A Introduction

1 Influence of rainfall on pesticide deposits

Agrochemical deposits on plant surfaces are constantly exposed to physical, biological, and chemical factors which may reduce the biological efficacy of the active ingredients (Schepers, 1996; Neely, 1970). Activity losses are attributed to impact of wind, UV-radiation, temperature, and biological degradation. Nevertheless, the main environmental factor responsible for residual activity of a given agrochemical is the influence of rain (Schepers, 1996; Leung and Webster, 1994; Kudsk *et al.*, 1991; McDowell *et al.*, 1987; Bruhn and Fry, 1982). Natural rainfall and overhead irrigation modify pesticide deposits on plants by dilution, redistribution and removal (Thacker and Young, 1999). Therefore, in order to assure pest control, treatments must be repeated, thus increasing production costs significantly (Thacker and Young, 1999; Troiano and Butterfield, 1984). Another negative consequence is the fact that rain-removed pesticides will reach non-target organisms, soil and water resources, resulting in unnecessary environmental contamination (Wauchope *et al.*, 2004).
On the other hand, rain-induced redistribution of active ingredients on leaf surface can induce positive effects, especially when a.i. is irregularly deposited (Kudsk *et al.*, 1991; Smith and MacHardy, 1984). In some cases, this could be used as a strategy for pathogen control (Rudgard *et al.*, 1990; Cooke *et al.*, 1989), providing enhanced fungicide efficacy (Schepers, 1996; Bruhn and Fry, 1982). Unfortunately, redistribution may also have a negative impact, since it can lead to a sub-toxic a.i. concentration on the whole surface, allowing or even stimulating the development of hazardous organisms (Steurbaut, 1993).

Several factors affect rainfastness of agrochemicals, but the majors are rain intensity, rain amount, interval of time between treatments and rainfall, commercial formulation of pesticides, pesticide water solubility and type of crop (Cabras *et al.*, 2001; Green, 2001). Moreover, the interaction of all these factors must be considered (Thacker and Young, 1999).
In the past, the term rainfastness was not always accurately used. Rainfastness denominates an intrinsic property of a given active ingredient or commercial formulation to resist the physical impact of rain droplets and the carry out effect of water film. Therefore, only those a.i. placed on plant surface can show its rainfastness. In contrast, if a.i. has already penetrated the plant tissue by the time of starting rain, rainfastness can not be determined. Several factors influence both rainfastness (directly or indirectly) and penetration (with respect to rain-induced wash-off) of agrochemicals. As exemplification we present the impact of adjuvants:

1 – If included in a formulation or when added to spray solutions, adjuvants can enhance adhesion of a.i. on plant surface, enhancing rainfastness in a direct way;

2 - Adjuvants modify the physicochemical characteristics of spray solutions, influencing the formation of deposits on plant leaves. Some deposit characteristics such as initial concentration, particle size, and a.i. distribution may alter rainfastness of a given agrochemical. As a result, adjuvants influence rainfastness indirectly;

3 - Adjuvants may improve penetration rate of systemic compounds, reducing the a.i. deposit on leaf surfaces before rainfall onset; this contributes to a reduction of rain-induced wash-off. Moreover, pesticide penetration implies alterations of deposit characteristics, which may influence rainfastness of the remaining a.i. indirectly.

2 Influencing factors on rainfastness and rain-induced wash-off

2.1 Active ingredient

Active ingredients have particular properties such as molecular weight, polarity, water solubility and others, which may influence their adhesion to plant surface and/or diffusion into wax layers. These characteristics may be decisive for the differences in rainfastness observed among several active ingredients (Spanoghe *et al.*, 2005; Suheri and Latin, 1991). Particularly the water-soluble pesticides are vulnerable to wash-off caused by rain (Green, 2001; Mashaya, 1993). However, even fungicides with low water solubility are easily removed by little amount of rain (Cabras *et al.*, 2001; Kudsk *et al.*, 1991).
In the case of systemic compounds, penetration of a.i. into the plant tissue reduces its exposition to environmental factors, reducing the risk of a rain-induced wash-off. Pick *et al.* (1984) suggest the speed at which an active ingredient penetrates the leaf determines its resistance to wash-off. Here, lipophilic compounds penetrate waxy, hydrophobic plant leaves more readily than hydrophilic compounds (Mashaya, 1993). Further, pesticide penetration may modify characteristics of the remaining deposit, exerting indirect influence on rainfastness.

