PLANT RESEARCH INTERNATIONAL

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1. Introduction

Both the damage to crops caused by herbicide vapors (Robinson & Fox, 1978) and the presence of pesticides in rain water and in air samples (Harris *et al.*, 1992; Chevreuil, 1996; Bucheli *et al.*, 1998; De Jong & Leendertse, 1999; Van Dijk & Guicherit, 1999) increased the awareness of the potential implications of pesticides in the atmosphere. It has been recognized that presence of pesticides in the atmosphere will contribute at least partly to the contamination of surface water (Harris *et al.*, 1992; De Jong & Leendertse, 1999) and groundwater (Bucheli *et al.*, 1998). Pesticides may come into the atmosphere during and after their application. During application emission can occur via drifted drops, aerosols and volatilization. So far, quantitative information on the importance of these different routes is not forehand. Drift of spray drops as an obvious loss of the pesticide has received much more attention than loss due to aerosol formation or volatilization during and after application. Drift depends on weather conditions, the application technology and the method of measurement. In spite of these variables, the literature indicates that drift from ground sprayers generally ranges from 0.1 to 10% of the applied amount (Combellack, 1982; Grover *et al.*, 1985; Kempenaar *et al.*, 1998). New nozzle- en sprayer types, developed for ground sprayers, showed large reductions of spray drift (Van de Zande *et al.*, 2000). The new technology reduced airborne spray drift of up to 60 fold when compared with a defined reference technique and situation (Huijsmans *et al.*, 1997). Spray drift deposition on a short distance of the field was reduced to a similar extent by this technology (Van de Zande *et al.*, 2002). After application of the pesticide, the pesticide may be emitted from the leaf and soil surface. Volatilization and formation of liquid or solid particle based aerosols may contribute to this emission. Experiments under field conditions revealed that this emission, expressed as percentage of the applied dose, can amount to 29% for tri-allate (Bor *et al.*, 1995), 24% for ethoprophos (Bor *et al.*, 1995), 75% for EPTC (Cliath *et al.*, 1980) and 21% for 2,4-D iso-octyl ester (Grover *et al.*, 1985).

Estimations for The Netherlands (fumigation not included) indicate that 5% of the applied amount is emitted via drift and 19% emits after application via volatilization (Anonymous, 1996). Volatilization from soil (Smit *et al.*, 1997) and from plants (Smit *et al.*, 1998) have been calculated for a large number of active ingredients that were used in The Netherlands at that time. Both reports indicate for several active ingredients a substantial loss of the applied amount due to volatilization from the soil surface and/or leaf surface.

Formulations and adjuvants have been used as tools to minimise emission of pesticides during and after application. Polymers (Zhu *et al.*, 1997) and emulsifiable oils (Western *et al.*, 1999, Dexter, 2001) can be used as drift retardant by increasing drop size and some adjuvants are used as an anti-evaporant (Hall *et al.*, 1993b). An anti-evaporant may lower the water evaporation of the drop in flight and thus lowers the fraction of small drops susceptible to drift. Controlled release formulations have been developed to control the volatilization after application (Schreiber *et al.*, 1988; Gorski, 1991). In spite of these developments, there is still a substantial loss of active ingredient after application. Pesticide emission to the atmosphere is not yet a criterion for registration by an active ingredient by the Dutch and several other authorities. As a consequence the agrochemical industry pays little attention to the emission. As part of the Dutch research program Pesticides and the Environment (DWK-359), the possibilities to reduce volatilization by using improved formulations and adjuvants in combination with the right application technology were investigated. The aim of this literature study is to provide an overview on the theoretical and practical possibilities of reducing emission by formulations and adjuvants.

In Chapter 2 we list available quantitative information regarding emission of pesticides. Chapter 3 deals with the physical-chemical principles governing emission during and after application. Chapter 4 informs the reader about the formulation/ adjuvant tools to reduce drift. Chapter 5 provides general information on adjuvants and formulations. Chapter 6 comprises conclusions based on this survey of the literature. In spite of the different approaches in the chapters, it was difficult to prevent some overlap between chapters. We hope that this overlap increased the informative value and will not puzzle the reader.

2. Literature data on volatilization of pesticides and its reduction by formulations and adjuvants

2.1 Literature data on post-application volatilization of pesticides

Data of post-application volatilization of pesticides under field conditions (Table 2.1), under laboratory conditions (Table 2.2) and calculated cumulative volatilization from soil and leaves after modeling (Tables 2.3 and 2.4) have been listed to provide an indication of the extent of volatilization. More references on volatilization from soil and plants can be found in previously published reports (Jansma & Lindners, 1995; Smit *et al.*, 1997 and Smit *et al.*, 1998).

Table 2.1. Literature data on volatilization of pesticides under field conditions.

Active ingredient	Days after application	Volatilization (% of applied amount)	Reference (alphabetical order)
tri-allate	14	29	Bor *et al.*, 1995
ethoprophos	14	24	Bor *et al.*, 1995
EPTC	2	75	Cliath *et al.*, 1980
alachlor	35	14	Gish *et al.*, 1995
atrazine	35	9	Gish *et al.*, 1995
2,4-D iso-octyl ester	5	21	Grover *et al.*, 1985
metalochlor	10	22	Prueger *et al.*, 1999
tri-allate	24	21	Smith *et al.*, 1997
trifluralin	24	18	Smith *et al.*, 1997
ethalfluralin	24	14	Smith *et al.*, 1997

Table 2.2. Literature data on volatilization of pesticides under laboratory conditions.

Active ingredient	Days after application	Volatilization (% of applied amount)	Reference (alphabetical order)
terbuthylazine	10	6.9-23.1	Lembrich *et al.*, 1999
propyzamide	1	10	Maas *et al.*, 1988
phenmedipham	1	70	Maas *et al.*, 1988
pendimethalin	1	70	Maas *et al.*, 1988
trifluralin	1	50	Maas *et al.*, 1988
lindane	1	90	Maas *et al.*, 1988
tri-allate	1	90	Maas *et al.*, 1988
metalochlor	1	84	Prueger *et al.*, 1999
trifluralin	1	90	Rüdel, 1997
parathion-methyl	1	50-70	Rüdel, 1997
endosulfan	1	50-70	Rüdel, 1997
fenpropimorph	1	50-70	Rüdel, 1997
lindane	1	50-70	Rüdel, 1997

All volatilization data need to be used carefully, because the extent of volatilizations depends much on the climatic conditions, the soil moisture and soil type, the type of formulation and the methodology used to measure or to calculate volatilization. The calculated volatilization from the soil (Table 2.3) were restricted by the following pre-conditions (Smit *et al.*, 1997):

- Only fallow soils without plant litter were considered.
- Only surface applications were included, ruling out the soil incorporations.
- Granular and encapsulated formulations were excluded.

Table 2.3. Calculated cumulative volatilization from soil surface 21 days after application.[1]

Active ingredient	CumulFieldVol (% of applied amount)	Active ingredient	CumulFieldVol (% of applied amount)
bendiocarb	27	methylbromide	90
bromophos-ethyl	60	methylisothiocyanate	73
buminaphos	33	pendimethalin	44
cycloate	42	pentachlorophenol	29
alpha-cypermethrin	26	piperonylbutoxide	70
diallate	29	procymidon	31
dial. dichl. aceetamid (cdaa)	29	pyrethrins	46
dichlobenil	38	pyridathioben (pyridaben)	31
dichlorvos	25	quintozeen	39
diethofencarb	26	tefluthrin	31
dinoseb	28	terbufos	34
dinoterb	43	thiodicarb	28
DNOC	25	thiram	35
EPTC	44	tolclofos-methyl	47
etridiazole	27	tolylfluanid	26
etrimfos	36	tri-allate	28
fenpropathrin	30	tri-fluralin	34
flucycloxuron	65	1,3-dichloropropene	76
folpet	28	cis-dichloropropene	77
fonofos	26		
lindane	25		

[1] *Volatilization values (restricted to values ≥25%) were extracted from Smit et al., 1997.*

The Tables 2.3 and 2.4 do not comprise all pesticides used in The Netherlands in 1997-1998.
A restriction was made by selecting those pesticides with a cumulative volatilization ≥25%. Further, volatilization of a number of compounds was not calculated by the authors due to lack of data or lack of sufficient data.

The information provided in Tables 2.1, 2.2, 2.3 and 2.4 demonstrates the importance of volatilization as route of emission to the atmosphere.

Table 2.4. Calculated cumulative volatilization from leaves 7 days after application.[1]

Active ingredient	CumulVol (% of applied amount)	Active ingredient	CumulVol (% of applied amount)
asulam	34	malathion	34
bromoxynil	34	methamidophos	50
buminaphos	100	methomyl	60
buprofezin	28	metolachlor	48
butocarboxim	100	metoxuron	67
chlorfenvinphos	25	mevinphos	100
chlorpropham	34	monolinuron	100
chlorpyriphos-ethyl	41	omethoate	59
diazinon	89	oxamyl	100
dicamba	50	oxydemeton-methyl	64
dichlobenil	100	parathion	32
dichlorvos	100	parathion-methyl	47
dienochlor	28	pendimethalin	47
diethofencarb	91	phosphamidon	36
dimethoate	26	primicarb	35
dinoterb	100	primiphos-methyl	47
DNOC	85	procymidon	100
etridiazole	100	propachlor	100
etrimfos	92	propoxur	38
fenpropathrin	25	pyrifenox	32
fenpropimorph	50	thiocylam hydrogen oxalate	25
flucycloxuron	67	thiometon	100
flutolanil	44	thiram	37
folpet	38	tolclofos-methyl	100
fonofos	100	tri-allate	100
heptenophos	100	tridemorph	80
hymexazol	100	2,4-D	34
ioxynil	34		
lindane	75		
linuron	43		

[1] *Volatilization values (restricted to values $\geq$25%) were extracted from Smit et al., 1998.*

2.2 Reduction of volatilization by formulations and adjuvants

In the past, a limited number of strategies have been developed to reduce the loss of an active ingredient to the atmosphere. Design of controlled release formulations using polymers and substitution of volatile esters by much less volatile amine salts do not fall within the scope of this study and will be mentioned shortly below. More attention is paid to the use of adjuvants for direct reduction of volatilization and the indirect reduction by reduction of the drift and concomitant the fraction of airborne particles.

