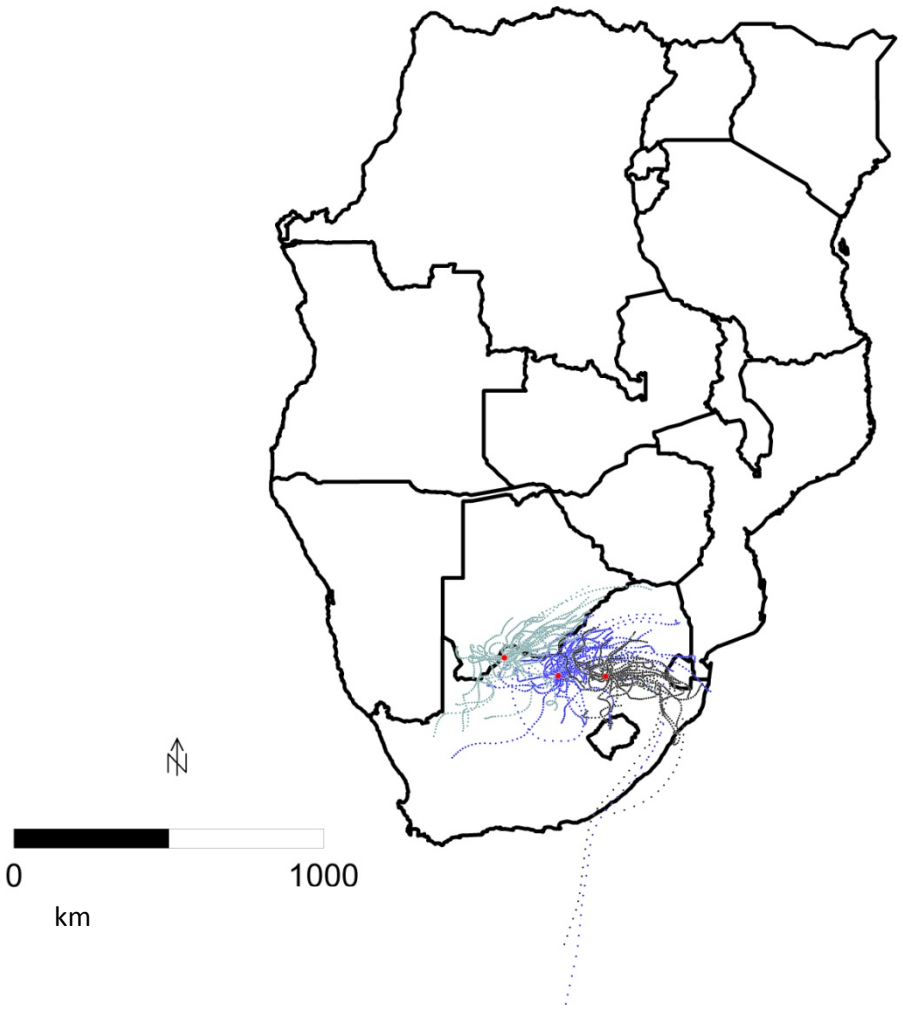

Figure 31: Backward air mass trajectory map for the month of March, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

Figure 31 shows that the sources of the air masses to the sampling areas originated from much further away when compared to February. Streams of air masses to Vanderbijlpark and Barberspan originated mainly from Limpopo and Mpumalanga. Molopo received some air masses from the northern part of South Africa, including Limpopo.

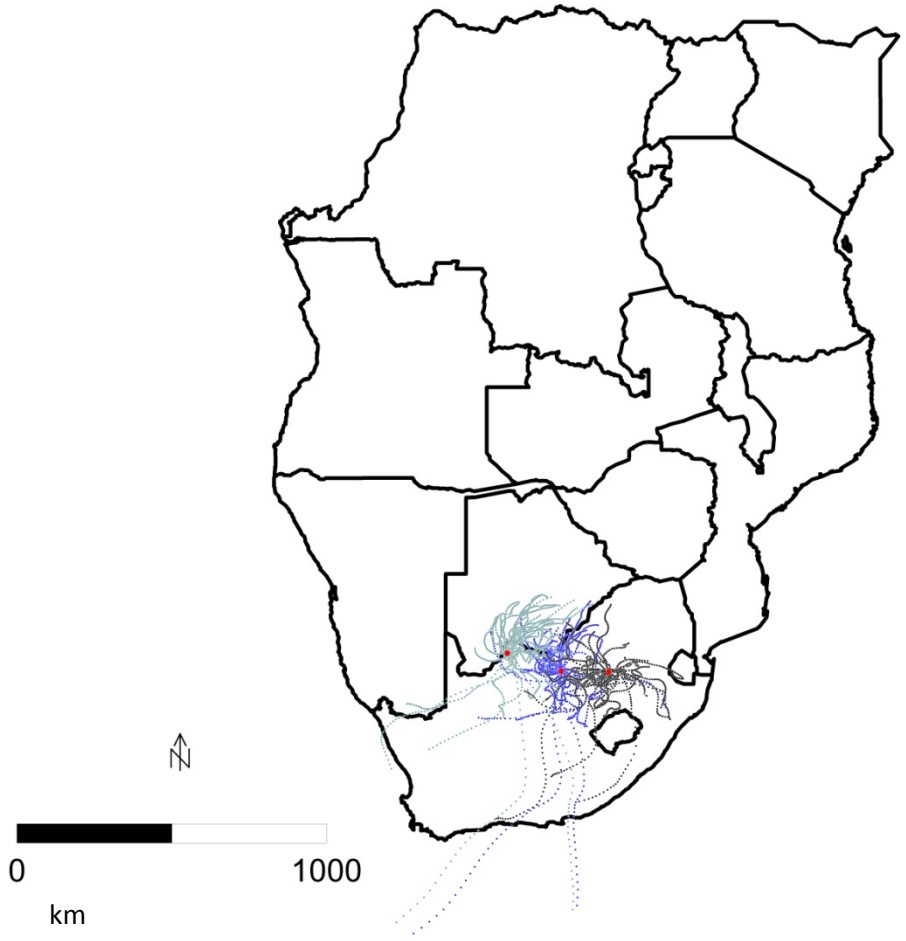

Figure 32: Backward air mass trajectory map for the month of April, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

Origin of April air mass movements to the sampled areas appeared confined to a small area around the sampling sites (Figure 32) when compared with other months. However, there were a few days when air masses to all three sites came from as far as the Indian Ocean and even the Atlantic.

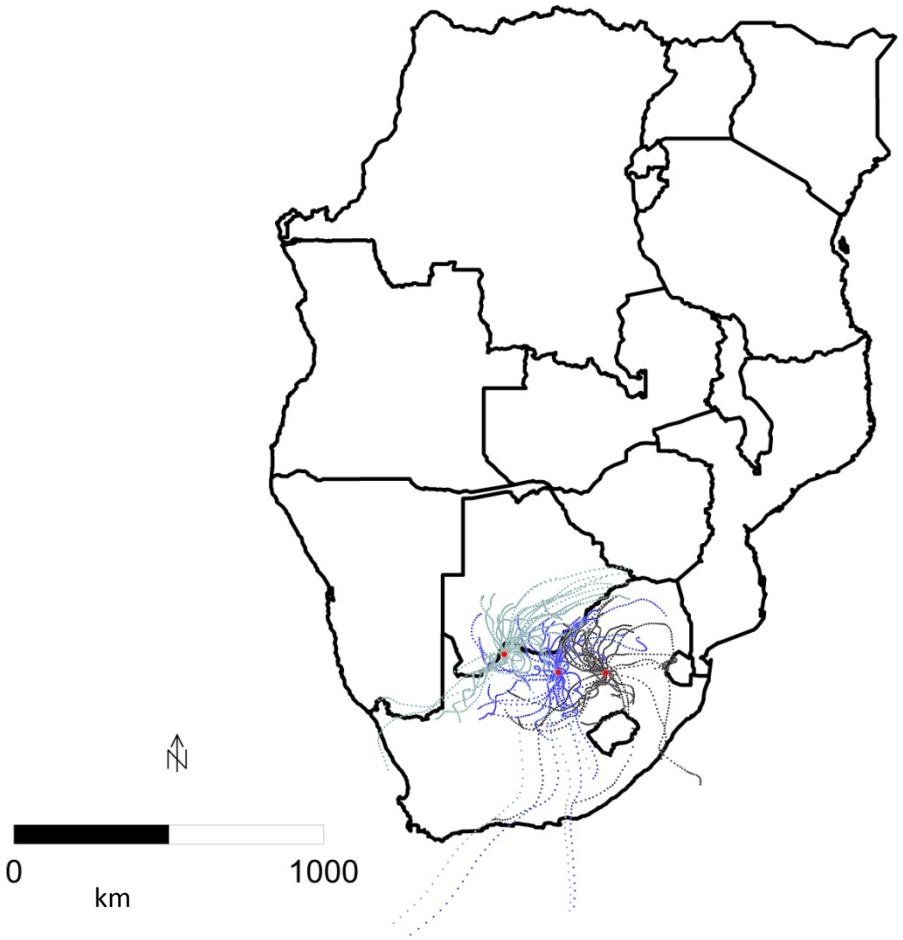

Figure 33: Backward air mass trajectory map for the month of May, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

In May the sources areas were more diffuse compared to April (Figure 33). Air masses from Limpopo reached all sampling sites. Vanderbijlpark and Barberspan had many air masses from central South Africa. The back trajectories also showed air streams from as far as the Indian and Atlantic oceans. Molopo received air from the eastern part of Botswana and the western parts of South Africa.

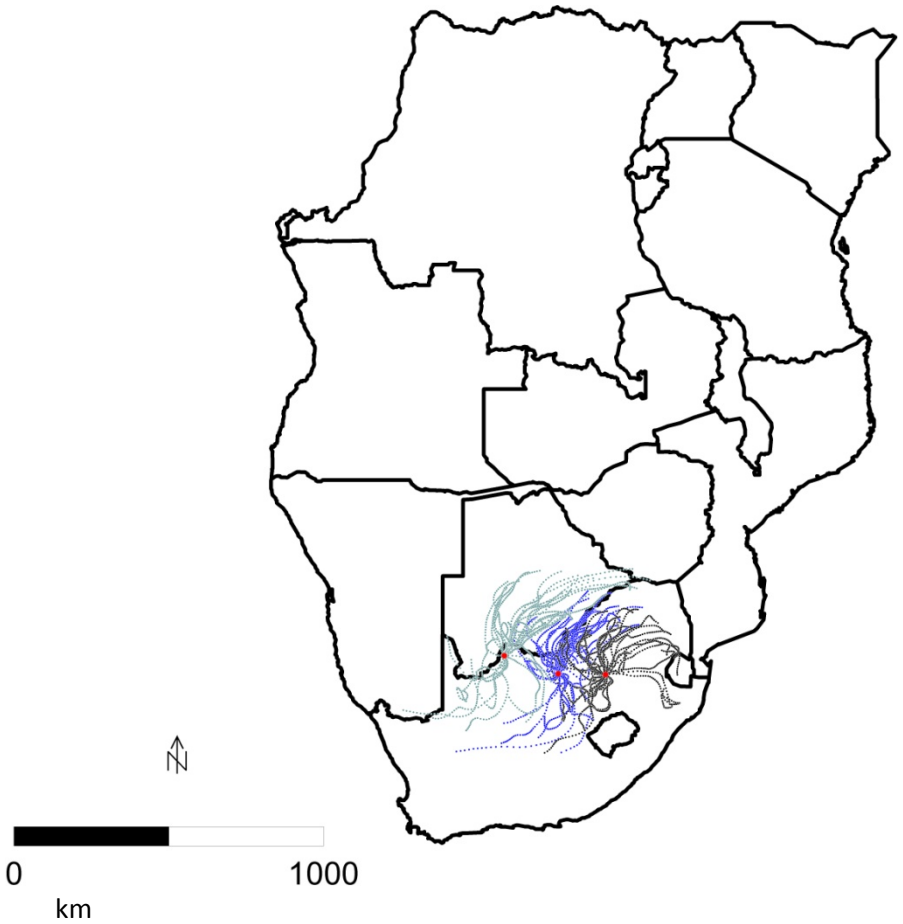

Figure 34: Backward air mass trajectory map for the month of June, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

In June, the source areas for the air masses were generally localised (Figure 34). Vanderbijlpark received air from the IRS areas. Barberspan also got air masses from Limpopo. Molopo was also affected by air movements from Limpopo but to a much lesser extent compared with the other two sampling sites.