2.2 Physical form of the pesticide formulation and deposit characteristics

The physical form of a commercial formulation (Tab. 1) has a great impact on pesticide rainfastness. As a rule, powders and granule formulations are removed more easily from plant surfaces than flowables and suspensions (Willis *et al.*, 1996; Kudsk *et al.*, 1991; van Bruggen *et al.*, 1986). Van Bruggen *et al.* (1986) observed that WP formulations of five fungicides had lower rainfastness than the respective flowable formulations. Pick *et al.* (1984) tested rainfastness of pesticides with different physical forms acquired by different producers and observed that rainfastness is drastically influenced by type of formulation; however, considering a given a.i. and physical form, rainfastness of agrochemicals was comparable, regardless of producers.

Table 1. Properties of water-mixable pesticide formulations.

Formulation	Physical form	Physical form in the tank
Wettable Powder (WP)	Powder	Suspension
Wettable Granule (WG)	Granule	Suspension
Suspension Concentrate (SC)	Suspension	Suspension
Emulsifiable Concentrate (EC)	Real solution	Emulsion (o/w)

Source: Haefs, 2001; Knowles, 1995; Börner, 1995; Heusch, 1981.

The physical type of formulation influences deposit characteristics and distribution patterns on leaf surfaces (Cooper and Hall, 1993; Hess and Falk, 1990). Pesticides formulated as wettable powders or granule yield deposits with greater median diameter (Kudsk *et al.*, 1991), which are less tenacious than small particles (Somers and Pring, 1967). Bukovac *et al.* (1995) observed droplets from spray formulations containing solids (e.g. WP) often deposit in irregular forms, so that many deposits bridge depressions and fail to make uniform contact with leaf surface. In addition, SC formulations generally contain more adjuvants than dry formulations (Gent *et al.*, 2003; Steurbaut, 1993), which can additionally influence rainfastness.

The amount of pesticide deposited on leaves may influence rainfastness of a given agrochemical; however, a consensus is missing. Willis *et al.* (1992) observed that wash off methyl parathion and fenvalerate from cotton plants is related to the square of insecticide amount loaded on plants. In another work, Willis *et al.* (1994) observed that removal of permethrin and sulprofos from cotton plants is related to the mean of insecticide deposited on plant surface. In contrast, Smith and MacHardy (1984) verified that relative decrease of captan residues from leaf surface due to rain is not a function of initial deposit. Also Bruhn and Fry (1982) have not observed an influence of the deposit magnitude on rain-induced wash-off. Leung (1994) noted that initial concentration of glyphosate does not affect intensity of degradation and removal processes like volatilization, photolysis and rain-washing.

2.3 Adjuvants

Adjuvants already incorporated in pesticide formulations or tank-mixed may influence both rainfastness and wash-off processes in distinct ways. Adjuvants can be arranged in groups according to several parameters, but usually they are classified taking into account their charge, origin, chemical composition, and objective of use (Green, 2001; Abribat, 2001; Tu *et al.*, 2001; Stock and Briggs, 2000; Hill, 2000; Green, 2000; Hazen, 2000; Stock, 1997; Knowles, 1995; Steurbaut, 1993; Stevens, 1993). The greater influence on enhancing rainfastness and reducing rain-induced wash-off is provided by stickers and penetration adjuvants respectively. It is not rare that a single adjuvant influences both processes; in such cases it is difficult to distinguish which effect acts in a greater extent.

2.3.1 Influence on rainfastness

Sticker-adjuvants enhance attachment of a chemical on leaf surface and make deposits less susceptible to removal by rain and other environmental factors (Martz, 2004; Hazen, 2000). Usually the sticker-components are nonevaporating materials with a viscous nature, allowing them to adhere, along with the pesticide deposits, for a longer time (Hazen, 2000). Stickers fall broadly into two categories: those that polymerize on the leaf surfaces, and those that are already high molecular weight polymers, such as latex derivates (Stevens, 1993). Particularly the high molecular weight stickers have a natural adherent tendency to plant surfaces (Hazen, 2000). These have many anchoring points, giving a.i. long term stability (Knowles, 1995). The most common stickers are heavy petroleum oil, acrylic latex, terpenes, epoxidised oil, alkyl resins, and block co-polymers (Green, 2001; Hazen, 2000).