2.2.1 Controlled release formulations (CR)

A number of pesticides are so volatile that a substantial loss (for instance 100% in 48 h) will occur if precautions like soil incorporation and/or use of a controlled release formulation are not taken. The primary function of a controlled released formulation is to maintain during several days a certain concentration of pesticide in the upper soil layers, in the crop canopy or in an orchard. Well-documented examples are the herbicide tri-allate (Grover *et al.*, 1978; Smith *et al.*, 1997; Bor *et al.*, 1995) and the pheromone insecticides (Ridgway *et al.*, 1990). Examples of other active ingredients whereby release of vapor could be controlled by CR formulation: atrazine and alachlor (Wienhold & Gish, 1994), chlorpyrifos (Ling *et al.*, 1994), dichlobenil (Spencer-Jones & Wilson, 1976), EPTC (Schreiber *et al.*, 1988), metalachlor and napropamide (Gorski, 1991), parathion (Riley, 1983) and trifluralin (Wilkins & Zhao, 1997). Controlled release formulations using polymers for encapsulation of pesticides (Gorski, 1991; Schreiber *et al.*, 1988) or application of micro-encapsulation (Lewis & Lee, 1976; Scher *et al.*, 1998), are useful vehicles for low-emission applications of pesticides. Because these options are outside the scope of this study we did not pay much attention on this the option.

2.2.2 Ester and amine formulations

The chemical structure of a number of pesticides enable the production of both ester and amine salt derivatives of a pesticide. Well-known examples are 2,4-D, MCPA, bromoxynil and ioxynil. Ester derivatives are more lipophilic and penetrate into leaves more easily and faster than 2,4-D salts (De Ruiter *et al.,* 1993; Price & Anderson, 1985). Drawbacks of esters are the requirement of a solvent in emulsifiable concentrate formulations and their volatile character (Breeze *et al.*, 1992; Grover *et al.*, 1985). The presence of 2,4-D esters in the atmosphere has been reported (Robinson & Fox, 1978). Amine salts are much less volatile (Grover, 1976) and by using an appropriate surfactant, the penetration and thus the performance of an amine salt derivate can be improved to a large extent. The latter has been demonstrated for 2,4-D amine salt (De Ruiter *et al.*, 1995), bromoxynil K-salt (De Ruiter *et al.*, 2001), and ioxynil K-salt (De Ruiter *et al.*, unpublished data). Substitution of ester derivatives by amine salts is a tool that contributes to reduction of emission of active ingredients to the atmosphere. A similar approach is followed with the fungicide pyrimethanil (Green *et al.*, 1998). Salt formation using organic acids strongly reduced the volatility.

2.2.3 Adjuvants

An adjuvant is defined as a substance without significant pesticide properties, added to an agricultural chemical to aid or modify the activity of this chemical. Adjuvants can fulfil different functions to enhance the activity of a pesticide. The addition/use of adjuvants to reduce volatilization (evaporation of a.i.) during and after application is rather unexploited. More is known about the possibility to use adjuvants for reduction of the fraction drift-susceptible drops and thus reduction of airborne particles. The result of literature search on adjuvants as a tool to reduce volatilization is presented on the next page. For reduction of drift we mention a few representative examples.

Volatilization

After application of the herbicide, adjuvants could reduce the volatility of 2,4-D *iso*-octyl ester under controlled conditions (Schubert *et al.*, 1993). The authors mentioned that this reduction could result from an adjuvant-accelerated penetration of the herbicide into the leaves. The same statement seems to be valid for the observation that an adjuvant reduced to volatilization of tri-allate applied on plants (Pestemer & Krasel, 1992). Particularly lipophilic adjuvants could strongly reduce the presence of the fungicide fluazinam in the headspace above fluazinam-adjuvant solutions (Mol *et al.*, 2001).

Volatilization experiments with glass-slides were conducted to measure the volatilization of the herbicide fluazifop-butyl (Chandrasena & Sagar, 1986). The experiments demonstrated that 42% of the applied fluazifop-butyl (EC formulation; temperature chamber 23.8 °C) was lost within 6 h and 62% after 48 h. Loss of fluazifop-butyl was also measured by trapping fluazifop-butyl after volatilization from the leaf surface (Grafstrom JR & Nalewaja, 1988). The loss of fluazifop-butyl (EC-formulation, temperature chamber 30 °C) was 4.1% within 72 h. The lower level in this study is at least partly caused by the foliar absorption of fluazifop-butyl which amounted to 44% after 12 h and 61% within 72 h. Addition of an oil reduced the volatilization from 4.1 to 0.6% and increased foliar uptake from 61 to 77.4% after 72 h. Volatilization of DDT (unformulated, chamber temperature 20-25 °C and period 24 h) was reduced by 45 to 70%, when surfactants were added (Stevens & Bukovac, 1987). The authors suggested that DDT may be partly trapped within the surfactant deposit. Wax-based dispersions, forming a film after application and evaporation of water, reduced volatilization of herbicides, insecticides and fungicides (Heinrichs *et al.*, 2001). A laboratory approach provided evidence that these wax products reduce the volatilization of fenpropimorph (fungicide) and methamidophos (insecticide) (Zeisberger, 2001).

Potential of adjuvants to reduce air-borne particles

In this section we hypothesize that reduction of the fraction small driftabled drops (<100 μm) will also reduce the emission of airborne particles to the atmosphere. To indicate the potency of this strategy we refer to studies (Table 2.5) on drift potential (windtunnel) and drift. It can be concluded that appropriate adjuvants can have a great potency to reduce emission of airborne particles. The study on ethyl parathion (Clark *et al.*, 1993) demonstrates the adjuvant strongly reduced presence of ethyl-parathion in the air up to a distance of 200 m downwind.

Table 2.5. Influence of adjuvants on (potential) drift reduction.

Adjuvant	Spray solution	Experiment	Distance downwind (m)	Reduction of drift potential or drift (%)	Reference
Lecithin-based	glufosinate (Basta)	windtunnel	2.3	76	Maas & Krasel, 1988
Rapeseed oils	water + dye	windtunnel	2	60	Western *et al.*, 1999
Polymer-guar gum blend	glyphosate (Roundup Biactive)	windtunnel	2	80	Hewitt *et al.*, 2001
Liquid ammonium sulfate/invert suspension blend	glyphosate (Roundup Biactive)	windtunnel	2	70	Hewitt *et al.*, 2001
Inverted emulsion	ethyl parathion (Aqua 8)	helicopter application	over 50-200	80	Clark *et al.*, 1993

3. Physical-chemical aspects of pesticide volatilization and the influence of adjuvants

3.1 Occurrence of pesticides into the atmosphere

During crop spraying events, pesticides are introduced into the atmosphere as solid or liquid airborne matter, termed aerosols, and as vapor. Depending on the size of the aerosol, it will return quickly to the surface a short distance downwind (> 100 μm), it will be deposited more slowly further downwind, or (< 10 μm) it will become airborne for a much longer time, will be diluted further in the atmosphere and will return to the surface very slowly. Typical droplet diameters for most spray application conditions range between 200-300 μm. Larger droplets would be favorable with respect to drift, but gives a less favorable target coverage which has to be compensated for by, e.g., greater application rates.

The quantity of pesticide that ends up in the atmosphere depends on a number of factors including amount of material sprayed, physical-chemical properties of the pesticide and dispersion vehicle, the particle size distribution, height at which the material is released, wind speed, and atmospheric turbulence. The particle size distribution of the spray is believed to be the most important factor contributing to off-target drift (Lewis & Lee, 1976). Obviously, the application method is also a determining factor, ground ward directed sprays cause less drift (ca. 5x) than aerial methods, which in turn cause less drift than orchard radial and axial fan mist blowers. The latter directs the spray away from the ground in order to reach the tree canopy and drift can be up to six times higher than aerial applications (Majewksi & Capel, 1995).

In the atmosphere exchange of pesticides takes place between the aerosols and the vapor phase, i.e. pesticides can adsorb on solid aerosols or dissolve in liquid aerosols (e.g. fog) and evaporate again. The size of the aerosol and meteorological parameters govern the transport of the associated pesticides. Aerosols smaller than 2 μm have very small settling velocities and may be treated as gaseous particles (Pitter & Baum, 1975).

Pesticides are not only directly introduced during the application but also thereafter by evaporation from the fields (soil, plants, water) and, adsorbed on dust/particles, by wind erosion of treated/ contaminated soil. The application of wettable powder formulations (WP) over dry soils can lead to removal of small pesticide particles by wind erosion (Taylor & Glotfelty, 1988).

Evaporation of pesticides can be a dominant pathway into the environment, not only for volatile but also for so-called ‘non-volatile’ pesticides. Therefore, parameters affecting the evaporation of pesticides will be discussed below.

3.2 Evaporation

Generally, the evaporation rate of a pesticide into air is determined by the effective vapor pressure of the substance at the evaporating surface and the rate of diffusion through the layer of air immediately adjacent to the surface (Glotfelty & Caro, 1975). Air close to the surface from which evaporation takes place does not move and molecular diffusion determines the evaporation rate (Spencer & Cliath, 1975). Volatilization increases if the depth of this stagnant air layer (normally 2-3 mm) decreases or if the concentration gradient across the layer increases. Variables that affect the two basis factors and thus the volatilization rate, include nature of the pesticide (solubility, adsorption coefficient), temperature, concentration of pesticide at the surface, type of formulation, rate of mass transport to the air-surface interface, supply of latent heat of vaporization, rate of air flow above the surface (wind), and atmospheric turbulence.

3.3 Evaporation from aqueous solutions

Evaporation of pesticides from aqueous solution is controlled by Henry's law constant (k_H). This constant is the ratio of equilibrium water concentration of the solute (S) to the solute partial pressure in the air (P) and is used to describe water-air partitioning of the solutes ($k_H=S/P$). The tendency of a pesticide to volatilize from water solution to air is largely determined by k_H. A high value means a relatively high concentration of the molecules in water and low partial pressure. The vapor pressure only indirectly influences vaporization from water, in combination with solubility. Pesticides with a low vapor pressure and also a very low solubility in water (e.g. DDT), can be subject to evaporative loss.
A critical review of Henry's law constants for pesticides has been published previously (Suntio *et al.*, 1988); k_H and other physico-chemical properties of 96 pesticides are given. Care should be taken with interpretation of tabulated k_H values as they are very temperature sensitive and the presence of dissolved electrolytes, organic matter, detergent and emulsified materials will affect the 'solubility' of the pesticide in water and thus alter k_H.