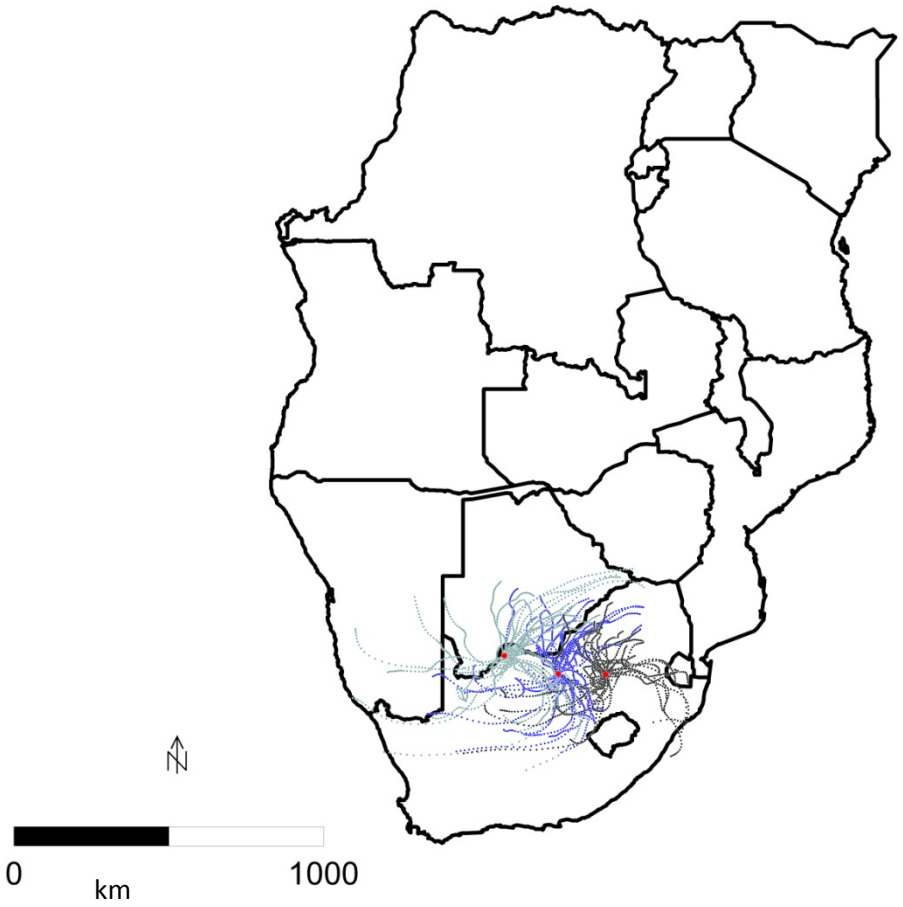

Figure 35: Backward air mass trajectory map for the month of July, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

Figure 35 shows air movement to the sampled areas for July. The air masses to Molopo originated from as far as the Zimbabwe-South Africa border. Some of the air originated from Namibia and central South Africa. Barberspan also received air masses from the Limpopo Province and central South Africa. Vanderbijlpark had air masses originating from the eastern provinces and central South Africa as well. The spread of origin areas was somewhat larger than the earlier months.

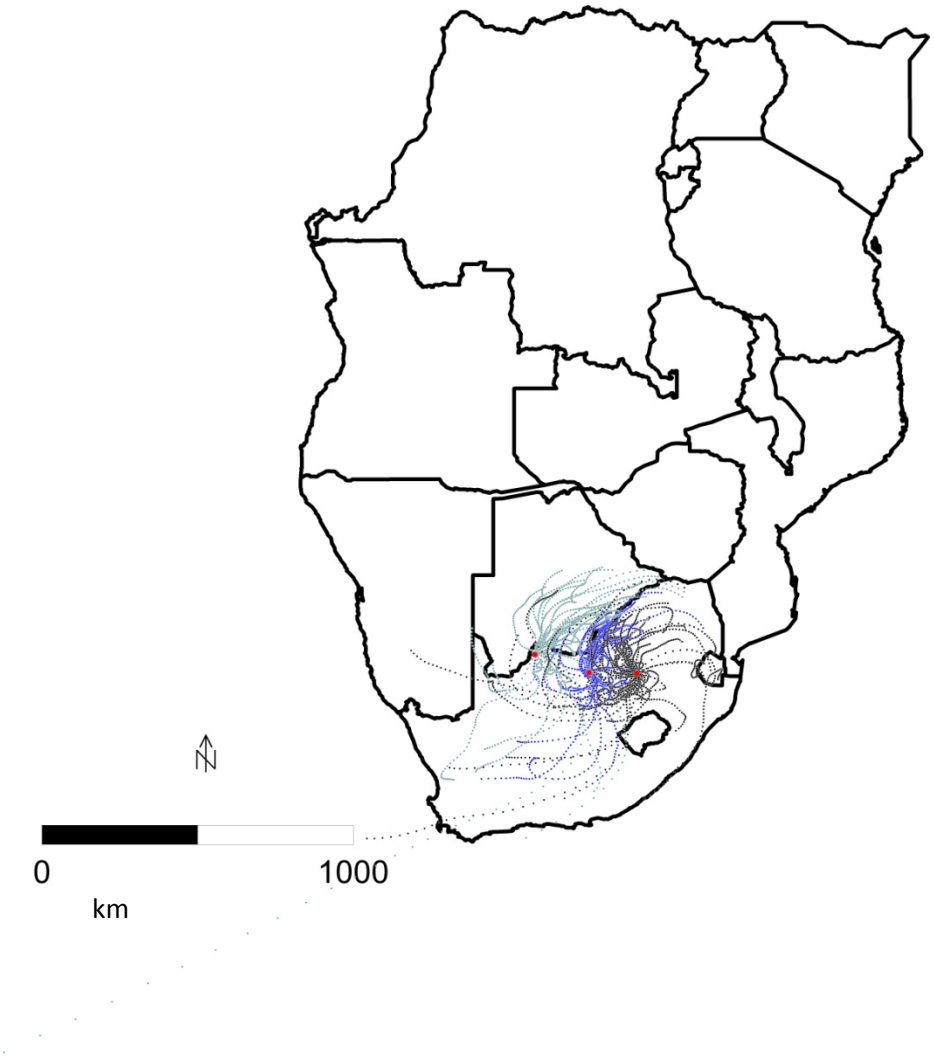

Figure 36: Backward air mass trajectory map for the month of August, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

The month of August (Figure 36) was characterised by a general movement of air from the northern parts of the country to the sampling areas, with some originating from the south. The distribution of air mass origins was wider compared with previous months. All sampling areas received air from the southern part of the country. One air mass crossed Cape Town towards Vanderbijlpark. It is clear that fewer air masses from the source area reached the sampling sites further east.

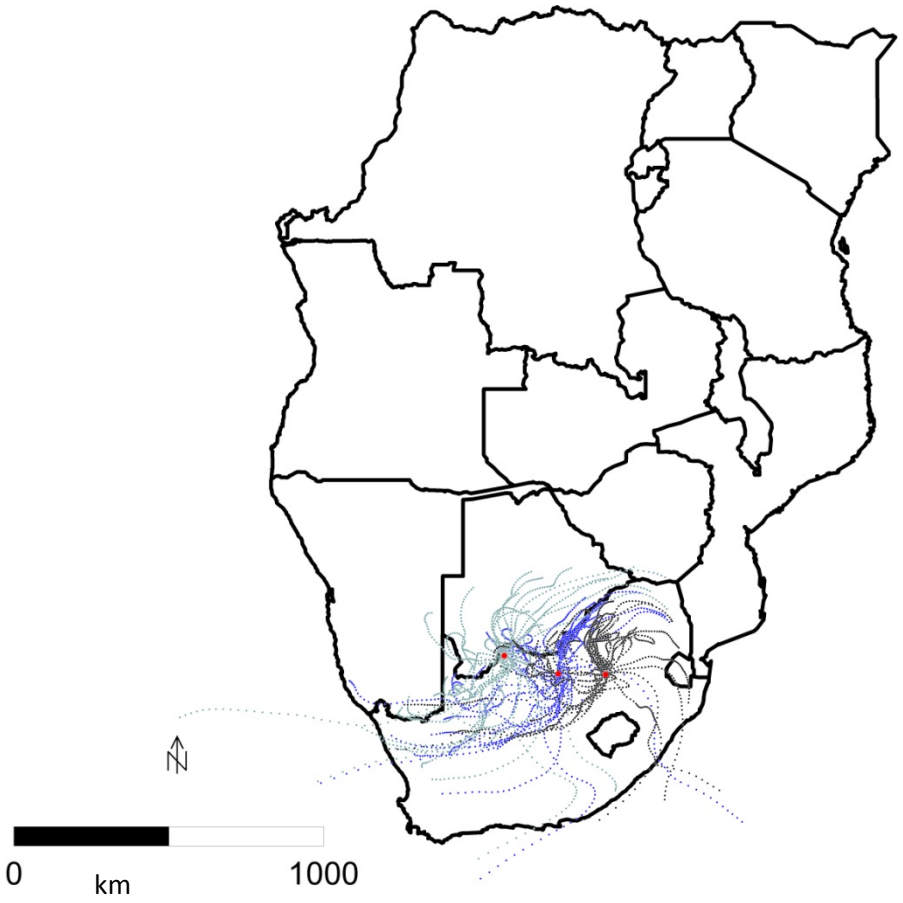

Figure 37: Backward air mass trajectory map for the month of September, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

The spread of trajectory origins in September (Figure 37) was much greater when compared to earlier months (Figures 29 and 30). Air travelled from eastern and northern South Africa to all three sampling sites. Vanderbijlpark had the most air mass origins from the IRS areas followed by Barberspan and lastly Molopo.