The second potential base for enhancing rainfastness in a direct way is water repellency of the deposit (Roggenbuck *et al.*, 1993). Some adjuvants form a hydrophobic layer over the pesticide deposit and protect it against water contact, preventing wash-off (Green, 2001). The degree of tackiness and resistance of the deposit vary according to water solubility of the adjuvant and its relative concentration to pesticide (Hazen, 2000).

The indirect effect of adjuvants on rainfastness is related to deposit characteristics. Several adjuvants improve spray deposition on the surfaces (Faers *et al.*, 2004; Balsari *et al.*, 2001), due to their ability in reducing surface tension of pesticide solutions. This decisively reduces the influence of adverse effects such as leaf topography, epicuticular wax, and trichomes (Hess and Falk, 1990). Mainly affected are pesticide placement on leaves, initial a.i. concentration, particle size, and grade of coverage (Scherhag, 2005; Gent *et al.*, 2003; Green, 2001; Green and Hazen, 1998). According to Leung and Webster (1994) and Steurbaut *et al.* (2001), solutions with low surface tension and low contact angle may dry up rapidly on foliage, resulting in crystalline, rainfast deposits.

2.3.2 Influence on penetration

A penetration agent is a compound that assists the pesticide movement from target surface through natural barriers into plant tissue (Hazen, 2000). They can influence coverage, droplet retention, physical state of the residue on cuticle surface, and additionally change structure and composition of the cuticle (Kirkwood, 1999; Kirkwood, 1993). As a result, they greatly enhance penetration rate of systemic compounds (Gent *et al.*, 2003; Zabkiewicz, 2000; Nalewaja and Matysiak, 2000; Laerke and Streibig, 1995; Gauvrit and Cabanne, 1993; Gaskin and Stevens, 1993; Stevens and Baker, 1987). Generally, hydrophilic adjuvants with high HLB values are most effective in enhancing penetration of highly water soluble herbicides, whereas lipophilic surfactants with low HLB are most effective in enhancing uptake of low water soluble herbicides (Hess and Foy, 2000). Actually, several combinations of adjuvant types, active ingredients, and formulations were already tested in diverse plant species (Müller *et al.*, 2002; Roggenbuck *et al.*, 1993; Gaskin and Holloway, 1992; Wells, 1989; Field and Bishop, 1988). The effect of adjuvants on a.i. penetration with consequences on wash-off depends on interactions of all involved factors, such as type of adjuvant and its concentration, active ingredient and its concentration, type of formulation, surface characteristics, and environmental factors (Gent *et al.*, 2003; Schönherr, 2002; Haefs, 2001; Combellack *et al.*, 2001; Kogan, 2001; Leaper and Holloway, 2000; Sun, 1996; Sandbrink *et al.*, 1993; Gaskin and Stevens, 1993; Coble and Brumbaugh, 1993; Reddy and Singh, 1992; Cranmer and Linscott, 1991; Roggenbuck *et al.*, 1989; Wells, 1989). Therefore, the great variability in the results is not surprising.

Finally, a.i. penetration *per se* modifies characteristics of the remaining deposit on leaf surfaces. Form and nature of remaining residue on the surface may be important for performance of some compounds (Bukovac *et al.*, 1995), and possibly for their rainfastness.

2.4 Drying time and environmental conditions

The time elapsed between pesticide application and rainfall onset decisively influences magnitude of a.i. wash-off by rain. Agrochemical deposits need a minimum of time to dry up and so resist impact of rain droplets. Several studies have shown that enhancement of rainfastness or reduction of wash-off can be achieved by longer drying times (Reddy and Locke, 1996; Schepers, 1996; Willis *et al.*, 1994; Mashaya, 1993; Willis *et al.*, 1992; Bryson, 1987; Pick *et al.*, 1984; Bruhn and Fry, 1982). However, there is no consensus, since other studies have shown that drying time has no influence on rainfastness of active ingredients (dos Santos *et al.*, 2002; Ditzer, 2002; Schepers, 1996; Clay and Lawrie, 1990).

Actually, contradictory observations are common, once standardized methods are not available and experiments can not always be conducted at same conditions. As a consequence, the evaluated drying times range from few minutes to several days (Willis *et al.*, 1992; Bruhn and Fry, 1982). In addition, environmental conditions during drying time play a decisive role. Ditzer (2002) showed that retention and rainfastness of contact fungicide dithianon was influenced by dew on the leaf surface. The same author studied influences of relative humidity during the drying time on rainfastness of the active ingredient.