3.4 Pesticide volatilization from aqueous solutions and the influence of adjuvants

Pesticide volatilization from aqueous solutions will occur during the flight and during the first 10 to 30 minutes after application when the drops are deposited on the leaf or soil surface. Adjuvants may influence this volatilization in different ways. Below we discuss the different options from the physical-chemical point of view. We stress that, during application, the emission into the air is possible via molecular volatilization, airborne particles and drift and that these routes are related to each other. In general terms: reduction of the fraction of small, drift susceptible drops will also reduce the emission via the other routes. In addition to the role of adjuvants or formulations, drift can be managed quite well by application technology. An overall view on drift is presented in Chapter 4.

3.4.1 Influence of adjuvants on the evaporation of water

Evaporation suppressants (Lewis & Lee, 1976) can be added to decrease the vapor pressure of the carrier (water in most applications). This reduces the evaporation rate and slows down the reduction in droplet size during the flight. As a result emission of pesticide by the routes mentioned above can be lowered. Hydrophilic polymers can reduce the loss of water during the flight from 55% (tap water) to 39% (polymer included) (Hall *et al.*, 1994). We suggest that the capacity of these polymers to bind and to retain water in the bulk solution, reduces evaporation.

3.4.2 Influence of adjuvants on the drop size distribution during atomization

Although there is still a dispute going on, the general view is that both a high dynamic surface tension and a high extensional viscosity increase the drop size and reduces the fraction of drift susceptible drops (Hewitt, 1998). Polymers increase the extensional viscosity (Zhu *et al.*, 1997). A high dynamic surface tension or high extensional viscosity will hinder the break-up of the liquid sheet leaving the nozzle and with increased drop size as result. Evidence is forehand that a number of adjuvants can alter the drop size distribution by influencing the break-up mechanism of the liquid sheet that comes from the nozzle. A recent report (Dexter, 2001) mentioned the great potency of emulsion-forming adjuvants (emulsifiable oil, emulsion, partly water-insoluble surfactant) to increase the drop size substantially.
A crop oil concentrate increased the median droplet size from 180 to 290 μm). The hypothesis is that the hydrophobic particles create weak spots in the liquid sheet during atomization and the sheet break up earlier in relatively bigger drops (Dexter, 2001).

3.4.3 Use of low volatility carriers

The use of low volatility carriers (Lewis & Lee, 1976) will also contribute to a reductions of small droplets by preventing loss of drop volume by evaporation. Depending on their composition, oils will loss much less volume during the flight of drops than water.

3.4.4 Influence of adjuvants on molecular volatilization from aqueous solutions

Although adjuvant producers sometimes claim the property of their product to reduce volatilization of the pesticide during application, the experimental evidence is scarce (see Chapter 2 sub-section 2.2.3). It can be argued that lipophilic particles in the spray solutions can increase the solubility of the active ingredient by acting as a sink and thus lower the volatilization according Henry's Law. On the other hand, the situation during atomization is very dynamic, which may hinder the sink function and the existing commercial formulation may already fulfil this function. In addition, the flight-time and thus the time available for volatilization is very limited. A substantial influence of adjuvants on molecular volatilization during application does not seem very likely but experimental evidence was missing at the start of the project. A reduction of volatilization during the first 10-30 minutes after application seems more likely: evaporation of water may reduce solubility of the ai and this may be compensated by the adjuvants. Further adjuvant-induced penetration into leaves may also reduce the availability for volatilization (see also Chapter 2 section 2.2.3).

3.5 Evaporation from surfaces

Factors that influence evaporative losses from treated surfaces include vapor pressure and environmental conditions that control movement away from the treated surfaces via molecular diffusion (Seiber & Woodrow, 1995; Spencer & Cliath, 1975). A volatilizing pesticide will diffuse through a stagnant air boundary layer and then be carried away by turbulent flow of the air. When the wind speed increases, the depth of the stagnant air boundary layer will decrease, which results in an increased rate of volatilization of the applied pesticide. The roughness of the surface will also influence volatilization by leading to greater turbulence closer to the surface as the roughness increases, resulting in greater turbulent transfer of residue to the atmosphere.

Unstable atmospheric conditions may lead to further enhancement of volatilization, and occurs when the temperature of the surface is greater than the overlying air. This results in rising heat plumes and dispersive turbulence. Volatilization is typically maximized at solar noon, when the solar energy input and the atmospheric turbulence are highest.

Spencer *et al.* (Spencer *et al.*, 1973) calculated rates of volatilization of a number of pesticides from drop deposits. The calculates rates agreed reasonably well with evaporation rates from nonadsorbent sand and varied from 0.01 kg/ha/day for p,p-DDT to 1.4-2.4 and 3-5 kg/ha/day for lindane and trifluralin, respectively (Lewis & Lee, 1976).

3.5.1 Evaporation from soil and the possible influence of adjuvants

A range of soil and weather factors (Smit *et al.*, 1997) affect the volatilization of a pesticide from the soil by influencing the vapor pressure and the availability of the pesticide to move away from the soil. Soil factors are: surface roughness, moisture content, organic matter content, bulk density and soil temperature. Weather factors are: temperature, wind speed, relative humidity, solar radiation and rainfall. Extensive discussion of these factors falls outside the scope of this study. Here we pinpoint some interactions because adjuvants or formulation constituents may influence these interactions.

The water content of the soil is an important parameter with respect to volatilization which is much more pronounced for wet soils. It is believed that this is mainly caused by displacement of the pesticide from the soil active sites (Spencer & Cliath, 1975). This effect is also observed when dry soil containing pesticides is wetted. When pesticides are applied to soil surfaces, pesticide flux often remains high until the surface dries. Flux will then be limited by soil sorption, and when surface residues become depleted, diffusion of pesticides from deeper soil layers becomes more important. In this regard, depth of soil incorporation is a factor influencing volatilization; movement through soil to the surface, which is in part accomplished by diffusion through soil vapor spaces and through soil moisture, is slowed with greater incorporation depths. Diffusion coefficients for pesticides in water and vapor are important here, as well as soil porosity. Furthermore, the movement of water to the soil surface can carry pesticide residues to the soil surface (caused by capillary action). In this regard, the pesticide's Henry constant (k_H, defined as S/P, see sub-section 3.3) becomes important. When the water solubility is relatively high (high k_H), pesticide residues accumulate at the surface faster than the emission via evaporation, resulting in an increasing evaporation flux over time. In contrast to this, pesticides with relatively low water solubilities (low k_H) would show declining flux via evaporation over time regardless of the movement of water to the surface (Seiber & Woodrow, 1995).

For weakly polar and non-ionic compounds, the amount of organic matter is the most important soil factor for adsorption and, consequently, decreasing vapor pressure. Doubling the soil organic matter content can cut volatilization rates by a factor of two (Majewski & Capel, 1995). For polar and ionic molecules, clay minerals can be more important. Soil surface applications or pesticides falling on the soil surface from foliar applications, can result in relatively high concentrations at the evaporating surface and limited or no interaction of the pesticide with the soil. This results in vapor pressures that equal those of the pesticides without soil.

The question whether adjuvants or formulation constituents may reduce the leaching of pesticides to deeper soil layers has been addressed since the start of the use of synthetic pesticides. The idea is to keep the pesticides in the upper soil layer without loss of efficacy or preferentially improved efficacy (Foy, 1992; Jain & Singh, 1992). It seems reasonable to assume that 'fixing' the pesticide in the upper soil layer will also reduce the volatilization. Data on the latter aspect are very scarce. One report suggested that emulsifiable oils and a fatty amine surfactant reduced volatilization of trifluralin as a slower dissipation in the soil was observed in the presence of these adjuvants (Swarcewicz *et al.*, 1998).

A previous report (Beigel & Barriuso, 2000) outlined that surfactants may enhance the water solubility of hydrophobic pesticides, may mobilize pesticides sorbed on the soil and may enhance the sorption of pesticides on the soil matrix after sorption of the surfactant itself. The relevance of these processes depends on the concentration of the surfactant. Surfactants, at relatively high concentrations, were able to enhance the mobility of several pesticides in soil columns and in soil thin-layer chromatography (Foy, 1992). The author concluded that low concentrations of surfactant that result from commonly used application rates under agricultural conditions will have no or little effect on the distribution of pesticides in the soil following irrigation. Although from another perspective, it was concluded in another study that low concentrations of surfactant will not significantly affect the soil sorption of triticonazole (Beigel & Barriuso, 2000). At this stage we tend to conclude that it is doubtful whether surfactants are a useful tool to reduce volatilization of soil applied active ingredients, particularly in those situations where abundant water dilutes the applied chemicals.

Other compounds like polymers, pine kraft lignins and starch have been tested to control the release of active ingredients when applied to the soil. This approach has been successful for several pesticides (Jain & Singh, 1992). A synthetic polymer reduced the mobility of simazine on soil TLC plates and in soil columns (Jain & Singh, 1992). However the authors mention that a slower release of simazine from the polymer can reduce its herbicidal activity. Polymers seem to be a useful tool to control the release and thus the volatilization as well, but solutions are found on a case-by-case optimization.

The combined application of thiosulfate fertilizer with 1,3-dichloropropene (1,3-D) is an example of a very specific way of reducing volatilization. Thiosulfate transforms 1,3-D in the soil in non-volatile ions and reduced the volatilization by 61% (Jianying *et al.*, 2000).

3.5.2 Evaporation from vegetation and the influence of adjuvants

As for soils, initially deposited pesticides on the vegetation surface are likely to vaporize at a rate closely resembling the pure material, because only a small fraction of the applied pesticide would be in direct contact with the leaf or fruit surface. Once the pesticides become solubilized in plant waxes or oils the effective vapor pressure will be greatly reduced. Obviously, uptake of pesticides by the plants will also reduce the post application emission into the atmosphere. The same is true when degradation of the pesticide (by sunlight or hydrolysis) occurs. Crop species and wind speed can create air turbulence which in turn can increase the evaporation rate by increasing mass transport. (Waymann & Rüdel, 1995).This can be important with respect to the laminar layer where molecular diffusion limits the evaporation rate. Due to lack of adsorption capacity of plants, evaporative losses from leaf surfaces have been reported to be much higher than from soil surfaces (Boehncke *et al.*, 1990; Waymann & Rüdel, 1995). Volatilization from plants varies for the crop and developing stage and will depend on the properties of the cuticle (roughness, thickness, type of waxes, etc.) (Stork *et al.*, 1994). Several investigators have attempted to correlate pesticide volatilization with the various influencing factors in descriptive equations with the aim to predict losses from treated surfaces. However, their ability to predict absolute volatilization rates in the environment has not been validated (Seiber & Woodrow, 1995).