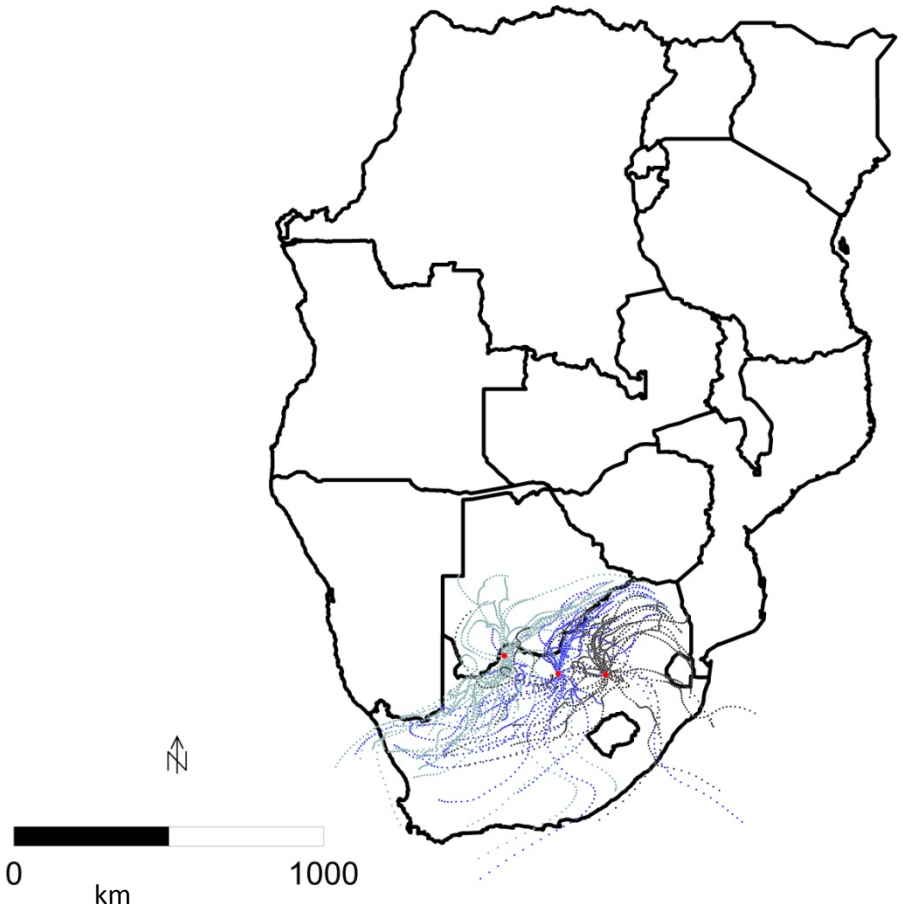

Figure 38: Backward air mass trajectory map for the month of October, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

Figure 38 shows air distribution for October. All three sites received air masses from all over the region. Air masses as far as Mpumalanga reached all three sites. Limpopo was the origin for air masses reaching all three sites. Air masses from the Western Cape also reached the sampling sites.

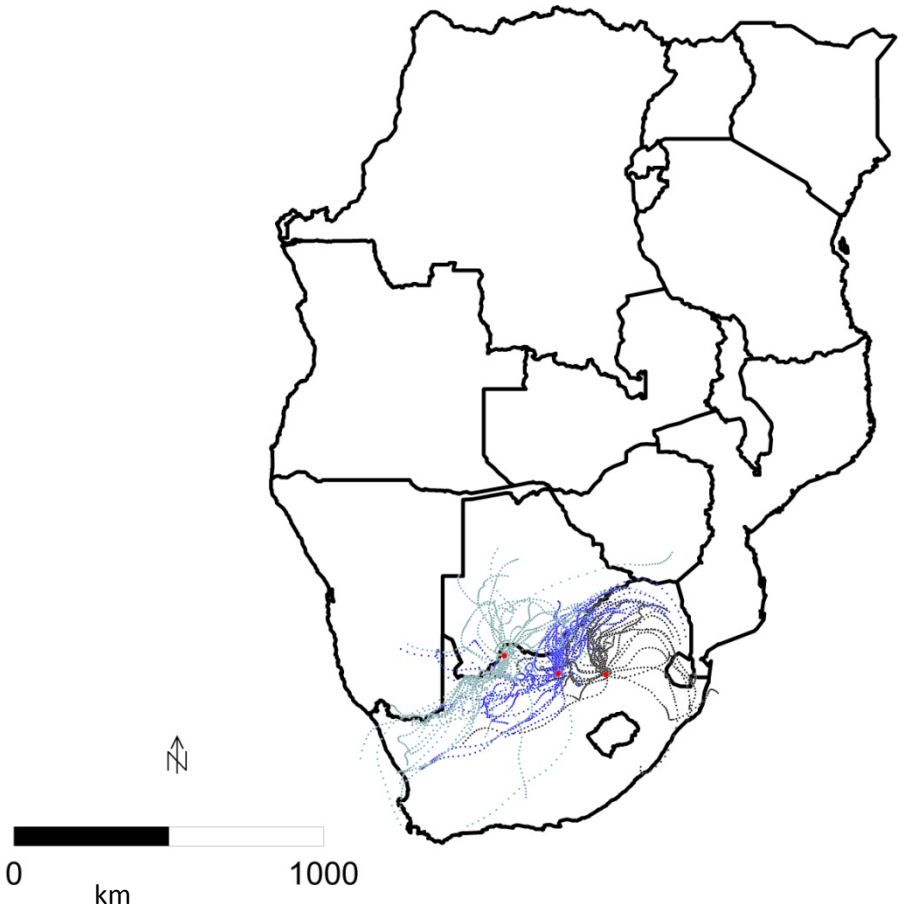

Figure 39: Backward air mass trajectory map for the month of November, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

In November (Figure 39), the length of trajectories shortened compared with August, September and October (Figure 37-40). Most air masses originated from the northern part of South Africa. Limpopo province continued to be the origin of the air masses at all the three sites.

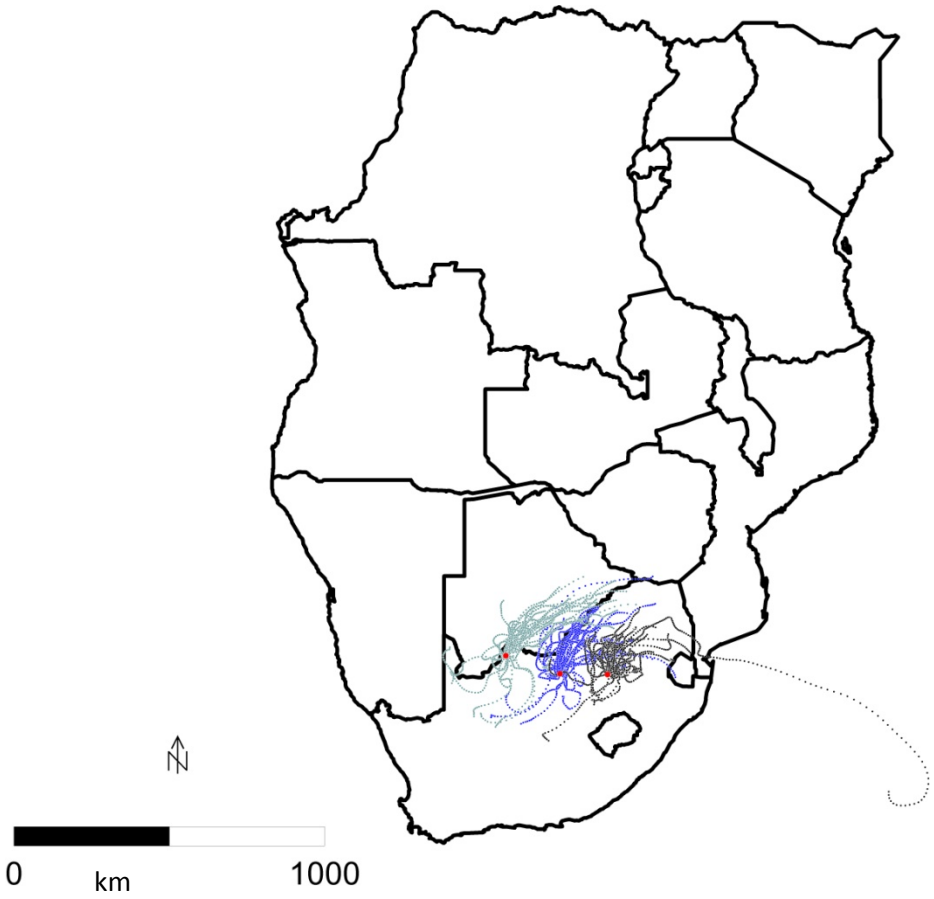

Figure 40: Backward air mass trajectory map for the month of December, 2008, from three sampling sites, each trajectory is a 24-hour backward trajectory of one site for each day of the month. Black = Vanderbijlpark, Blue = Barberspan Nature Reserve, Green = Molopo Nature Reserve.

December (Figure 40) had the smallest area of origins of air mass sources of the year. Air mass origins to Barberspan were restricted to the North West Province and Botswana. A similar pattern was noted at Molopo. Vanderbijlpark was also limited to air masses originating close to Gauteng.

CHAPTER 5: DISCUSSION

The fifth chapter is divided into three sections. Section A discusses the trends and levels of DDT metabolites at the three passive sampling sites. Section B turns its focus on the spread and, distribution of airborne DDT using forward trajectory maps, and identify areas possibly affected due to precipitation and impaction of the DDT out of the air mass. The last section, Section C, looks at the backward trajectories generated from the three sampling sites to see where the DDT in the filters may have come from.

5.1 SECTION A: The trends and levels of DDT and its metabolite at the passive sampling sites.

5.1.1 *o,p'*-DDT

o,p'-DDT is not a breakdown product but a constituent of the applied formulation, making up about 15% of the DDT used in IRS for malaria control (WHO, 2001; Bouwman *et al.,* 2006). Concentrations of *o,p'*-DDT (Figure 10) at the beginning of the year were low at all three passive sampling sites. This could be due to a high rate of wet deposition caused by the wet season. Ritter *et al.* (2005) states that rainfall and snow my remove chemicals in the air. Blais *et al.* (1998), states that deposition is speeded up by precipitation, and aids in removing the contaminants from the atmosphere and depositing them on the surface. Rainfall may have led to most of the pollutants (particulate and gas phase) being scrubbed out of the air and therefore not available for accumulation by the PUF filter.

The low concentrations recorded at the beginning of the year could also be due to prolonged degradation of the compound from the time of spraying in 2007. POPs are degraded through photolytic degradation (Berdowski *et al*., 1997). Photolytic degradation of *o,p'*-DDT in solid and gas phase may therefore also have contributed towards the low concentrations at the beginning of the year. Temperatures, which are high at the beginning of the year, may also lead to a high rate of degradation resulting in low concentrations (Berdowski *et al*., 1997).

DDT is sprayed for IRS around September to January, depending on conditions (Chapter 2). Due to vapour pressure, the compound volatilizes into gas phase and may then also adhere to

particulates. Most POPs are reintroduced into the atmosphere through this process (Berdowski *et al*., 1997; Ritter *et al.,* 2005). Windblown dust will also contribute towards DDT in air. However, because of breakdown and initial volatilization, fewer compounds will progressively be available for volatilization over time at the sites of application, causing a decrease in concentrations, after application stops, further downwind.

In June, concentrations in Vanderbijlpark began to increase (Figure 10). Photolytic degradation potential may have reduced in winter as nights in winter are longer, resulting in less photolytic potential. This may explain the increase in concentration in winter months. Halsall *et al*. (1998) explains this theory using the poles as an example where length of day affects POPs degradation. Photolytic degradation is high during periods of light, and minimal in darkness.

DDT is sprayed around September to January. By September, *o,p'*-DDT concentrations almost reached 7 ng/filter. The increase may be due to the latest application of DDT in the sprayed provinces. The increase might also be a result of volatilization of previously deposited *o,p'*-DDT. Seasonality and summer time maxima may be due to usage patterns and increased volatisation from soil at higher temperatures (Batterman *et al.,* 2008). Vanderbijlpark *o,p'*-DDT concentrations rose a month earlier than the other two sites. This site could have received earlier and greater concentration of *o,p'*-DDT mainly because of its relative proximity to the DDT sprayed areas, and hence explaining why Molopo had the least values. Over a long distance and time after the compound has been applied, it would have mixed with many air masses, hence a reduction in compounds on the filters due to dilution.

The presence of *o,p'*-DDT at remote areas such as Barberspan and Molopo indicate that LRT of the *o,p'*-DDT occurred. POPs are able to travel long distances and beyond national boundaries (AMAP, 1997; Ritter *et al.,* 2005), making them an international concern as Molopo is located close to Botswana. According Iversen (1996), wind speed affects airborne concentrations as it may introduce the compound back into the atmosphere. In dry desert areas, POPs will travel for longer distances as there are fewer geographical disturbances and vegetation to scrub the compounds from the air. Molopo maintained steady concentrations throughout the year, never

reaching higher than 1 ng/filter. Molopo is located the furthest from the potential source of *o,p'*-DDT (Figure 7). Barberspan also had a significant increase in monthly concentrations after July.

All of the factors and processes described above (time of application, volatilization, breakdown by photolysis and temperature, deposition, impaction, LRT, wind speed, wind direction, dilution, and distance from source) are also in effect for the other DDT compounds, so they will be treated in less detail, following.

5.1.2 *p,p'*-DDT

p,p'-DDT (Figure 11) had the highest concentrations of any of the DDT metabolites at all three sites. Batterman *et al.* (2008) also found levels of *p,p'*-DDT in Durban. The compound is predominant at 75% in the IRS formulation (WHO, 2001; Bouwman *et al.,* 2006), hence it's consistently detectable presence in air. The concentration of the compound decreased in between January and March, most likely as a result of increased wet deposition. The period between January and March is characterised by rainfall and this may have led to increased deposition. The floods experienced within the region during 2008 may have contributed to the dip in concentration. A slight increase in concentrations was also noted at all three sites between April and July. This could be due to a reduction in wet deposition as the rainy season had ended.

p,p'-DDT concentrations rose sharply from August onwards at all three sites. This could be attributed to the *p,p'*-DDT, applied during the 2nd half of the year, being semi-volatile, and reaching the passive sampler stations via wind. The increase in temperature around this time could also have volatised settled *p,p'*-DDT from previous seasonal applications. *p,p'*-DDT still remains in the environment due to its extensive historic use from previous years (Harrad, 2008). An increase in wind speed and therefore also of airborne dust may also have contributed.

The period between August and September gave the highest concentrations of *p,p'*-DDT at all three sites. Stronger winds and wind patterns may have resulted in LRT of *p,p'*-DDT to Molopo Nature Reserve and Barberspan Nature Reserve, located further away from the sprayed sites. Vanderbijlpark has a greater concentration most likely because of its relative proximity to the IRS areas (Figures 7 and 8a).

As for the other parent compound, *o,p'*-DDT (Figure 11), *p,p'*-DDT also showed a noticeable October to November dip in concentrations, at Vanderbijlpark and Barberspan, but not at Molopo.

5.1.3 *p,p'*-DDD

p,p'-DDD (Figure 12) concentrations were generally low throughout the year at all sampling sites, except between January and March. *p,p'*-DDD is a breakdown product from the initially sprayed *p,p'*-DDT, possibly explaining the lower concentrations compared to *p,p'*-DDT (Figure 11). Molopo had a fairly constant concentration, ranging between 0-1 ng/filter. Barberspan followed and then Vanderbijlpark with the highest, but concentrations remained below 5 ng/filter. Concentrations were highest at the beginning of the year, most likely due to the breakdown of *p,p'*-DDT from previous years of IRS, volatilization, and windblown dust.

Factors such as wet deposition during the rainy season, between January and April, and dry deposition through dust particles, could have led to the reduction in concentration in air. 2008 experienced floods and this could explain the increased wet deposition. Dilution of the compound could also be a major explanation for the reduction in concentrations as the year progressed. The compound may have reached the Vanderbijlpark sampling site still in greater concentration as it was subject to less dilution and degradation because of distance when compared to samplers further away. Molopo had a lower concentration that was more consistent throughout the year. In April, a slight increase was noted at all three sites. This may be because the rains had stopped and deposition was reduced, with the compound in the air being more available for trapping by the filters. Concentrations further reduced after April as

the winter became cooler. Cold temperatures do not promote volatilisation of POPs which was the only likely source at that time of the year.

Vanderbijlpark recorded the highest concentrations in any month. As for *p,p'*-DDT and *o,p'*-DDT, it is also probably because of its relative proximity to the DDT sprayed areas.

5.1.4 *o,p'*-DDD

o,p'-DDD (Figure 13), a breakdown product of *o,p'*-DDT, also had very low concentrations when compared with *o,p'*-DDT and *p,p'*-DDT (Figures 10 and 11). Until June, all sites had no detectable *o,p'*-DDD except for January and March at Vanderbijlpark. Low concentrations can again the attributed to the breakdown of the 15% of the o,p'-DDT of the sprayed formulation (WHO, 2001; Bouwman *et al.,* 2006). The concentrations of *o,p'*-DDD were so low most of the time that they probably remained present but below detectable levels.

An increase in levels was first detected in June-July at Vanderbijlpark, July-August at Barberspan, and August-September at Molopo. This is in the same order as increasing distance from the sprayed areas. The October-November dip, seen for *o,p'*-DDT and *p,p'*-DDT (Figures 10 and 11) was not evident for *o,p'*-DDD, but there was a flattening between September and October. This may have been due to the start of the rainy season when more compound was scrubbed out of the air by rain, and therefore not available for accumulation by the filters.

The presence of *o,p'*-DDD in a place as far as Molopo is evidence of the LRT the compound went through, even in its initially low quantities. The same factors regulating concentrations in air (time of application, volatilization, breakdown by photolysis and temperature, deposition, impaction, LRT, wind speed, wind direction, dilution, and distance from source) is therefore also likely in effect for *o,p'*-DDD.

5.1.5 *p,p'*-DDE

p,p'-DDE (Figure 14), the most prominent breakdown product of *p,p'*-DDT, had slightly higher concentrations when compared to other compounds, except for *p,p'*-DDT, and was detectable

throughout the year. Although there were changes in concentrations throughout the year, these changes did not seem as sharp as for the other compounds. Vanderbijlpark recorded the highest concentrations throughout the year. The chemical is highly persistent (Ritter *et al.,* 2005); hence it can still be detected months after application. Between January and April concentrations at all sites decreased, but the decrease was most prominent at Vanderbijlpark.

An increase in concentration was also noted from July-August onwards. It was pronounced in Vanderbijlpark. This could be because of volatilisation of the compound back into air from soil and from application.

Molopo generally had a steady concentration throughout the year. The relatively greater distance between Molopo and the sprayed areas (compared with the other two sites) may account for the lower relative concentrations as the compound undergoes more deposition, degradation and dilution as it moves further away from the source, with distance and attenuation of this most stable DDT compound, explaining the low but relatively steady concentrations. The effect of distance on concentration is clearly illustrated by the graphs as Vanderbijlpark had the highest concentrations and the reduction is noted at sites further away from the source areas.

5.1.6 *o,p'*-DDE

Together with *o,p'*-DDD, *o,p'*-DDE (Figure 15) generally had the lowest levels of all DDT compounds studied. From the beginning of the year till June, no *o,p*'-DDE was recorded at any site. Although traces of the compound were quantified later in the year, the quantities were low. The relatively (compared to the other compounds) low concentrations are also attributed to *o,p*'-DDE being a breakdown product of the sprayed *o,p'*-DDT, which originally only made up about 15% of the applied formulation. The climatic conditions of South Africa in the beginning of the year are characterised by high rainfall. Such conditions encourage greater wet deposition, reducing *o,p*'-DDE in the air (vapour phase and particulate) available for trapping by the filters.

The first quantifiable recordings were in June. From then on, the changes were very much the same except for absolute amounts on the filter. Concentrations decreased the further away the sites were from the sprayed areas. *o,p*'-DDE decreased sharply from September to October for all three sites, but at Molopo, detectable concentrations were only seen for November-December.

5.1.7 ΣDDT at all three sites

ΣDDT is the sum of all six DDT compounds measured and therefore integrates all of them proportionally, and will therefore follow the trends of the dominant components of ΣDDT, consisting, in this case, of *p,p'*-DDT, *o,p'*-DDT (the parent compounds), and, to a lesser extent, also *p,p'*-DDE. ΣDDT was detected at all three sites every month of the sampling period, with all three sites showing a similar pattern of change (Figure 16). Concentrations of DDT at Barberspan and Molopo were always lower than for Vanderbijlpark, most likely because of the relative distances between the sampling areas and the areas under IRS. Concentrations were relatively high at the beginning of the year, and decreasing following the end of the spraying season, due to dilution degradation, and scrubbing by precipitation.

ΣDDT levels increased from around August till yearend, with sharp increases seen at Barberspan Nature Reserve and Vanderbijlpark. The likely source is residual DDT from previous years and the DDT sprayed in the Limpopo, KwaZulu-Natal and Mpumalanga provinces for malaria control.

5.1.8 mean % *p,p'*-DDT of ΣDDT

p,p'-DDT is the active isomer in DDT sprayed for malaria control (Longnecker 2005; Wolff *et al*. 2000). It makes up about 77% of the DDT solution sprayed in IRS (Bouwman *et al*. 2006). Figure 16b shows that the mean percentages of the isomer through out the year is similar to the trends of ΣDDT (Figure 16a) and that this trend is subject to the same factors as stated above. Figure 16b shows that the increase in %*p,p'*-DDT of ΣDDT is consistent with IRS spraying months in South Africa and Swaziland. This support the deduction that the DDT detected at the

three sampling sites were (to an unknown extent) as a result of IRS in South Africa and Swaziland.

5.1.9 Overall interpretation

The detection of DDT on all sampling sites is consistent with the findings by GAPS study and Batterman *at el.* (2008). It is remarkable that even at the low levels in air, the geographic pattern of lower levels further away from the source areas was so consistent at all sites for all compounds. Although there were slight differences in trends between compounds, the general decreases following cessation of spraying at the beginning of the year and the increases from the middle of the year implicates the DDT used for IRS in malaria control much stronger than from any other possible legacy sources. Legacy sources of DDT are suspected to be almost countrywide from previous wide-scale use in agriculture. If legacy sources played a major role, much more even patterns (as perhaps *p,p'*-DDE does, Figure 14) would have been seen. Further support for implicating DDT from malaria control as the main driver for the observed patterns was the relatively higher concentrations of the parent *p,p'-DDT* and *o,p'*-DDT detected in the filters. Legacy sources would have had *p,p'*-DDE predominating as the major breakdown product. *p,p'-DDT* is the active isomer in DDT used for malaria control and its concentration increases during the summer months when it is applied is consistent with IRS spraying areas. Figure 16b about the %*p,p'*-DDT of ΣDDT reveals that the rise in percentages was associated with IRS as the %*p,p'*-DDT percentages increased during this period. The backward and forward trajectories also indicate that air mass movements (on some days) come from known areas where DDT is used for malaria control occurred. The combination of findings offer support for the deduction that the DDT sampled at the three sites are likely, in part, to have come from IRS areas in South Africa and Swaziland.