The surface-active agents among the adjuvants can enhance the size of the wetted leaf surface. An enhancement of the treated leaf surface may reduce the volatilization as has been reported for lindane (Waymann & Rüdel, 1995). Adjuvants without and with hydration water may act as a solvent for a pesticide when most water has been evaporated from the leaf surface (Briggs & Bromilow, 1994). It is rather unexploited in how far the volatilization pattern from a dissolved pesticide differs from the patterns of the crystalline or liquid pesticide. It is well known that adjuvants may also substantially increase the foliar penetration of pesticides and thus lower the availability for volatilization from the leaf surface. However, the relation between uptake kinetics and volatilization pattern has not been investigated as far as we know.

4. Physical and chemical modifications of spray liquid to affect spray drift

4.1 Introduction

During a spray application the occurrence of spray drift may be a significant loss of spray liquid to downwind areas. Small drops may remain airborne long enough to evaporate considerably before impacting onto the ground. This evaporation comprises that of the solvent (usually water) and that of the solute (the pesticide and various adjuvants). With respect to volatilization of chemicals from the crop or ground surface the time scale for the presence of airborne spray is very short, yet even a small drifting drop contains a relatively large amount of pesticides compared to the rate of volatilized molecules after spraying.

Several methods can be used to suppress spray drift during application. One may distinguish three options:
(a) diminish the production of small drift-prone droplets at the nozzle outlet;
(b) promote a rapid deposition of the drops;
(c) suppress the evaporation of drops in air.

The use of nozzles with a relatively coarse drop size distribution is one possibility to achieve option (a). Conventional nozzles with a coarse spray often imply relatively high dose rates. So-called 'drift reducing' nozzles may produce a relatively coarse spray, yet do not increase the applied dose. The draw-back is that initial velocity of the drops for these nozzles is relatively low, which partly undoes the advantage of the coarser spray. Another type op nozzles, producing drops with a narrower size distribution, clearly have an advantage, yet the commonly used hydraulic nozzles all have a similar (wide) 'span' of drop sizes.

To decrease the time that drops need to travel from nozzle to target (option (b)), the use of air-assistance to guide drops downward is a well-known but costly possibility. Charging drops is another option to promote deposition, yet in practice this is only possible for fine sprays. Besides, it can have the opposite effect as charged drops repel each other and a cloud of drops will tend to spread out.

Another option to diminish spray drift involves a 'non-technical' approach, and will be the topic of this chapter. This approach implies the use of adjuvants to modify the physicochemical properties of the spray liquid. Roughly, two groups of adjuvants can be distinguished. The first group coarsens the drop size spectrum (i.e. option (a)), the second group suppresses evaporation (i.e. option (c)). In principle, deposition can be promoted by increasing the mass density of the spray liquid (option (b)). This is not a feasible option with adjuvants, yet using a 'heavy' solvent occasionally may have some advantages.

4.2 Increasing drop size

Physical properties of the spray liquid may affect the drop size distribution of a spray. A major explanation for spray coarsening by physicochemical modifications is thought to be due to early break-up of the liquid sheet that forms at the nozzle outlet. In that case the liquid sheet is still relatively thick, which is directly related to the sizes of the produced drops.

The most relevant physical properties to affect the moment of break-up are viscosity, surface tension. Homogeneity of the bulk liquid, particularly in case of suspensions and emulsions, can be an important factor as well. In the following sections the effect of these properties on drop size distribution will be dealt with.

4.2.1 Viscosity

Adjuvants that increase viscosity of the spray liquid coarsen the spectrum of the spray (Moser & Schmidt, 1983). Dynamic viscosity (η) of pure water is about 1.0 mPa·s (at 20 °C). A liquid with dynamic viscosity of about 1.6 mPa·s significantly affects drop size distribution (Moser & Schmidt, 1983). Though many additives hardly affect viscosity, some may affect viscosity considerably. Occasionally, even a relatively dilute 0.1% solution of the proper adjuvant may increase dynamic viscosity up to 1.9 mPa·s, and thus decrease spray drift due to coarsening of the spray (Moser & Schmidt, 1983).

Viscosity is usually temperature dependent. Even for a 'simple' fluid like water, a change in temperature may affect drop size distribution through a change in viscosity. Table 4.1 shows values of the dynamic viscosity for water at various temperatures (Margenau *et al.*, 1953).

Table 4.1. Dynamic viscosity of water as a function of liquid temperature.

Temperature (°C)	Dynamic viscosity [1] (mPa·s)	Relative change in SMD [2]
0	1.79	1.09
20	1.01	1.00
40	0.66	0.94
60	0.47	0.89

[1] *Margenau et al., 1953.*

[2] *Taking SMD (Sauter Mean Diameter) at 20 °C as a reference; see text.*

By interpolation one may estimate viscosity of water at intermediate temperatures. Figure 1 is obtained this way. From this curve it can be estimated that at 20 °C the rate of change in viscosity of water is about -0.026 mPa·s per °C.

Often the Sauter Mean Diameter (SMD) is expressed as being proportional with η^b. Experimentally obtained values for b range from 0.06 up to 0.22 (Lefebvre, 1989). The parameter b appears to be related to flow rate: an increased flow rate will decrease b (Lefebvre, 1989). Using an average value of $b = 0.15$, SMD for a water spray changes only slightly for practical temperatures (see Table 4.1). Even when cooling the water from 20 °C down to (just above) zero, on average only a 9% increase in mean drop size is to be expected.

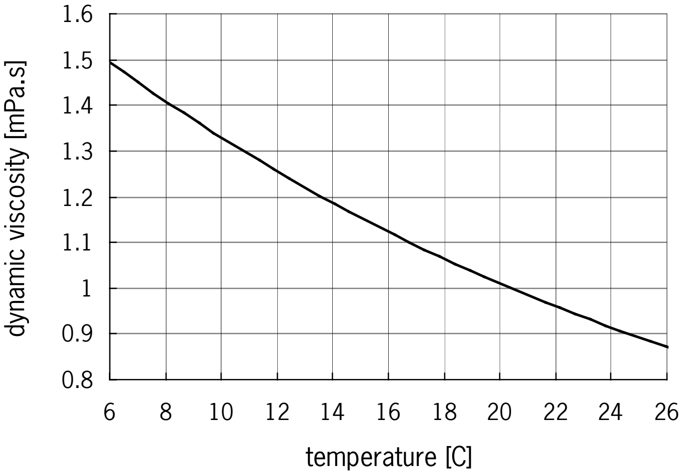

Figure 4.1. Dynamic viscosity of water as a function of temperature. Obtained by interpolation using the values of Table 4.1.

Aqueous solutions often are Newtonian liquids, i.e. their dynamic viscosity is independent of shear rate. However, adjuvants that intend to reduce drift by an increase in viscosity behave like non-Newtonian liquids: dynamic viscosity of the solution is a function of shear rate. For drop formation the shear rate at the nozzle outlet is important. Typically, shear rates at the nozzle outlet range from 10^4-$2 \cdot 10^5$ s^{-1} (Butler *et al.*, 1969). For those solutions, viscosity decreases with increasing shear rate ('shear-thinning' behavior). Therefore, to obtain a dynamic viscosity at the outlet of the nozzle that is significantly higher than that of water, the (low-shear) viscosity of the tank liquid must be even higher still (note that shear rates in the tank are low: typically 50 s^{-1}).

Highly viscous liquids however cause problems with stirring and therefore with creating a homogeneous spraying liquid (Hartley & Graham-Bryce, 1980).

Non-Newtonian liquids have both viscous and elastic properties. Non-Newtonian behavior often is accompanied by other (time-dependent) behavior. Thixotropic liquids are shear-thinning when stirred, and the low-shear viscosity recovers only slowly after stirring has stopped. A high viscosity can lead to long threads in the formation of drops. These threads may break up in a number of small satellites. In case of a highly elastic liquid, after rupture the thread and drop will recoil and stick together again, without formation of satellites (Hartley & Graham-Bryce, 1980).

For non-Newtonian liquids, Hewitt *et al.* (2001) distinguish extensional and shear viscosity. Extensional viscosity is particularly important when polymers with high molecular weight (typically $>10^6$) are used in the formulation. Even very low concentrations (~100 ppm) of such a polymer can lead to a significant increase in averaged drop size. The effect of extensional viscosity is related to the flow pattern through the nozzle; therefore the effect on drop size may differ for different nozzles.

4.2.2 Surface tension

Another important physical factor is surface tension (σ) of the liquid. A lower surface tension will decrease averaged drop size. Several investigations state that SMD is proportional with σ^a, where a is about 0.25 (Lefebvre, 1989). Surface tension of pure water is 72.8 $mN \cdot m^{-1}$ (at 20 °C; Moore, 1978). Suspending or solving various additives can easily decrease surface tension to about 30 $mN \cdot m^{-1}$, which causes a decrease in SMD of approximately 20%.

Aqueous solutions can both increase and decrease surface tension. Substances like fatty acids, whose molecules have both a polar (hydrophilic) group and a non-polar (hydrophobic) group, decrease surface tension when dissolved in water (Moore, 1978). The rate of decrease with concentration depends on the relative size of the hydrophobic group: the larger the non-polar group, the more pronounced the effect will be. Ionic solutions (salts) increase surface tension slightly, because the salty ions tend to pull water molecules into the interior of the liquid (by ion-dipole interaction), away from the liquid surface.

It should be noted that dynamic surface tension may differ from equilibrium (or static) surface tension, because obviously it takes some time for the molecules in the solution to form an equilibrium surface (Moore, 1978). If migration of molecules to the surface is very fast (typically $<10^{-3}$ s) static surface tension is applicable (Schmidt, 1980).

Surface tension of water is only slightly dependent on temperature, decreasing about 0.14 $mN{\cdot}m^{-1}$ per degree increase, averaged between 0 ^{o}C and 20 ^{o}C (Margenau *et al.*, 1953). This means that in the practical range of temperatures mean drop size of sprays of pure water is hardly affected by changes in temperature, as far as surface tension is considered.

In experiments often tracers (dyes) are used, dissolved in water. Although these tracers do not affect viscosity or density significantly, the surface tension usually is lowered (typically to 60-65 $mN{\cdot}m^{-1}$ for some common fluorescent dyes at 1 g/l; according to Schmidt, 1980).

4.2.3 Homogeneity of the bulk liquid

Dexter (2001) suggested that with emulsions the hydrophobic droplets, when they are stretched in the liquid sheet, form weak spots which promote early break-up of the liquid sheet and thus result in coarsening of the spray. There may be an effect of initial size of the emulsion droplets in the bulk liquid as well.