The trends in concentrations is therefore attributable to varying combinations throughout the year of time of application, volatilization, breakdown by photolysis and temperature, deposition, impaction, LRT, wind speed, wind direction, dilution, and distance from source.

The above results show the utility value of the relatively low-cost passive sampling systems used, by providing data that would have been far more costly to obtain by using active samplers. The data also shows that the use of forward and backward trajectories from source and towards target areas is valid and warranted, as will be discussed in the following two sections.

5.2 Section B: Forward trajectories

A major motivation for the SC was the discovery of POPs contamination in relatively remote Arctic regions, thousands of miles from any known source. Kurt-Karakus *et al.* (2006) and Ritter *et al.* (2005) both state that a series of pesticides used in the past have been found in areas in which they were not known to have been used. Under different climatic conditions, atmospheric circulation patterns may play a role in POPs movement and distribution. POPs can be transported by wind, water, and biota, and therefore POPs generated in one country can and do affect people and environments further away from where they were used or released (Ritter *et al.,* 2005; AMAP, 1997). The compounds are persistent for long periods in the environment and can accumulate and pass from one species to the next through the food chain.

This section looks on a monthly basis at the forward trajectory patterns generated through HYSPLIT to determine the movement of air masses from areas under IRS. The assumption underlying the following Sections 2 and 3 is that DDT is transported by air from the sprayed areas – the data from Section 1 is sufficient to assume that LRT of DDT from these areas is indeed happening and present in air at ground level. There are assumptions inherent in using trajectories as was done here. The starting height was 10m at the source point. Subsequent air movements do not necessarily follow this height and much admixture would occur. However, the large-scale approach used here was done to identify the major air mass movements, with less certainty and importance to be given to single trajectories or trajectory streams with few trajectories. The air mass trajectories were also run for 24 hours per trajectory, so longer movements are possible, but considered to be less of a factor due to dilution, breakdown, and scrubbing of the DDT compounds as illustrated by the relatively lower concentrations in filters at Molopo when compared with the other stations, discussed in Section 1.

The forward trajectory maps (Figures 17-24) show the possibility of LRT of DDT from the sprayed area reaching areas as far as the Indian and Atlantic oceans and the Kalahari Desert in a single day. Though the shape and distribution of the trajectory patterns may appear similar and

consistent between months, the patterns vary. This is because of the different sampling periods, weather patterns, rainfall, wind speed, and temperature. Temperature, sunshine, wind speed or wet depositions are some of the factors affecting the fate and lifespan of the DDT compounds in the atmosphere, as discussed in Section 1.

Overall, when considering Figures 17-24, it can be seen that there is a dominant trajectory stream from the sprayed areas towards the north-west. A secondary stream is often discernable going west and to the south around Lesotho. Another trajectory stream heads south and then west following the coast, also pivoting around Lesotho, and then out into the southern Indian Ocean. April to August (Figures 20-24) sees some air masses moving north-east towards and over Mozambique and then out to the central Indian Ocean. Some air masses reached as far as Zambia, Namibia, the eastern parts of South Africa, and even Angola, within one day. These movements will be considered in more detail below.

5.2.1 Trans-boundary movement

Forward air mass trajectories reveal an important aspect of trans-boundary air pollutant movement. Most countries surrounding South Africa and Swaziland are potentially subjected to DDT contamination from the sprayed areas (Figures 17-24). The countries affected include Botswana, Lesotho, Mozambique, Zambia, Zimbabwe, and even as far as Namibia and Angola. Air movements (Figures 17-24) generally moved to the north-west away from sprayed areas. During months with a wider spread of trajectories such as January, February, April, July, August, September and December (Figures 17, 18, 19, 22, 23 and 27), most parts of Botswana received air masses from the sprayed areas of South Africa and Swaziland. The greater part of Botswana is therefore likely to experience DDT contamination as the chemical is able to travel and spread over a vast area (Wania and Mackay, 1996; Ritter *et al.,* 2005; Scheringer, 2009). The month of September (Figure 25) was of particular importance as it is usually the month when spraying starts. DDT concentrations can be expected to be particularly high and increasing (as shown in Figures 10-16) and hence the degree of elevated levels. Botswana is a desert area with little vegetation and disturbance in air movement. In dry desert areas and during summers, POPs will

travel for longer distances as there are fewer disturbances (Iversen, 1996; Macdonald *et al*., 2000). The relatively flat land also offers less potential for impaction. However DDT also has the ability to bind to dust particles (Campbell, 1998), travel with it, and eventually be deposited when the dust settles or when scrubbed out of the air with precipitation.

Air masses also moved towards Zimbabwe (Figures 20-25). The southern part of Zimbabwe is a malaria area (Masendu *et al.,* 2005) and it should be kept in mind that DDT may also be used for malaria control in this region, thereby not only becoming a potential sink area, but also a source area. Trajectories from the sprayed areas in South Africa and Zimbabwe were generally limited to the southern part of Zimbabwe, (Figures 20-25), with very little moving up into the Midlands Province of Zimbabwe. Impaction may be a major factor here as the vegetation is more when compared with Botswana, which is an arid area (Iversen, 1996; Macdonald *et al*., 2000). Impaction on vegetation may contaminate vegetative life together with the associated soil with DDTs as the compounds may be washed off the trees during rainfall. DDT is hydrophobic and well absorbed by soils; the chemical may be present in these soils for years to come. DDT in soil can also be absorbed by some plants and by the animals or people who eat those crops (ATSDR, 2002). This poses a risk of unknown magnitude to the environment and human health.

Air masses also moved to the western part of Zimbabwe and Kariba through the Zambezi Valley (Figures 20 and 24). Masendu *et al.* (2005) reports that Kariba town is a malaria area also under IRS. The air movement from South Africa and Swaziland would contribute towards the DDT levels in air, but the extent of relative LRT contribution would likely be low as this area is also a potential DDT source area. Kariba is a world-renowned tourist destination attracting people from all over the world.

Swaziland also received air masses from the sprayed areas (Figures 17-28). On the trajectory maps, the whole of Swaziland is covered by the trajectories of air masses coming from the sprayed areas in South Africa, and from Swaziland herself (not clearly visible on the maps shown, but the individual trajectory maps shows the clearly). This was the case throughout the

year including during the spraying seasons. Like Zimbabwe, Swaziland uses IRS for malaria control making use of DDT. With that in mind, the concentrations of DDT in Swaziland air may be elevated especially during spraying as spraying may take place around the same time as air masses from South Africa, potentially also with DDTs, cross the country. The whole population and biota of Swaziland might therefore be exposed to DDT through inhalation and other secondary modes of contamination.

The southern part of Mozambique received air masses from the sprayed areas (Figures 17-20). Few air masses moved towards Mozambique in the beginning of the year. The months that followed between April and July (Figures 20-22) saw an increase in air mass distances into Mozambique. Maputo is the capital of Mozambique with a population of 1 800 000 people. Throughout the year, air masses from the sprayed sites moved towards the Maputo area. Southern Mozambique is therefore likely to be contaminated by DDTs from the South African and Swaziland sprayed areas. The Maputo corridor is very busy as a result of the port. A number of people move through the Corridor every day and are potentially exposed to the DDT in air. Traffic increases towards the yearend as people return home from South Africa for the festive season. This coincides with the IRS spraying activities. The concentrations of DDTs in this part of the year are much higher (Figures 10, 11 and 16) and may pose an increased risk to human and environmental health.

The Indian Ocean is also likely to be polluted by DDT in air coming from the sprayed areas covered here. Air masses moved off-land eastwards towards the sea, especially May till yearend (Figures 21-28). The number of air masses reaching the ocean increased as the year progressed. The trajectories are air mass movements for a single day, indicating that air masses may even carry the pollutant further towards other regions in the Indian Ocean. Since POPs can be transported through air and water, the deposition of POPs in the Indian Ocean may lead to the spread of POPs to even further regions via oceanic currents. The presence of POPs in these media to places such as the Arctic has been recorded (Hung *et al.,* 2010).

Semi-volatile contaminants such as the DDTs are volatilized in regions of use, transported via air and deposited in colder climates at higher altitudes (Mark *et al.,* 2004). This is due to the high precipitation in many mountain regions. On the Drakensberg Mountains, heavy winter snow is experienced. This may lead to deposition of POPs in mountainous areas (Blais *et al.,* 1998). However, although Lesotho is reasonably close to the malaria sprayed areas, only few air masses reached Lesotho. June, July, August, and December (Figures 22-24 and 28) were the only months with a few air masses reaching Lesotho. The air masses may have been influenced by the Drakensberg Mountains, hence seemingly protecting Lesotho from airborne contamination. It would be interesting to analyse snow and sediments from the upper reaches of the Drakensberg Mountains to confirm whether DDT is indeed reaching the Drakensberg, or if it would be lower than levels from similar mountainous regions.

Namibia may also experience DDT transported from South Africa and Swaziland. Though the frequency of air masses from the sprayed area reaching Namibia was low (Figure 24), the air masses presumably carrying DDT covered the distance in a single day. Monitoring of such movements is important for planning and coming up with solutions.

5.2.2 Potential areas with increased potential of airborne DDT contamination

Because of their lipophilic nature, POPs tend to accumulate in matrices rich in organic matter such as soil, sediment, and biota, and can bio-accumulate in the food web (ATSDR, 2002; Schecter *et al.,* 2006). Studies have linked POPs exposures to declines in health, diseases, or abnormalities in wildlife and humans (Jones *et al,* 2008; Sagiv *et al.,* 2008). It is therefore important to investigate areas where DDT is not currently used for the potential of receiving airborne DDT. The following section will investigate some but not all areas that potentially may be of concern.

5.2.2.1 Environmental exposure

The Kruger National Park is close to DDT sprayed areas and has a history of DDT used in the camps for malaria control, although this is likely to be small amounts. The Park's close proximity

to DDT sprayed areas puts it at increased risk of receiving airborne DDT. DDT travelled into the southern part of Mozambique (Figures 17-20), an area rich in wildlife. Wildlife in the area is therefore potentially at risk of DDT exposure from South Africa and Swaziland. Across the border shared by Zimbabwe, Mozambique, and South Africa is the Limpopo National Park (large cross-border park between Zimbabwe and South Africa). According to the forward trajectories, wildlife in these parks is likely to be continuously exposed to the DDT in air from the sprayed areas. Banhina National Park is located between the Limpopo and Changane rivers and also has rich wildlife. All the flora and fauna in this region may be at risk of possible contamination. Waterways are also at risk, including humans that use this water for domestic purposes. Continuous drinking and consumption of these contaminated water sources may lead to future adverse impacts as DDT is able to bio-accumulate in body tissue and fat (Ritter et al., 2005).

The North West Province has a number of nature reserves. Areas, such as Barberspan Nature Reserve, are likely to receive air masses from the sprayed areas (Figures 10-16 and 23-28). On the border between Botswana and South Africa is the Molopo Nature Reserve. DDTs and air masses reached this area (Figures 10-16 and 23-28). The reserve is potentially at risk of DDT as it may affect birdlife through accumulation. DDT contamination is likely during the spraying months. Many birds of prey such as osprey, eagles, pelicans, falcons, and hawks can be heavily impacted by DDT (Gregor *et al.*, 1998). DDTs (especially p,p'-DDE (Colburn *et al.,* 1996)) pose a risk to their reproduction and survival as it causes eggshell thinning and hence reducing the chances of the chick hatching properly. Predatory birds are the most sensitive to this effect by DDT (Gregor *et al.*, 1998; ATSDR, 2002; Lovette, 2010). Birds with accumulated DDT can also aid in DDT LRT.

The Indian Ocean received DDT from South Africa (Figures 21-28). The DDT may not have a direct impact on the coastal and off-shore ecosystem, but at a bigger scale it may. A computer simulation of the environmental fate of DDT has revealed that substantial quantities of the pesticide are still being released from the world's oceans, despite widespread restrictions on its use during the 1970s (Lovette, 2010). Lovette, (2010), referred to a computer model to simulate the circulation of DDTs between ocean and atmosphere between 1950 and 2002. The model

shows that since the 1970s, the re-emission of DDT from the ocean has increased in comparison to the three known current release sources of new DDT; its continued use in some countries for malaria control, degrading storage canisters, and other pesticides that contain DDT as a contaminant. The DDT carried by the air masses may be deposited in the Indian Ocean together with that coming into the ocean through waterways, and then accumulate in the colder Southern Ocean and Antarctic, as has been found for the Arctic (Li *et al.*, 2002). This is of ecological concern because marine organisms concentrate DDT by factors of millions through bio-accumulation. As DDT moves up the food web, the concentration reaches levels where it can have toxic effects on fish or the animals that eat them (Lovette, 2010; Ewald *et al.*, 1998; Wahlström, 1987).

5.2.2.2 Human exposure

DDT is used for malaria control as IRS in the Limpopo Mpumalanga and KwaZulu-Natal provinces. Studies by Bouwman *et al.* (2006; 2012) show that DDT accumulates in human breast milk and is passed on to breastfeeding infants indicating risk to mothers and infants. Due to LRT, DDT can travel over long distances to regions where it is not in use (van Dyk *et al.,* 2010). The DDT sprayed in South Africa and Swaziland may have travelled to the southern part of Zimbabwe (Figures 20-25), and central South Africa (Figures 22-27). The Gauteng Province had a consistent inflow of air coming from the sprayed areas throughout the year. Gauteng is highly populated and its population is likely exposed to DDT coming from malaria control.

Human exposure may also come from eating contaminated food. Kariba is a malaria zone and under IRS (Mpofu, 1987). Together with the DDT sprayed in Kariba and that from South Africa and Swaziland, the risk to the residents and the environment is increased. Through scrubbing of DDT from the air during rains, DDT may end up in water systems and bio-accumulate in fish (Wahlström, 1987). The months of January, February, April, July and September (Figures 17, 18, 20, 23 and 25) are characterised by heavy rainfall and may lead to increased deposition of DDT in water. This poses a human health risk by consuming dietary fish that have accumulated DDT.

More than 62% of people in Africa live in rural areas (although this is changing rapidly) and the main source of water in rivers and water streams (WHO-UNICEF WSS Assessment Report, 2000). The same water from rivers is used for domestic purposes in rural areas in most parts of southern Africa, (which is the region mainly affected by DDT sprayed in South Africa and Swaziland). The hydrophobic nature of DDT also allows it to be well absorbed by soils, therefore present and available in the soil for long periods and may increase human exposure through contact, ingestion, inhalation, and via food (ATSDR, 2002). Airborne DDT may therefore contribute directly and indirectly towards human contamination, together with DDT from other routes.

5.3 Section C: Backward trajectories from the passive sampling sites

This section looks at the backward trajectories generated through HYSPLIT. The trajectories help to determine the movement of air masses to the passive sampling sites at Molopo, Barberspan, and Vanderbijlpark. The previous two sections have shown that the assumption that DDT can travel from DDT-sprayed areas longdistances and still be detectable in air a remote sites is valid.

A daily back trajectory was run for each month of 2008 to detemine the origin of the daily air mass (Figures 29-40). Months between August and November (Figures 36-39) had a wide spread of air mass origins, influenced by factors such as weather, wind speed and direction. August is a known windy month in the southern parts of Africa (van Zyl, 2003). The maps show an increase in movement of air from the Limpopo Province toward Barberspan during summer. This may have increased the concentration of DDT metabolites at the sampling areas. The back-trajectory maps (Figures 37-40) indicate air originating from DDT sprayed areas, Limpopo, and this coincides with the increase in DDT concentrations at the three sites. This may explain the increase in concentrations at yearend (Figures 10, 11, and 16). Between February and June (Figures 30-34) the wind speeds may have dropped and this may explain the closer proximity of the air mass origins to the sampling sites.

The dry windy air in months such as June, July, August and September (Figures 34-37) allowed for the movement of air over longer distances. In dry dusty months, DDT may travel longer distances as transportation is aided by DDT associated with dust particles (Campbell, 1998). DDT particles can travel much easier to dry areas like Molopo because of the limited wind breaks and other vegetation. The presence of DDT metabolites in Molopo Nature Reserve and Barberspan is evidence of LRT over dry semi desert areas. Back trajectories indicate possible air mass origins to be in areas where IRS is used for malaria control. Air mass movement towards and in Vanderbijlpark may have been affected by the industrial buildings, other man made structures, and urban secondary woodlands.

Back trajectories also showed that the sampling sites received a number of air masses from the northern part of South Africa such as Limpopo. This may have carried DDT metabolites to the sampling sites especially during spraying months like September (Figure 37). Air mass movements from the sprayed areas towards the passive sampling sites were frequent throughout the year (Figures 29-40). These movements presumably played a large role in the LRT of DDT metabolites to the sampling areas.

Therefore, there are air masses reaching the sampling sites originating from both 'clean' sites and DDT source areas. The different origins may have reduced the concentrations of the DDTs by dilution with 'clean' air at the sampling sites. Active, daily sampling, together with the the back trajectories from the active sampling sites, would show whether different origins indeed carry different amounts of DDTs.

Chapter 6: CONCLUSIONS AND RECOMMENDATIONS

The paradox of DDT has been debated over many years and disputed the world over (Bouwman et al., 2011). The debate on whether DDT use for malaria control should be continued or whether it is causes insidious diseases or conditions continues. This study aimed to shed more knowledge on the origin, movement, distribution, and fate of DDT in air of southern Africa and the adjacent oceans.

Over the years, the knowledge on air quality in southern Africa has been limited. An industrialised area, agricultural area, and nature reserve on a transect of increasing distance away from the DDT-sprayed areas was chosen for passive air sampling. The movement of contaminates was tracked through forward (from the source areas) and backward (towards the sampling sites) trajectories, supported with DDT concentration and trend information from the three sampling stations. Air mass origins and areas at risk of exposure and/or contamination were noted.

The aims of the project are listed and annotated below:

- *Passive sampling and analysis of airborne DDT at three sites; Vanderbijlpark, Barberspan Nature Reserve, and Molopo Nature Reserve.*

  DDTs were detected at all three sampling sites. Passive air sampling showed that the concentrations of DDT decreased with increased distance from the potential sources of DDTs. DDT concentrations decreased from Vanderbijlpark to Barberspan, and Molopo consistently having the lowest concentration. Together with the higher levels of *p,p'*-DDT and *o,p'*-DDT (the parent compounds) closer to the source areas, confirmed that the assumption that DDT came from IRS areas is valid, and that backward and forward trajectories would be informative. The increase in %*p,p'*-DDT of ΣDDT is also consistent with IRS spray patterns and supports the deduction that the DDT detected came from IRS areas.

- *Determine the distribution of DDT by air movements from DDT-sprayed areas on a monthly basis from 54 sites using HYSPLIT.*

  Forward trajectories revealed that the airborne DDT is likely to move away from the sprayed areas to adjacent and further regions. The trajectories showed that the spraying of DDT in South Africa and Swaziland is likely to be a source, via LRT, of DDT contamination on a sub-continental scale and contributing to the spread of DDT to oceans and possibly from there, via ocean currents, to the Antarctic.

- *Compare model data with passive air sampling data*

  The data from the passive sampling sites was consistent with the information from the forward trajectories. It seemed that fewer trajectories originating from the source areas reached the sampling sites, and more during the spaying season when the concentration of DDTs in the PUFs were also higher.

- *Determine the populations and ecosystems that may be exposed to airborne DDT.*

  A vast spread of air mass trajectories of DDT metabolites places many ecosystems at risk. The Kruger National Park is at presumably high risk due to its close proximity to the sprayed area. The bird reserves and other parks in the region are also at risk. Urban areas in and around the sprayed areas are also at risk, the risk decreasing with an increase in distance. It is also clear that DDT carrying air masses will also reach the oceans, especially the Indian Ocean.

- *Establish the spraying period with the longest and shortest air transportation distances.*

  Forward trajectories and data from passive air sampling sites reveal that DDT spread from sampling sites is high around August to December. To reduce the spread of DDT, it may be more advisable to conduct IRS in less windy months (if compatible with malaria control requirements), such as February to June, to help reduce DDT spread.

- *Determine any trans-boundary LRT of DDT via air.*

  The forward trajectories illustrated air mass movements for a single, 24 hour, day. It is interesting to see that in 24 hours, air masses in some months travelled to most of the southern African countries, namely, Zambia, Botswana, Namibia, Angola, Mozambique, and Zimbabwe. Forward trajectories also showed that air masses travelled as far as the Indian and Atlantic oceans. Trans-boundary LRT movement was evident with the potential of the DDTs to go even further to other regions via oceanic currents.

- *Identify potential airborne DDT sampling sites as a result of long range transport of DDT.*

  A number of areas were identified to be areas of interest for future studies on LRT of DDT. The Drakensberg Mountains is an important area of study to confirm whether this mountain range is a sink for DDT and other POPs, or if the air currents moving around it may be deflected. The Kruger National Park is also a potential site to help assess the environmental risks of DDT is the environment. Passive sampling in the sprayed areas will provide information on how much DDT is actually in the air, exposing residents, and how much of the DDT there w could reach other areas. The maps will also provide information for site selection for future projects, depending on the issues to be investigated.

Traces of DDT were detected using passive air samplers at all three sampling sites. Forward trajectories showing that air masses moved from the DDT sprayed areas towards the passive air sampling sites, as well as higher %*p,p'*-DDT of ΣDDT during the spraying months, both strongly imply that DDT sprayed areas were the sources of the DDT detected at the passive air sampling sites. The backward trajectories from the sampling sites further confirmed that some of the air masses reaching the sampling sites had indeed originated from the sprayed area. Air masses moved far and wide from the source areas, confirming LRT of DDT and DDT's air borne trans-boundary movement.

Recommendations

- Conduct passive sampling in sprayed areas.
- Establish passive sampling sites at border towns and possibly neighbouring countries, to confirm and semi-quantify trans-boundary LRT of DDT.
- Conduct passive air sampling in the food producing regions of the Lowveld, adjacent to the sprayed areas.
- An adjustment of the spraying seasons to months that reduce the likely sprayed of DDT, for example between February and May, may be considered.
- Conduct a similar exercise for Zimbabwe, a potential source of DDT to southern Africa.
- More collaborations between countries using IRS for malaria control in the SADC region.
- More studies to estimate the amount of DDT deposited at difference stages of its movement from sprayed areas and hence quantify the concentrations deposited at particular areas. Modelling could be done with more advanced modules on HYSPLIT.
- Conduct studies to investigate other airborne compounds.
- To raise public awareness on the effects of DDT in order to motivate for alternative methods and means to deal with malaria in Africa.