In general, dispersions do not appear to affect drop size distribution (apart from the effect of the physical properties described in previous sections), while emulsions show an increase in average drop size due to early break-up caused by hole formation, as well as a narrower size distribution (Hewitt *et al.*, 2001).

4.2.4 Adjuvants for coarsening drop size spectrum

Butler *et al.* (1969) investigated several additives (Vistik 6.5 g/l: a hydroxyethyl cellulose; Dacagin 6.5 g/l: a polysaccharide; Norbak 7.5 g/l: a water-swellable polymer) that increased viscosity. The amount of small drops decreased indeed. However, the drop size spectrum only shifted to larger drops, and the amount of large drops consequently increased. Due to non-Newtonian (shear-thinning) behavior relatively high concentrations had to be used to ensure a viscosity that was significantly higher than that of water at shear rates occurring in the outlet of the nozzle.

Schmidt (1980) tried solutions of Nalco-625 (a polyacrylamid-based emulsion) in water. Even a solution of 0.1 g/l significantly increased VMD (about 20%). The corresponding viscosity (1.27 $mPa{\cdot}s$) of this non-Newtonian liquid was measured using a falling-ball viscometer, which should only be used for Newtonian liquids, and therefore the resulting viscosity is merely indicative. At the outlet of the nozzle the viscosity probably will be much closer to that of water. The reported surface tension was 32.9 $mN{\cdot}m^{-1}$. This means that viscosity and surface tension hardly can account for the observed differences in drop size spectrum.

Bouse *et al.* (1990) investigated the effect of several herbicide spray mixtures and polymer adjuvants on drop size spectrum. Although they found significant differences in VMD for herbicide mixtures without polymer adjuvants, variations in surface tension and viscosity were only small and could not explain the differences in drop sizes. Subsequent addition of polyvinyl polymers (Sta-Put or Nalco-Trol (Nalco Chemical Co.)) increased averaged drop size considerably, even at low polymer concentration. Increasing polymer concentration did not result in further increase of drop sizes. The dynamic viscosity of the mixture increased with polymer concentration (up to 3.6 mPa·s for 0.04% Sta-Put; 6 mPa·s for 0.04% Nalco-Trol), but surface tension was not affected (about 29 $mN \cdot m^{-1}$ for all mixtures).

Zhu *et al.* (1997) investigated the effect of recirculating spray liquid in a test stand, with respect to polymer composition and drop size spectrum. Polymer adjuvants based on the common components polyacrylamide, polyethylene oxide and a polysaccharide (xanthan gum) were used in different concentrations. All solutions showed degradation (decrease of volume median diameter) due to recirculation. It is reasonable to assume that degradation is due to breaking of the polymer chains under shear or extensional stress. It appeared that the longer the polymer chains were, the easier they were broken and the more rapid degradation occurred. Solutions of non-ionic polymers degraded more rapidly than those of anionic polymers. For non-ionic polymers, regardless of molecular weight and concentration, volume median diameter has decreased to about the value of pure water after circulating only two times. Solutions of anionic polymers appeared to be more resistant to degradation, especially at higher concentration and higher anionicity. This is probably due to the formation of a network of polymers, which is more resistant to shear stresses and prevents breakage of polymer chains. Top-down ranking of the polymers tested with respect to resistance to breakdown: xanthan gum, anionic polyacrylamides, non-ionic polyacrylamides, polyethylene oxide.

Liquids can be divided in solutions and emulsions. Oil-in-water (o/w) emulsions often behave similar to solutions with respect to viscosity, density and surface tension (Schmidt, 1980). With the use of 'invert emulsions' (water-in-oil, w/o) much higher viscosities can be obtained (Hartley & Graham-Bryce, 1980).

Butler Ellis *et al.* (1997) investigated physical properties of aqueous sprays containing 0.5% Ethokem (cationic surfactant with polyoxyethylene tallow amine) or 0.5% LI-700 (acidifying surfactant with soyal phospholipids). The former adjuvant appeared to reduce drop size, the latter increased drop size. Using Phase-Doppler Anemometry (PDA) they found that the effect on drop size was related with the location inside the spray cloud: the changes were largest near the center of the cloud. Further, with Ethokem the average velocity of drops of a certain size appeared to be lower than with water, while with LI-700 drop velocities appeared to be higher than with water. Drops (>300 μm diameter) of the mixture containing Ethokem, when caught in oil trays, seemed to show air inclusions. Occasionally drops as small as 150 μm diameter showed air inclusions also. The authors assumed that the observed changes in drop size spectrum, liquid sheet geometry could be explained by dynamic changes in surface tension and surface viscosity in the aging liquid sheet. More recently, Butler Ellis & Bradley (2002) found in wind tunnel experiments that drop size reduction when using surfactant 0.5% Ethokem not always led to increased drift, but this seemed to depend also on nozzle type and wind speed. However, their experiments involved flat fan nozzles as well as hollow cone nozzles, which might have obscured a clear interpretation.

Often no clear relation between changes in drop size and concentration of the adjuvant can be given. E.g. while at low concentrations drop size may increase, at higher concentrations the increased drop size may decrease to its initial value (Dexter, 2001). The type of spray nozzle used may be an essential factor as well, yet still not clarifying the observed effects (Spanoghe *et al.*, 2002).

4.3 Reduction of in-flight vaporization

The evaporation rate of additives is determined largely by their saturated vapor pressure, which is much lower than that of water. The effect of a lower diffusion coefficient and a higher density roughly is compensated by the increase in molecular weight. The net result is an evaporation rate for additives which is much lower than that of water, even for additives known as 'volatile'. Therefore, for aqueous sprays evaporation of water occurs much more rapidly than that of the suspended ingredients. Water will evaporate until a more or less dry particle remains. This particle may drift a considerable distance without a notable change in size.

Non-aqueous solvents may evaporate with similar speed as water (e.g. diethylbenzene, n-decane) or even faster (e.g. xylene).

A possible way to reduce drift is to prevent the drops from shrinking, i.e. prevent the solvent from evaporating. Though a non-volatile surfactant may act as an 'evaporation retardant' by shielding the droplet, only few authors investigated this aspect. Hall *et al.* (1994) describe an apparatus to determine the evaporation rate of a relatively large pendant drop in a static environment. They found that several adjuvants appear to reduce evaporation. Unfortunately, a possibly drift reducing effect under practical conditions cannot be deduced from such an experimental method. Besides, an evaporation-retardant adjuvant does not *prevent* drift to occur, it merely may reduce the distance traveled by drift-prone drops. Probably more importantly, the use of such non-volatile surfactants affects the drop size distribution, which is a more effective way to influence spray drift.

On the other hand, vapor loss of active ingredients in air is more likely to originate from spray deposits than from evaporating airborne drops (Hartley & Graham-Bryce, 1980). Only the smallest residual particles (after complete evaporation of the solvent) that may stay airborne over long distances may contribute significantly to vapor loss. Using the spray drift model IDEFICS (Holterman *et al.*, 1997) it has been estimated that roughly 3% of the spray liquid is lost into air (as vapor and 'dry' particles) during a conventional application on field crops (Smidt, 2000).

4.4 Effect on spray pattern

In general, adjuvants not only may affect drop size distribution, but also a change in spray pattern (i.e. the angular volume distribution inside the spray cone) sometimes is observed (Dexter, 2001; Wills *et al.*, 2001; Hewitt *et al.*, 2001). Typically polymer-based adjuvants tend to decrease the top angle due to the effect of extensional viscosity. On the other hand, surfactants promoting a decrease in surface tension tend to broaden the top angle. Not only top angle is affected, but also the shape of the angular distribution may be changed.

5. General information on adjuvants for agrochemicals

5.1 Introduction

In many countries there is increasing pressure to reduce the total loading of pesticides applied to crops and the environment generally. This can sometimes be achieved by introducing new highly active pesticides or by increasing the biological activity of existing pesticides. Because of the very high cost of introducing a new pesticide compound, it is becoming a common practice to investigate the use of surfactants to enhance the activity of existing products. In these cases, the surfactants are known as adjuvant (literally 'helpers') and may be added to the formulation in the same pack, added separately with the formulation in a twin-pack, or added by the user directly to the spray tank. The exact mode of action of the surfactant adjuvant in enhancing biological activity is not fully understood, but is likely that improved leaf wetting, spreading, retention and penetration are important factors, coupled with the basic mode of action of the pesticide itself (Knowles, 1995). Pesticide formulations contain the active ingredient plus other chemicals, including surfactants, which serve several purposes such as wetting and emulsification. Adjuvants may also be added to pesticides at the time of application for a variety of reasons, all ultimately to increase the efficiency of action and application. There are three main reasons to use adjuvants (Knowles, 1995).

Adjuvants are used to facilitate the physical handling characteristics of an agrochemical during storage, mixing and application of the spray solution. Adjuvants are used to improve efficacy and consistence in performance. The ability of adjuvant materials to impact this area is perhaps the most important reason that they are used. First there is the ability to minimise chemical loss and second, the maximization of the agrochemical's effect once it is placed on the target. The main losses are drift, in-flight evaporation, in-flight volatilization, droplet shatter, bounce and or runoff, wash-off, and removal by wind or plant growth. These losses result in agrichemicals never reaching the target or achieving only a transitory deposit. Adjuvant materials have been designed to modify spray droplet characteristics to minimise these kinds of losses. Maximizing the effect of agrichemicals once delivered to the target can also be seriously affected by adjuvants. Coverage of the spray solution can be improved by lowering the surface tension of the spray. Penetration or uptake into the target pest can be enhanced with special types of adjuvant materials, particularly with herbicides, systemic fungicides and insecticides, growth regulators and nutrients. Adjuvants are used to comply with legal requirements. Many pesticides registered have recommendations for adjuvant use. In the US there are some geographic or state statutes requiring the use of certain adjuvants with certain pesticides. They usually involve cotton defoliants, hormone herbicides, and drift-reducing adjuvants. As spray adjuvant uses increases, there is legitimate concern that the products should be registered and regulated, as are the pesticides with which they are used.

Types of adjuvants are surface-active agents (surfactants), emulsifiable oils, polymers, polymer-forming compounds, phospholipids and inorganic salts (Copping, 2000).

5.1.1 Adjuvant use

The value of the world's adjuvant market is estimated to be approximately $1000 million (Copping, 2000). Thousands of adjuvants are available and nowadays their sales in the US represent 5% (value $400 million in 2000) of the pesticide market (with sales totaling $8.5 billion in the US). Pesticides represent a $33-billion industry world-wide. Most herbicides require surfactants and other adjuvants to maximize their efficacy or utility, either as ingredients in the formulated product, as spray-tank additives or both.