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REFERENCES

Aislabie, J., Richards, N. & Boul, H. 1997. Microbial degradation of DDT and its residues — a review. *New Zealand journal of agricultural research,* 40:269-282.

ATSDR. 2002. Agency for Toxic Substances and Disease Registry. Dicholrodiphenyldicholoroethane: Toxicological profile. [Web:] http://www.atsdr.cdc.gov/tfacts38.pdf.

ATSDR. 2007. Agency for Toxic Substances and Disease Registry. Dichloro-diphenyl-trichlorethane: Toxicological profile. [Web:] http://www.atsdr.cdc.gov/tfacts43.pdf.

Bahadur, J. 1993. The Himalayas: A third polar region. Snow and glacier hydrology, Kathmandu, 1992. http://iahs.info/redbooks/a218/iahs_218_0181.pdf (Date of access: 24 April 2013).

Baker, H.G., Opler, P.A. & Baker, I. 1978. A comparison of the amino acid complements of floral and extrafloral nectars. *Botanical gazette,* 3:322-332.

Barron, M.G. Galbraith, H. & Beltman, D. 1995. Comparative reproductive and developmental toxicology of PCBs in birds. *Biochemistry and Physiology*: Part C, 112C: 1-14.

Bartkova, J., Hořejší, Z., Koed, K., Krämer, A., Tort, F., Zieger, K., Guldberg, P., Sehested, M., Nesland, J.M. & Lukas, C. 2005. DNA damage response as a candidate anti-cancer barrier in early human tumorigenesis. *Nature,* 434:864-870.

Batterman, S.A, Chernyak, S.M, Gounden, Y, Matooane, M, & Naidoo, R. 2008. Organochlorine pesticides in ambient air in Durban, South Africa. *Science of the total environment*, 39:119–130

Bernes, C. 1998. Persistent organic pollutants: A Swedish view of an international problem. *Swedish environmental protection agency,* 16:147-153.

Bernes, C. & Lundgren, L. 2009. Use and misuse of nature's resources: An environmental history of Sweden. *Swedish environmental protection agency,* 21:16–27.

Bernes, C. & Naylor, M. 1998. Persistent organic pollutants: A Swedish view of an international problem. Almqvist & Wiksell International, Stockholm, Sweden.

Bouwman, H., Becker, P.J., Cooppan, R.M. & Reinecke, A.J. 1992. Transfer of DDT used in malaria control to infants via breast milk. *Bulletin of the World Health Organization,* 70: 241-250.

Blais, J.M., Kimpe, L.E., McMahon, D., Keatley, B.E., Mallory, M.L., Douglas, M.S. & Smol, J.P. 2005. Arctic seabirds transport marine-derived contaminants. *Science,* 309:445-455.

Blais, J.M., Schindler, D.W., Muir, D.C., Kimpe, L.E., Donald, D.B. & Rosenberg, B. 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. *Nature,* 395:585-588.

Bornman, R., Kylin, H., Sereda, B. & Bouwman, H. 2012. DDT in breast milk: Intake, risk, lactation duration, and effect of gender. *Environmental pollution,* 709:152-163.

Bouwman, H. & Kylin, H. 2009. Malaria control insecticide residues in breast milk: The need to consider infant health risks. *Environmental health perspectives,* 117:1477-1480.

Bouwman, H., Sereda, B. & Meinhardt, H. 2006. Simultaneous presence of DDT and pyrethroid residues in human breast milk from a malaria endemic area in South Africa. *Environmental pollution,* 144:902-917.

Bouwman, H., Van den Berg, H. & Kylin, H. 2011. DDT and malaria prevention: Addressing the paradox. *Environmental health perspectives,* 119:744-747.

Burkow, I.C. & Kallenborn, R. 2000. Sources and transport of persistent pollutants to the Arctic. *Toxicology letters,* 225:11287-11292.

Carson, R. 2002. Silent Spring: 40th anniversary edition. Mariner books, New York.

Campbell, P. 1998. Guidance document: Higher-tier aquatic risk assessment for pesticides: From the SETAC-Europe/OECD/EC workshop, held at Lacanau Ocean, France on the 19-22 April 1998. Lacunae Ocean: SETAC-Europe.

Carrera, G., Fernández, P., Vilanova, R.M. & Grimalt, J.O. 2001. Persistent organic pollutants in snow from European high mountain areas. *Atmospheric environment,* 35:245-254.

Chaemfa, C., Barber, J.L., Moeckel, C., Gocht, T., Harner, T., Holoubek, I., Klanova, J. & Jones, K.C. 2009. Field calibration of polyurethane foam disk passive air samplers for PBDEs. *Journal of environmental monitoring,* 11:1859-1865.

Chen, A. & Rogan, W.J. 2003. Non-malarial infant deaths and DDT use for malaria control. *Emerging infectious diseases,* 9:960-964.

Chen, D., Bi, X., Liu, M., Huang, B., Sheng, G. & Fu, J. 2011. Phase partitioning, concentration variation and risk assessment of polybrominated diphenyl ethers (PBDEs) in the atmosphere of an e-waste recycling site. *Chemosphere,* 82:1246-1252.

Chikuni, O., Nhachi, C., Polder, A., Bergan, S., Nafstud, I. & Skaare, J. 2002. Effects of DDT on paracetamol half-life in highly exposed mothers in Zimbabwe. *Toxicology letters,* 134:147-153.

Cohn, B.A., Wolff, M.S., Cirillo, P.M. & Sholtz, R.I. 2007. DDT and breast cancer in young women: New data on the significance of age at exposure. *Environmental health perspectives,* 115:1406-1414.

Colburn, T., Myers, J.P. & Dumanoski, P. 1996. Hormonal sabotage. *Natural history,* 34:105-112.

Coticelli, P. 2007. WHOPES and its impact on long lasting insecticidal net availability. *Africa fighting malaria occasional paper.* http://fightingmalaria.org/research.aspx?id=773 Accessed [6 April, 2013]

Craig, G.R. & Ogilvie, D.M. 1974. Alteration of t-maze performance in mice exposed to DDT during pregnancy and lactation. *Environmental physiology and biochemistry*, 4:189–199.

de Jager, C., Farias, P., Barraza-Villarreal, A., Avila, M.H., Ayotte, P., Dewailly, E., Dombrowski, C., Rousseau, F., Sanchez, V.D. & Bailey, J.L. 2006. Reduced seminal parameters associated with environmental DDT exposure and *p,p'*-DDE concentrations in men in Chiapas, Mexico: A cross-sectional study, *Journal of Andrology,* 21:16–27.

Dommergue, A., Ferrari C.P, M. Amyot, *S. Brooks*, F. Sprovieri, F. & Steffen, A.: Spatial coverage and temporal trends of atmospheric mercury measurements in Polar Regions. In: Mercury fate and transport in the global atmosphere, emissions, measurements and models*. Atmospheric chemistry and physics,* 10:3309-3329.

Eskenazi, B., Chevrier, J., Rosas, L.G., Anderson, H.A., Bornman, M.S., Bouwman, H., Chen, A., Cohn, B.A., De Jager, C. & Henshel, D.S. 2009. The Pine River statement: Human health consequences of DDT use. *Environmental health perspectives,* 117:1359-1367.

Evenset, A., Christensen, G., Carroll, J., Zaborska, A., Berger, U., Herzke, D. & Gregor, D. 2007. Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. *Environmental pollution,* 146:196-205.

Ewald, G., Larsson, P., Linge, H., Okla, L. & Szarzi, N. 1998. Bio-transport of organic pollutants to an inland Alaska lake by migrating sockeye salmon (*Oncorhynchus nerka*). *Arctic,* 42*:*40-47.

Fan, Z.H.T. 2011. Passive air sampling: Advantages, limitations, and challenges. *Epidemiology,* 22:132-138.

Franz, T.P., Eisenreich, S.J. & Holsen, T.M. 1998. Dry deposition of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons to Lake Michigan. *Environmental science & technology,* 32:3681-3688.

Gascon, M., Vrijheid, M., Martinez, D., Forns, J., Grimalt, J.O., Torrent, M. & Sunyer, J. 2011. Effects of pre and postnatal exposure to low levels of polybromodiphenyl ethers on neurodevelopment and thyroid hormone levels at 4 years of age. *Environment International,* 31:605–611.

Gordon, T.J. & Helmer, O. 1964. Report on a long-range forecasting study, Oxford, London.

Gorecki, T. & Namieśnik, J. 2002. Passive sampling. *Trends in analytical chemistry,* 21:276-291.

Grimalt, J.O., Carrizo, D., Gari, M., Font-Ribera, L., Ribas-Fito, N., Torrent, M. & Sunyer, J. 2010. An evaluation of the sexual differences in the accumulation of organochlorine compounds in children at birth and at the age of 4 years. *Environmental research,* 110:244–250.

Gyalpo, T., Fritsche, L., Bouwman, H., Bornman, R., Scheringer, M. & Hungerbühler, K. 2012. Estimation of human body concentrations of DDT from indoor residual spraying for malaria control. *Environmental pollution*, 309:445-453.

Halsall, C.J., Sweetman, A., Barrie, L. & Jones, K.C. 2001. Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. *Atmospheric environment,* 35:255-267.

Hargreaves, K., Koekemoer, L., Brooke, B., Hunt, R., Mthembu, J. & Coetzee, M. 2001. *Anopheles funestus* resistant to pyrethroid insecticides in South Africa. *Medical and veterinary entomology,* 14:181-189.

Harris, J.M., Martin, N.E. & Modi, M. 2001. Pegylation, a novel process of modifying pharamacokinetinetics. *Clinical pharmacokinetics,* 40:539-551.

Harris, R.S., Bishop, K.N., Sheehy, A.M., Craig, H.M., Petersen-Mahrt, S.K., Watt, I.N., Neuberger, M.S. & Malim, M.H. 2003. DNA deamination mediates innate immunity to retroviral infection. *Cell,* 113:803-809.

Hecht, M. 2004. In Africa, DDT makes a comeback to save lives. *Scientific American*, 23:362-376.

Holoubek, I., Klánová, J., Jarkovsky, J. & Kohoutek, J. 2007. Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part I. Ambient air and wet deposition 1988–2005. *Environmental monitoring,* 9:557–563

Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J.M., Leppänen, S., Bossi, R. & Skov, H. 2010. Atmospheric monitoring of organic pollutants in the arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Science of the total environment,* 408:2854-2873.

IARC (International Agency for Research on Cancer). 1991. DDT and associated compounds. 53:179–249.

Iversen, G., Friis, E.P., Kharkats, Y.I., Kuznetsov, A.M. & Ulstrup, J. 1998. Sequential and coherent long-range electron transfer close to resonance with intermediate bridge groups, and new perspectives for in situ scanning tunnelling microscopy of adsorbed metalloproteins. *Journal of biological inorganic chemistry,* 3:229-235.

Jones, C.G., Heck, W., Lewis, R.E., Mungroo, Y., Slade, G. & CADE, T. 2008. The restoration of the Mauritius kestrel *Falco punctatus* population. *International journal of avian science,* 137:173-180.