Spray adjuvants are used more extensively with herbicides than with other classes of pesticide. The market in the US represent about 150 000 tonnes in the US and 22 000 tonnes in Western Europe. It must be indicated that the US adjuvant market share is more than 75% mineral and vegetable oils and only 15% surfactants while in Europe mineral and vegetable oils represent nearly 50% of the sales and surfactants 52% (Copping, 2000). The present change in acreage in the US from conventional crops to transgenic crops has also dramatically altered pesticide usage and consequently the adjuvant usage. The dominant position of the herbicide glyphosate and its loss of patents creates a need for adjuvants appropriate for safe application of this herbicide (Graham, 2001). Emulsifiers and spray adjuvants in the US have an almost equal share of the market. The spray tank adjuvants are the realm of the formulator/distributor (Helena, Loveland, etc.) but also basic manufacturers market spray adjuvant products. The spray adjuvant market can be divided into two distinct markets: the competitive displacements market and, the non-use markets. The non-use market is potentially much larger than the spray adjuvant market that exists today. In general, formulators market a complete line of spray adjuvant products while basic manufacturers of pesticides market only one or two specific types. This is due to the lack of proprietary chemistry and therefore the lack of patentability of the products.

5.1.2 Adjuvant registration

Registration also plays an important role, influencing from country to country whether adjuvants can be used or not. In the USA many EPA labels neither recommend nor prohibit adjuvant use. In Canada all adjuvants need registration. In the UK stickers and wetters already present in the formulation need registration but when adjuvants are used in the tank mix with no claim of enhancement of pesticidal action no registration is needed. In Germany tank-mix adjuvants are not allowed. In France anything added to the spray tank requires registration. In The Netherlands the use of tank-mix adjuvants is not restricted by rigid registration rules.

5.1.3 Current perspectives for adjuvants

Because of the considerable shift towards the rational design of agrochemical formulations, it is expected that the emphasis with newer products to optimize formulations will reduce new developments in tank-mix practice. However, the use of tank-mix adjuvants to enhance many of the older pesticide formulations will remain common practice. Combinations of generic pesticides and adjuvants are still usually less expensive than the latest agrochemicals (Hochberg, 1996).

At a time of increasing regulatory constraints and public awareness of the health and environmental costs of the broadcast use of pesticides, it is a matter of some urgency to rationalize the spray-application process, itself a major contributor to the wasteful nature of pesticide-based crop protection. The application equipment is unlikely to change significantly in the immediate future. Any technique that increases the efficient utilization of crop protection chemicals, such as the use of spray modifiers, can potentially protect the life span of both new and existing ai's. Delivery of agrochemicals to plants is a very inefficient process (Hall *et al.*, 1993a); just a few promilles of the dose applied will reach the target in the plant or targets on the leaf surface like fungi or insects. There is clearly considerable room for improvement. Improving the efficiency of use of ai has obvious advantages e.g. (a) reducing the quantity of biocide that is released into the environment, (b) reducing input costs, and (c) greater cost effectiveness compared with the development of new ai's. Adjuvants, however, are not without controversy. There is still much confusion surrounding their use, including vague claims and lax reporting requirements. Some of the confusion concerning adjuvants comes from the lack of understanding of adjuvant terminology. Some people use the terms 'adjuvants' and 'surfactants' interchangeably.

5.2 Surfactants

Surfactants are an important group of chemicals among the adjuvants. Surfactants are added to formulated products to aid in the manufacturing process and to improve the application. Surfactants act as emulsifiers as well as wetters and spreaders (Hall *et al.*, 1993a). Normally they are already present the formulation of the ai. Surfactants used for wetting are typically small molecules since small molecules will diffuse more rapidly to the interface. The oldest types of surfactants are soaps, normally sodium or potassium salts of weak fatty acids, e.g. sodium stearate, which have a polar-hydrophilic (water-soluble) and a non-polar lipophilic (oil-soluble) end of the molecule. Although soaps are effective anionic surfactants, they precipitate as an insoluble scum in hard water or acidic solutions and surfactant properties are lost. It is increasingly important that all materials, active ingredients and formulation additives, should be used without endangering non-target species and the environment as a whole. To this end surfactant manufacturers are developing new products which are biodegradable and non-toxic to mammals and to fish. While fully biodegradable surfactants , such as lignosulphates are well known in pesticide formulations, an interesting new trend is the development of sugar ethers or alkyl polysaccharides.

Synthetic surfactants are split into anionic, cationic and non-ionic types. They are similar to soap in possessing a non-polar, lipophilic group (long 12-18 hydrocarbon chain) and a polar hydrophilic group. The hydrophilic group differs from that in soap. Anionic surfactants are very good wetters and detergents; they include aliphatic alcohol sulfates, alkylbenzene sulfonates, lignosulfonates, naphthalene sulfonate formaldehyde condensates and dioctyl and dinonyl-sulfosuccinates. Sulfosuccinates are powerful wetting agents in powder and water dispersible granulates. The alkylnaphthalene sulfonates and lignosulfonates are primarily active at the water/solid interface during the dispersion process. They do not produce much lowering of surface tension, and do not form micelles. They are therefore known as pseudo-surfactants and are often used in wettable powders (WPs) and suspension concentrates (SCs) (trade names are Atlox from ICI and Morwet from Witco).

Cationic surfactants are derived from ammonia and are generally phytotoxic and precipitate in hard water. Non-ionic surfactants do not ionize in solution and so there is no detrimental effect of hard water and high acid solutions. They are good dispersing agents and detergents and form stable emulsions. Wetting can be improved by addition of anionic surfactants. Non ionic surfactants have a lipophilic hydrocarbon chain, e.g. fatty acid and corresponding alcohol attached to a second, hydrophilic, ethylene oxide chain. The length of hydrophilic chain and the nature or lengths of hydrophobic chain determine the surfactant properties; the relation between the lengths of these chains is the hydrophilic-lipophilic balance of HLB scale. The HLB scale is arbitrary, ranging from 1 (lipophilic) to 20 (hydrophilic) (Anderson, 1983).

Table 5.1. HLB value and surfactant properties.

HLB	Property	Behavior in water	Uses
3-6	Invert (water-in-oil emulsion)	Immiscible at room temperature	Adding water-based mixtures to oil
7-9	Wetting agent	Stable but opaque dispersions	Adding oil based mixtures to water
8-15	Normal (oil-in-water emulsion)	Give hazy solutions	Adding oil based mixtures to water
13-15	Detergent	Give clear solutions	Adding oil based mixtures to water
15-18	Solubilizer	Give clear solutions	Adding oil based mixtures to water

The HLB system, so called from Hydrophilic-Lipophilic Balance, is based on the premise that all surfactants have one property in common. That is, they all exhibit a certain balance between the hydrophilic and lipophilic portions of their molecular structure. The lower the HLB value, the more lipophilic (oil-loving) is the material, and conversely, the higher the HLB value the more hydrophilic (water-loving) is the material. Those in the HLB range of 10-11 are intermediate. Emulsifiers, as used in industry, are almost always blends. When two or more emulsifiers are combined, their HLB values are additive. Attaining the proper HLB does not assure good emulsification, or solubilization, or other desired action. With the proper HLB you get the best action from the chemical type with which you are working. To obtain the best action you must have both the proper HLB and the correct chemical type. A low HLB (4-7) should be used for w/o and a high HLB (9-20) for o/w emulsions.

The principal classes of non-ionic surfactants are: alkylphenol ethoxylates, long chain alkanol ethoxylates, long chain alkylamine ethoxylates, sorbitan esters and their ethoxylates and ethylene oxide/propylene oxide block copolymers.

Alkylphenol ethoxylates (APEs) were among the first commercially available non-ionic surfactants and have enjoyed widespread use in e.g. agrochemicals (60 000 tonnes annually)(Knowles, 1995). Nonylphenol ethoxylates are by far the most important APEs, accounting for about 80% of total APE volume. Alkyphenol ethoxylates are relatively slow to degrade. In crop protection, APEs are widely used as wetters and emulsifiers because of their low cost and effectiveness. The amounts of nonyl-and octylphenol ethoxylates (like synperonic NP8, nonylphenol POE) applied to crops is typically equivalent to 50-200 g/ha. In the last few years, the metabolites of nonylphenol ethoxylates in water have been suspected of being potential endocrine disrupters. They are therefore being banned in some countries and further product development based on these compounds in Europe is unlikely. Tallow amine ethoxylate has become important in glyphosate formulations to enhance biological activity. Sorbitan esters are used mainly as emulsifiers. The main supplier is ICI (Span and Tween). In general, the partial esters such as the Span products are lipophilic and most of the polyoxyethylene derivates, such as the Tween products are hydrophilic. Other very good emulsifiers are the ethylene oxide/ propylene oxide copolymers (trade names from ICI are Synperonic PE, from BASF are Pluronic PE) and ABC type bock copolymers (trade names from ICI are Synperonic NPE, Atlas G and from Rohm and Haas is Triton). In recent years, the research for products that adsorb very strongly on surfaces and also have large stabilizing groups has led to the development of polymeric surfactants. A product of this type is Atlox 4913 from ICI (known as a ‘comb’ or ‘rake’ surfactant). Silicone surfactants can be useful where very low surface tensions are required, for example to give excellent wetting. The most common are polysiloxane-polyether copolymers (Trade names are Tegoplant from Goldschmidt and Silwet from Union Carbide).

For the creative, market focused surfactant manufacturer, the present greater environmental awareness has created the opportunity and challenge to identify or develop surfactants that meet performance, ecotoxicological and handling requirements without compromises. Examples are sugar ether-based surfactants (alkylpolysaccharides, APS, like Atplus APS 450 a C9-C11 APS) with unique properties when compared to other non-ionic surfactants, and ‘speciality’ alcohol alcoxylates like monobranched alcohol alcoxylates (MBA, Atplus MBA 871, Atplus 872) and amine- (Atlas G-3780A, tallowamine POE), amide- and glucamide-based surfactants like alkenic succinc anhydride diglucamides. Alcoxylated ethylene diamines (for example the Synperominc T range) are acceptable alternatives for the conventional alkoxylated tertiary alkyl amine surfactants.

5.3 Formulation types

The most common formulations are still soluble concentrates for water-soluble chemicals, emulsifiable concentrates for oil-soluble chemicals, and wettable powders for insoluble solids (Tadros, 1983). Granules and powders for direct application to soils and seeds respectively have been produced for many years. The general trend is now to move away from dusty powders and liquids based on flammable or toxic solvents towards aqueous-based suspensions or emulsions and water-dispersible granules.

Table 5.2. Different formulation types.

Formulations type	GIFAP code	Carrier concentration (%)	Water (%)	Emulsifier concentration (%)
Wettable powder	WP	15-70		
Emulsifiable Concentrate	EC			up to 20
Suspension Concentrate	SC		20-80	
Solution Concentrate	SL		50-80	
Suspoemulsions	SE		10-30	1-5
Water Dispersible Granules	WG	5-45		
Oil in water emulsions	EW			5
Microemulsions	ME			up to 30

There is also increasing interest in multi-component formulations such as mixed suspension concentrates and 'suspoemulsions' to broaden the spectrum of biological activity. Surfactants are also being used as built-in-wetter systems to increase the biological activity of the pesticide and thus reduce dose rate. With some products, it is not possible to incorporate the surfactant system into the formulations and in these cases surfactant wetters are used increasingly as tank-mix adjuvants.

5.3.1 Definitions

An adjuvant can be defined as a substance without significant pesticide properties, added to an agricultural chemical to aid or modify the activity of this chemical. A built-in adjuvant is part of the formulation as delivered by the producer of the active ingredient. A tank-mix adjuvant is an adjuvant that is added by the user to a commercial formulation just before application.

Other definitions (anonymous) are:

Additive: non-pesticidal ingredient added to a formulation for a specific purpose. May be incorporated in a product or added to a tank mix.

Carrier: bulking agent, diluent, filler, vehicle.

Dispersant: neutralizes the attractive interaction of like particles, maintaining them in uniform suspension in liquids.

Dispersible concentrate (DC): liquid, homogeneous formulation applied as a dispersion of solids in water.

Emulsifier: surfactant used with oil to emulsify the oil in water.

Flowable product suspension concentrate (SC): Suspension of particles in complex liquid, emulsifiable for water sprays but not for oil.

Granule:	free-flowing solid product.
Humectant:	additive that increases the moisture content of a product by absorbing water from the air.
Spreader:	additive that improves the spread of a spray over a plant surface by lowering surface tension.
Suspender:	additive that maintains in suspension solid particles in a spray.
Wettable powder:	powder to apply as suspension in water.
Wetter:	surfactant used with water, cf. emulsifier; improves mixing of a product with a liquid; reduces surface tension; improves spread of a spray over a plant surface.

5.3.2 Liquid suspensions

This range of formulations uses a liquid as carrier, usually water or oil. The most common are suspension concentrates and emulsions.

Suspension concentrates

Suspension concentrates (SC)-stable suspensions of active ingredients in a fluid intended for dilution in water before use- have grown rapidly in popularity because of several obvious and significant benefits such as absence of dust, ease of use and effectiveness when compared with other conventional formulation types, such as emulsifiable concentrates and wettable powders. The suspended active ingredient must be insoluble in, and insensitive to, the dispersing medium-usually water, sometimes and aliphatic or an aromatic solvent. Products such as ethoxylated alcohols and alkyl naphthalene sulphonates are responsible for the wetting of the particle. Dispersants-anionic, non-ionic or polymeric in nature- stabilize the particles in the dispersing medium.

Suspension concentrates are essentially suspensions of particles in liquids. Particles account for 10-40%, surfactant 3-8% and carrier liquid (oil or water) 35-65% by weight. Viscosity should roughly equal the setting rate of the particles. This is achieved by the use of dispersants i.e. colloidal clays, synthetic polymers, etc.

Concentrated emulsions

Concentrated emulsions (EW)-stable concentrated oil-in-water (o/w) dispersions of a liquid or a low melting point lipophilic active ingredient have the advantage that they are liquid, easy to handle and have reduced toxicity levels when compared with other formulation types such as water-dispersible granules and emulsifiable concentrates. Surfactants need to stabilize the emulsion in its concentrated form for the duration of its shelf life, and will also stabilize the emulsion upon dilution in the spray tank.

Emulsifiable concentrates

Emulsifiable concentrates (EC) - liquid, homogeneous formulations to be applied as an emulsion after dilution in water - usually consists of an organic active ingredient and emulsifiers dissolved in a suitable water-immisible organic solvent. Added to water, they form a sprayable oil-in-water (o/w) emulsion, with dispersed phase droplets in the range of 0.1 to 5 µm. ECs frequently contain a blend of surfactants (usually an anionic with a non-ionic) to produce an emulsion containing droplets within a specified size range instantaneously on mixing with water in the spray tank.

Microemulsions

The droplet size in a ME is around 0.1 μm meaning that microemulsions are normally clear or translucent. To achieve this droplet size a blend of water-soluble (high HLB value) and oil-soluble (low HLB value) surfactants are used.

Oil in water and Suspo emulsions

Oil in water formulations allows the levels of solvent used in an EC formulation to be reduced or to be eliminated altogether. Pairs of non-ionic surfactants are used and polymeric surfactants can be used as emulsifiers and thickeners.

A suspo emulsion (SE) consists of three phases: a discontinuous oil phase (solvent + dissolved ingredient) dispersed in a continuous aqueous phase to produce an oil-in-water (o/w) emulsion. Then, the third solid phase is dispersed through the continuous aqueous phase. Again the emulsifier pair can be non-ionic and polymeric.

5.3.3 Powders

Wettable powders

Wettable powders (WP) - powder formulations to be applied as suspensions after dispersion in water - consists of a single active ingredient or a number of them, blended and mixed with inert fillers (or carriers). These mixtures are dispersed in water and sprayed on the crops.

Water-dispersible granules

Water-dispersible granules (WG) - a formulation consisting of granules to be applied after disintegration and dispersion in water - allow the production of highly concentrated formulations which are wettable and easily disintegrated in contact with water. Water dispersible granules are easy to formulate at very high concentrations; they produce little or no dust and free flowing for easy and accurate measurement.

Wetters and spreaders

Wetters are particularly important components in SL, SC, SE, WG and WP formulations.

Table 5.3. Concentration of wetters in formulations.

Formulation	Wetter concentration (%)
Solution concentrate	3-10
Suspension concentrate	1-5
Suspoemulsion	0.1-2
Water-dispersible granule	1-5
Wettable powder	1-5

Wetters can be either anionic or non-ionic surfactants. The enhanced capability of silicone surfactants and fluorosurfactants to reduce surface tension makes these products useful (but expensive) wetting agents.

5.3.4 Dispersants

Dispersants are used to prevent solid particles from aggregate in the pre-mix or in the spray tank. These surfactants are anionic and the larger the surfactant molecule, the more particles can adsorb and thus provide long-term stability of the formulation. The surfactants used for this purpose are bulky anionic molecules such as lignosulfates and formaldehyde condensates of alkylnaphthalene sulfonates but also Atlox 4913, the polymeric surfactant is a good dispersant.

Table 5.4. Concentrations of dispersants in formulations.

Formulations	Concentrations of dispersants (%)
Suspension concentrates	< 10
Water-dispersible granule	5-20
Wettable powder	< 10

5.4 Application of liquid formulations

5.4.1 Water volume and drop size

In a liquid formulation the active ingredient is carried in a liquid, normally oil or water. Addition of surfactant or oil and emulsifier to water, or use of pure oil, form drops of more even size than those of water do alone, with consequently better controlled spray. Oil is preferred for ultra low-volume sprays (ULV); water is normally used as the diluent at higher volumes.

Table 5.5. Common volume application rates of liquid formulations (Matthews, 1992).

Classification	L/ha
High volume (HV)	> 600
Medium volume (MV)	200-600
Low volume (LV)	50-200
Very low volume (VLV)	5-50
Ultra low volume (ULV)	< 5

Reduction of volume increases the need to optimize spray droplet size to maximize coverage of the target.

Droplet size ranges for optimum application of foliage is 40-100 µm. Coverage is influenced by droplet size, impaction and retention. Drop sizes can be divided into two classes: small drops (<100-150 µm) and large drops (>150 µm) (Himel *et al.*, 1990). The small drops are primarily transported on turbulent eddies and therefore penetrate through foliage canopies. A spray cloud normally contains a range of droplets. The final size of the droplet reaching the target depends on the amount of evaporation of the formulation itself. The general characteristics of evaporation of water from water based droplets have been fairly well described by a theoretical model (Luo *et al.*, 1994). Oil evaporates much less than water as a result of different vapor pressure and viscosity. Also evaporation of formulation itself increases as droplet size decreases due to increasing surface to volume ratios. Oil carriers are most used for ULV sprays. If water is used, especially with small droplets, an anti-evaporant or humectant is used. Anti-evaporants may form a film at the droplet surface to reduce evaporation: often these are water-soluble polymers.

5.4.2 Reduction of water evaporation

The current trend toward reduced spray volumes and uniform active ingredient distributions by utilizing small droplets has increased the likelihood of spray mix evaporation. For ultra-low-volume (ULV) application where oil is the carrier, evaporation-stable formulations are readily available. This is not the case, however, for spray applications where water is the carrier. For this reason, several adjuvants have been introduced with recommendations for use in evaporation reduction (Roberts, 1992). Laboratory evaluation of evaporation reduction performance is hampered by the large number of variables encountered in actual field use. Laboratory procedures having applications in this area are available, but limited when applied to water-based spray mixes. (Sundaram & Leung, 1986). ASTM D972 is applicable (test temperature 100 °C!) but variables affecting evaporation rates in the field, such as humidity, wind speed, and spray velocity, however, are not addressed by the laboratory procedures.

Studies on evaporation rates for a falling water droplet show that its diameter decreases linearly with fall time for most of its life but that around 140 μm the slope changes to reflect a slower rate. There seem to be two internal streamlines within the droplet, which circulate the liquid up to six times per second. This exposes liquid from the center of the droplet to the evaporative process. Therefore when a non volatile viscous liquid is added to water the droplet will evaporate at the same rate as water until the concentration of the non evaporative component increases thus raising which in turn reduces the internal velocities of the streamlines thus reducing the rate of evaporation. After the volatile component has evaporated the droplet will be left with a skin of non-evaporative material. There is a need to explore complex liquids because droplet drift could be greatly reduced when droplet evaporation is reduced. However, increasing droplet size has drawbacks such as possible reduction in spray retention and coverage and an adverse effect on lateral spray distribution (Combellack, 1998).