Klánová, J., Čupr, P., Holoubek, I., Borůvková, J., Přibylová, P., Kareš, R., Tomšej, T. & Ocelka, T. 2009. Monitoring of persistent organic pollutants in Africa: Passive air sampling across the continent in 2008. *Journal of environmental monitoring,* 11:1952-1963.

Kylin, H. & Bouwman, H. 2012. Hydration state of the moss *Hylocomium splendens* and the lichen *Cladina stellaris* governs uptake and revolatilisation of airborne α-and γ-hexachlorocyclohexane. *Environmental science & technology,* 46:10982-10989.

LEAR, L. 1998. Reviews and commentaries. *Scientific American,* 99:1253-1267.

Lengeler, C. & Sharp, B. 2003. Indoor residual spraying and insecticide-treated nets. Reducing malaria's burden: Evidence of effectiveness for decision makers*. Tropical medicine and international health*, 16:17-24.

Lin, T.H. 2001. Long-range transport of yellow sand to Taiwan in spring 2000: Observed evidence and simulation. *Atmospheric environment,* 35:5873-5882.

Longnecker, M.P., Klebanoff, M.A., Dunson ,D.B., Guo, X., Chen, Z. & Zhou H. 2005. Maternal serum level of the DDT metabolite DDE in relation to foetal loss in previous pregnancies. *Environmental Research,* 97:127–133.

Lovett G. M., Burns D. A. & Driscoll C.T. 2007. Who needs environmental monitoring? *Ecological environment,* 5:253–600.

Mabasa, S., Leuschner, K. & Manthe, C. 1996. Screening sorghum cultivars for resistance to witchweed (*Striga asiatica*) in Zimbabwe. Drought-tolerant crops for southern Africa: Proceedings of the SADC/ICRISAT regional sorghum and pearl millet workshop, 25-29 July 1994, Gaborone, Botswana.

Mabaso, M.L.H., Sharp, B. & Lengeler, C. 2004. Historical review of malarial control in southern African with emphasis on the use of indoor residual house-spraying. *Tropical medicine & international health,* 9:846-856.

Masendu, H.T., Hunt, R.H., Govere, J., Brooke, B.D., Awolola, T.S. & Coetzee, M. 2004. The sympatric occurrence of two molecular forms of the malaria vector *Anopheles gambiaegiles* in

Kanyemba, in the Zambezi valley, Zimbabwe. *Transactions of the Royal Society of Tropical Medicine and Hygiene,* 98:393-396.

Masendu, H., Hunt, R., Koekemoer, L., Brooke, B., Govere, J. & Coetzee, M. 2005. Spatial and temporal distributions and insecticide susceptibility of malaria vectors in Zimbabwe. *African entomology,* 13:25-34.

MacDonald, G. 1956. Epidemiological basis of malaria control. *Bulletin of World Health Organization*, 26:613–626

Mendis, K., Rietveld, A., Warsame, M., Bosman, A., Greenwood, B. & Wernsdorfer, W.H. 2009. From malaria control to eradication: The World Health Organisation perspective. *Tropical Medicine and international health,* 14:802–809.

Moonasar, D., Asomugha, C., Baker, L., Blumberg, L., Barnes, K., Maharaj, R. & Benson, F. 2011. Preventing disease and saving lives: The malaria season is upon us. *South African medical journal,* 101:865-867.

Nobelprize.org., 2012, *Award ceremony speech for Paul Müller* (http://www.nobelprize.org/nobel_prizes/medicine/laureates/1948/press.html) accessed March 2012.

Pearce, M.J. 1988. Some effects of Lates spp. on pelagic and demersal fish in Zambian waters of Lake Tanganyika. Lewis, D. (ed.), Predator-prey relationships, population dynamics and fisheries productivities of large African lakes*. CIFA Occasional Paper,* 15:154-161. http://www.fao.org/docrep/005/S7047E/S7047E06.htm. Retrieved 19 September 2012.

Ritter, L., Solomon, K.R. & Forget, J. 2005. Persistent organic pollutants: An assessment report on DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, dioxins, and furans. Report for the International Programme on Chemical Safety (IPCS)

within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

Roberts, D.R. & Andre, R.G. 1994. Insecticide resistance issues in vector-borne disease control. *The American journal of tropical medicine and hygiene,* 50:21-29.

Rogan, W.J. & Chen, A. 2005. Health risks and benefits of bis(4-chlorophenyl)-1, 1, 1-trichloroethane (DDT). *The lancet,* 366:763-773.

Sachs, J. & Malaney, P. 2002. The economic and social burden of malaria. *Nature,* 415:680-685.

Sagiv, S.K., Nugent, J.K., Brazelton, T.B., Choi, A.L., Tolbert, P.E., Altshul, L.M. & Korrick, S.A. 2008. Prenatal organochlorine exposure and measures of behaviour in infancy using the neonatal behavioural assessment scale (NBAS). *Environmental health perspectives,* 116:666-672.

Sakellarides, T., Konstantinou, I., Hela, D., Lambropoulou, D., Dimou, A. & Albanis, T. 2006. Accumulation profiles of persistent organochlorines in liver and fat tissues of various water bird species from Greece. *Chemosphere,* 63:1392-1409.

Schecter, A., Päpke, O., Harris, T.R., Tung, K., Musumba, A., Olson, J. & Birnbaum, L. 2006. Polybrominated diphenyl ether (PBDE) levels in an expanded market basket survey of US food and estimated PBDE dietary intake by age and sex. *Environmental health perspectives,* 114:1515-1524.

Sereda, B., Bouwman, H., & Kylin H. 2009. Comparing water, bovine milk, and indoor residual spraying as possible sources of DDT and pyrethroid residues in breast milk. *Toxicology and environmental health*, 72:842–851.

Sharma, S., Shukla, R., Raghavendra, K. & Subbarao, S.K. 2005. Impact of DDT spraying on malaria transmission in Bareilly District, Uttar Pradesh, India. *Journal of vector borne diseases,* 42:54-62.

Sharp, B.L. & Le Sueur, D. 1996. Malaria in South Africa: The past, the present and selected implications for the future. *South African medical journal,* 86:83-89.

Shoeib, M. & Harner, T. 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental science and technology,* 36:4142-4151.

Shunthirasingham, C., Oyiliagu, C.E., Cao, X., Gouin, T., Wania, F., Lee, S., Pozo, K., Harner, T. & Muir, D.C. 2010. Spatial and temporal pattern of pesticides in the global atmosphere. *Journal of environmental monitoring,* 12:1650-1657.

Stockholm Convention on Persistent Organic Pollutants. 2010. What are POPs? [Web:]http://chm.pops.int 12/01/2010.

Streets, D.G., Tsai, N.Y., Akimoto, H. & Oka, K. 2001. Trends in emissions of acidifying species in Asia, 1985–1997. *Water, air, and soil pollution,* 130:187-192.

Tatarsky, A., Aboobakar, S., Cohen, J.M., Gopee, N., Bheecarry, A., Moonasar, D., Phillips, A.A., Kahn, J.G., Moonen, B. & Smith, D.L. 2011. Preventing the reintroduction of malaria in Mauritius: A programmatic and financial assessment. *Plos one,* 6:23832-23836.

Thomas, C. & Lindsay, S. 2000. Local-scale variation in malaria infection amongst rural Gambian children estimated by satellite remote sensing. *Transactions of the Royal Society of Tropical Medicine and Hygiene,* 94:159-163.

Thundiyil, J.G., Stober, J., Besbelli, N. & Pronczuk, J. 2008. Acute pesticide poisoning: A proposed classification tool. *Bulletin of the World Health Organization,* 86:205-209.

Toxicological Profile: for DDT, DDE, and DDE. Agency for Toxic Substances and Disease Registry, September 2002.

UNEP. 2001. United Nations Environment Programme. Stockholm Convention on Persistent Organic Pollutants. Geneva, Switzerland.

UNEP. 2005. United Nations Environment Programme. Ridding the world of POPs: A guide to the Stockholm Convention on Persistent Organic Pollutants. Geneva, Switzerland.

UNEP (United Nations Environment Programme), 2007. Guidance on the global monitoring plan for persistent organic pollutants, Preliminary version February 2007. Amended in May 2007. Stockholm Convention Secretariat, Geneva.

Yang ,H-H., Lia, S-O., Hsueh, H.-J., Chi, T.-W., 2002. Profiles of PAH emission from steel and iron industries. *Chemosphere*, 48:1061-1074.

van den Berg, H. 2009. Global status of DDT and its alternatives for use in vector control to prevent disease. *Environmental health perspectives,* 117:1656-1663.

van den Berg, H., Zaim, M., Yadav, R.S., Soares, A., Ameneshewa, B., Mnzava, A., Hii, J., Dash, A.P. & Ejov, M. 2012. Global trends in the use of insecticides to control vector-borne diseases. *Environmental health perspectives,* 120:577-582.

Wania, F. & Mackay, D. 1996. Tracking the distribution of persistent organic pollutants. *Environmental science & technology,* 30:390-396.

Watkinson, J.I., Sioson, A.A., Vasquez-Robinet, C., Shukla, M., Kumar, D., Ellis, M., Heath, L.S., Ramakrishnan, N., Chevone, B. & Watson, L.T., 2003. Photosynthetic acclimation is reflected in specific patterns of gene expression in drought-stressed loblolly pine. *Plant physiology,* 133:1702-1716.

Webster, E., & Mackay, D.F., Wania, F., 1998. Evaluating environmental persistence. *Environmental toxicology and chemistry,* 124:172148-172158.

Spencer, W.F. & Cliath, M.M., 1972. Volatility of DDT and related compounds. *Journal of agricultural and food chemistry,* 20:645-649.

WHO, 2006. Indoor Residual Spraying: Use of indoor residual spraying for scaling up global malaria control and elimination: WHO Position Statement. Geneva: Global Malaria Programme, World Health Organization.

WHO, 2006. Pesticides and their application for the control of vectors and pests of public health importance, WHO/CDS/NTD/WHOPES/ GCDPP/2006.1, Geneva: World Health Organization.

WHO, 2008. World Malaria Report 2008. Geneva: World Health Organization.

WHO-UNICEF WSS Assessment Report, 2000.

Wolff, M.S., Zeleniuch-Jacquotte, A., Dubin, N. & Toniolo, P. 2000. Risk of breast cancer and organochlorine exposure. *Cancer epidemiology biomarkers and prevention,* 9:271-277.

Wolff, M.S., Berkowitz, G.S., Brower, S., Senie, R., Bleiweiss, I.J., Tartter, P., Pace, B., Roy, N., Wallenstein, S. & Weston, A. 2000. Organochlorine exposures and breast cancer risk in New York City women. *Environmental research,* 84:151-161.

Wong, C., Li, X., Zhang, G., Qi, S. & Peng, X. 2003. Atmospheric deposition of heavy metals in the Pearl River delta, China. *Atmospheric environment,* 37:767-776.

Yakob, L. & Yan, G. 2010. A network population model of the dynamics and control of African malaria vectors. *Transactions of the Royal Society of Tropical Medicine and Hygiene,* 104:669-675.

Young, R. 2001. Postcolonialism: An historical introduction. Oxford: Blackwell Publishers, England.

Van Zyl, D. 2003. South African weather and atmospheric phenomena. Briza Publications, South Africa.