5.4.3 Fluid properties and spray quality

Compared to water, addition of a water-soluble polymer causes a dramatic decrease in fan width, attributable to an increase in the extensional viscosity (Dexter, 2001). At the same time there is a change in the fluid distribution: more liquid is found at the edges of the fan than is the case of water. Emulsions, in contrary form wider fans than water and all form high spray concentrations close to the edge of the fan. The droplet size of sprays form a flat-fan nozzle is increased by emulsions when present in the spray mix above a critical concentration. This concentration depends on the type of emulsion, and on the other surfactants present in the spray mix. Emulsions of an aromatic solvent, Silwet L-77, mineral oil, methyl canolate and other water-insoluble liquids including surfactants with droplet sizes ranging from 0.3 to 30 μm are all effective. When dispersions of solid particles are present there is no significant effect on spray droplet size. It appears that the dispersed particle in the spray mix must be liquid or deformable during the break-up of the sheet for an increase in droplet size to occur. Emulsion sprays form narrower droplet size distributions than water. When sheet break-up occurs, the droplets follow trajectories that spread at angles depending on the wave amplitude. A similar effect is seen in polymer solutions, but the sheet length is increased. Water-soluble surfactants have little effect on the spray thickness. With emulsions, the spray expands immediately from the nozzle at a narrow angle that remains constant and does not abruptly expand, as is the case for water. As a result the thickness of the fan is smaller for the emulsions than for water, surfactant or polymer solutions.

When surfactants are tank mixed with the pesticide, a liquid crystalline phase is formed as the spray droplet dries on the surface of the leaf (Knowles, 1995). These liquid crystals may improve rain fastness and increase pesticide activity since the active ingredient stays solubilized for a longer period. The phase behavior of systems at higher surfactant concentrations is likely to have an impact on biological efficiency. The presence of vesicles is claimed to increase the transport of the active component to the surface of the leaf and to enhance transport of the active component through membranes. A significant observation is that at low concentrations, monobranched alcohol alcoxylates form vesicles rather than conventional micelles.

The role of surface tension in the application process is complex (Tadros, 1983; Tadros, 1994). Equilibrium (static) surface tension is easily measured, but measurements of dynamic surface tension, especially at surface ages present at atomization, are more difficult to obtain. Dynamic surface tension clearly has a role to play in the atomization of a liquid but it is not surface tension forces alone that govern the break-up of liquid into drops. Viscosity is also important, and these two forces interact. At droplet impaction, dynamic surface tension forces are again important and, with viscous forces, combine to affect rebound, run-off, and spread of liquid upon the surface of the substrate. Once liquid has adhered to the substrate, equilibrium surface tension will affect the spread of the droplets over the surface and hence deposit formation.

Oil based adjuvants are used for a variety of different reasons, including the reduction of loss through the vapor phase. It was usual to use mineral oils as spray formulation or spray tank additives but it is now considered to be more environmentally friendly (and in many cases more cost effective) to use vegetable oils.

The modified lecithin adjuvant (LI-700) increased droplet size when added to Roundup (water soluble pesticide) reducing drift substantially but also increasing deposition on the crop (Butler Ellis *et al.*, 1998). The tallow amine surfactant T80 had a more predictable effect, reducing droplet size, increasing both drift and deposition. With Topik (EC) all three adjuvants resulted in similar droplet size distributions and similar amounts of drift. However, deposition on the target was significantly higher with LI-700 than with the oil adjuvant (EC, SM99) or the methylated seed oil (EC, Phase). In another study (Butler Ellis *et al.*, 1997), comparing six different adjuvants it was found that Etokem (cationic surfactant, polyoxyethylene tallow amine) had the greatest effect in reducing droplet size and Spraymate LI-700 (penetrating acidifying surfactant 750 g/l soya phospholipids) was one of the adjuvants that significantly increased droplet size. When comparing 'Ortho' X-77, a non-ionic surfactant and 'Direct', a drift-controlling polymeric adjuvant, there is 4.5% less volume in droplets that are <100 μm diameter compared to water, i.e. 0.35 of the total volume sprayed is in drops <100 μm in diameter (Hall *et al.*, 1993a). In contrast, "Direct" gives 19% more volume in droplets that are between 600 and 700 μm compared to water. Spreaders and stickers were found to have equilibrium surface tension values of 20-25 mN/m; penetrants/crop oil concentrates/extenders (for example Bond) have equilibrium values ranging from 30 to 40 and dynamic values from 40 to 70 mN/m.

The drift control agents (Agro-Flow, Direct, Nalcotrol, 38-F + Sta-Put, 41-A and Windfall) exhibit equilibrium and dynamic surface tension values of 70 mN/m. It is well known that linear, high molecular weight water-soluble polymers such as polyacrylamides, reduce the tendency of aqueous sprays and jets to break up (Chamberlain & Rose, 1998). It was found that polymer with higher MW would modify the spray pattern significantly, whilst the low MW products have little influence. Formulations containing polymeric adjuvants and a high concentration of a non-ionic surfactant provided pseudoplastic liquids with high viscosities (Sundaram *et al.*, 1987). These formulations resulted in large droplets with high recoveries of spray deposits on sampling units. When an anti-evaporant was added to a permethrin (insecticide) formulation (Thacker & Hall, 1993) the following was observed: a) a decrease in evaporation rate, b) a decrease in droplet retention, c) no change ion the ais intrinsic toxicity and d) and increase in the ais bioavailability.

For example, the linear equations predict that for a 200 μm droplet of Ambush (conventional Permethrin formulation), released at a height of 20 m (i.e. from an aircraft) into the air at a temperature of 30 °C, evaporation would be complete before it had an opportunity to deposit. In comparison, a droplet of D325 (with added anti-evaporant) would deposit with a diameter of approximately 140 μm under the same conditions. The dynamic surface tensions of Ambush and D325 are 43 and 47 dynes/cm, respectively.

It is common for adjuvants that are described as drift retardants to show no effects on droplet size for all formulation types. However, a product like Quilt (sold as wetter/spreader) did reduce the volume of spray carried in small driftable droplets by over 50%. It has been demonstrated (Dexter, 2001) that sprays containing oil emulsions reduce drift significantly.

The complexity of the process of pesticide delivery has been demonstrated (Dexter *et al.*, 1998). In many cases adjuvants are used to correct a problem of compatibility or drift. Physical properties, which are optimized for one stage may not be optimum for the following one. Pesticide efficacy can be increased by minimizing drift losses (high dynamic surface tension), minimizing droplet reflection (low DST), maximizing spreading (low EST) and maximizing penetration and uptake (chemical properties). Adjuvants can be selected by their physical properties to modify a deficiency in a particular stage of application, but on that basis no adjuvant can possibly optimize all other stages. Selection of an adjuvant should only be made after an analysis of the efficiency of each stage in the delivery process and should address that part of the process where the greatest increment in efficacy can be obtained.

When a spray liquid is applied in fine droplets, a much better coverage is obtained than the same volume would give in large droplets. As an example, one droplet of 400 μm diameter is equal to eight droplets of 200 μm obviously the same volume spray will be more efficiently spread over the target in eight smaller droplets than in one large one, and the finer droplets more easily attach to most targets. Common droplet sizes are:

Table 5.6. *Common droplet sizes for different spray categories.*

Spray category	Volume median diameter of droplet μm
Aerosol	< 50
Mist	50-100
Fine spray	100-200
Medium	200-400
Spray	> 400
Coarse spray	> 400

The best droplet size required for the target being sprayed is produced by careful selection of spray nozzle and operating pressure. Most herbicide spraying should aim at a droplet size of 100 to 300 microns. Larger droplets will give poor coverage, whilst smaller ones can result in excessive drift and evaporation losses.

Droplet density usually quoted, as the number of droplets per square centimeter is very important. Some systemic herbicides may be quite effective at droplet densities as low as 5 to 10 droplets per square centimeter when applied in larger droplets, whilst non systemic fungicides need to be applied at densities of 50-70 droplets per square centimeter for maximum effectiveness.

Table 5.7. Relation between droplet size and number of droplets per square centimeter.

Droplet diameter µm	Number of droplets per square centimeter
10	19097
50	153
100	19
200	2.4
500	0.2
1000	0.02

Table 5.8. The relation between droplet size and its effect on spray drift.

Droplet diameter (µm)	Time for droplet to fall 3 meters (s)	Distance droplet travels whilst falling 3 m in a 5 km/h wind (m)
5	3960	5000
100	10	15
400	2	2.5
1000	1	1.4

While it is now known how pesticide application could be modified to eliminate drop reflection, the constraints in these areas are enormous and the spray formulation and its method of application in the field must inevitably be a compromise. For example, aqueous pesticide solutions applied as very small droplets with low velocity would not bounce from leaves but evaporation and drift would result in a high proportion of the spray never reaching the target canopy (Grease *et al.*, 1991).

6. Conclusions and recommendations

Volatilization of an active ingredient can occur both during and after application of the pesticide. Emission data provided in Chapters 1 and 2 indicate that volatilization after application may exceed the emission during application. Data on volatilization during the flight of spray drops, considered separately from the emission by drift of small droplets, were not found. Joint experiments at IMAG-DLO have been started in 2001 to highlight this aspect.

Controlled release formulations using polymers and chemical modifications of the active ingredient have been used by the industry to control and to reduce the volatilization of pesticides as mentioned in Chapter 2. Data in this chapter also indicate that formulations of many existing products are such that high levels of volatilization can occur. In those cases where a reduction of volatilization does not impair the performance of the pesticide, many more opportunities are forehand to improve formulations such that emission can be lowered.

Adjuvants can reduce the fraction of driftable spray drops by enhancing the volume median diameter of spray drops as mentioned and discussed in all chapters. This adjuvant technology is not used in The Netherlands and we recommend to pay more attention on this aspect whereby performance of the active ingredient must be maintained.

Adjuvants are able to ‘stick’ an active ingredient in the drop residue on the leaf or soil surface. In other words the adjuvant creates a shift of the partition coefficient of the pesticide between drop residue and the air in the direction of the drop residue. This has been demonstrated for surfactants and wax-type adjuvants and is indicated by joint head-space experiments at TNO Food and Nutrition Research both mentioned in Chapter 2. More research is required to optimize this technology regarding the interaction between adjuvant type, pesticide and pesticide formulation.

Adjuvants are used frequently to enhance the foliar penetration of active ingredients as mentioned in Chapters 2 and 3. This penetration competes with volatilization from the drop residue and, depending on the pesticide functionality, can be considered as a tool to reduce emission. This aspect is subject of a literature study that is conducted in 2002.

This study was focused on adjuvant and formulations as tools to reduce emission both during and after application. The application technology, like nozzle type, strongly influences drop size and thus the fraction of drops susceptible to drift or aerosol formation. We recommend that more attention will be paid on the interaction between nozzle type and formulation/adjuvant type in order to optimize an emission-poor application.

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