In case of systemic compounds, interactions are more complex. Pesticide penetration into plant tissue is a function of time, regulated by several biological and environmental factors. For an optimal penetration into plant tissues, systemic a.i. must be in a liquid form (Bukovac *et al.*, 1995). In contrast, to be rainfast, a.i. must dry up rapidly on foliage. It is obvious that systemic compounds are designed to penetrate into the plant tissues, and therefore their wash-off is lower after longer drying times. In this case, the longer the rain-free period, the more active ingredient can penetrate the plants (Sun, 1996) and the better is the biological efficacy (Werlang *et al.*, 2003; Bariuan *et al.*, 1999; Willis *et al.*, 1994; Mashaya, 1993; Willis *et al.*, 1992; Wells, 1989).

2.5 Rain characteristics

2.5.1 Amount and intensity

A rain event (Tab. 2) is characterized by its quantity and intensity as well as by droplet spectrum, energy of the droplets and time of duration (Park *et al.*, 1983; Simmons, 1980). According to Green (2001), the most important characteristics of rainfall are amount, intensity and drop size. Anyhow, all characteristics of a rainfall can be adequately defined by rain intensity (Park *et al.*, 1983).

The withstand of a pesticide deposit to wash-off due to rain is given by its resistance to mechanical impact, particularly from big rain droplets, as well as dissolution rate (Kudsk *et al.*, 1991). Experimental results concerning the influence of intensity and amount of rain are not always in consonance. Some of them show that cumulative rain amount affects the wash-off at a greater extent than rain intensity (Willis *et al.*, 1996; Mashaya, 1993; Kudsk *et al.*, 1991; Sundaram, 1991; Pick *et al.*, 1984), while others have shown the opposite (Taylor and Matthews, 1986). Complementing, some authors observed similar impact of rain amount and rain intensity (Mashaya, 1993), while others observed that rain intensity and duration affect active ingredient removal from the plant foliage independently (Fife and Nokes, 2002). Diversity in results may be explained due to differences in experimental conditions such as active ingredient, plant material, drying time, drying conditions, rain characteristics, etc.

Fact is that intense rains are characterized by bigger droplets which fall at greater speed, having a greater mechanical impact on the surfaces (Park *et al.*, 1983; Simmons, 1980). This greater impact can easily dislodge pesticide deposits (Kudsk *et al.*, 1991; Park *et al.*, 1983). The removal process is finished by the water film which is formed on the surface; it carry out the pesticides from the leaves (Lauver and McCune, 1984). Heavy rainfall produces a constant water film on surface, making the carry out process easier (Hartley and Graham Bryce, 1980). In contrast, by misting and light rain, run-off occurs only periodically, after junction of water drops on the surface (Suheri and Latin, 1991).

Table 2. Classification of rainfall types according to their major characteristics (adapted from several authors).

Type of rain	Rain intensity [mm h^{-1}]	Droplet radius [µm]	Droplets fall speed [m s^{-1}]	Duration
Mist	< 0.4	50 - 250	low (0.25 – 2)	short to long
Drizzle / Light rain	0.42	250 - 500	medium (2 - 2.8)	long (8 h -24 h)
Hard rain	4.2	500 - 1500	medium (4-6)	medium (6 h)
Torrential rain	42	1500 - 2500	high (6 – 8.9)	short (10 min.)

Sources: Lauer and Bendix, 2004; Weischet, 2002; Barth, 2002; Ditzer, 2002; Häckel, 1993; Liljequist and Cehak, 1984; Park *et al.*, 1983; Simmons, 1980.

Researches demonstrated that greatest part of a.i. is removed by comparatively little rain amount, while the remaining deposit remains in a stable form, difficult to displace with more rain (Wauchope *et al.*, 2004; Fife and Nokes, 2002; Rudgard *et al.*, 1990; Smith and MacHardy, 1984; Bruhn and Fry, 1982). Rain-resistant fungicide is most probably held in the leaf matrix (Fife and Nokes, 2002).

Lauver and McCune (1984) divided the wash-off process in four phases:

a) water accumulate on foliage, removing only little part of the deposit;
b) removal rate achieves the maximum as storage capacity of the foliage was reached and superficial water with dissolved or suspended material was displaced from the surfaces;
c) exponential decline in removal rate;
d) no additional removal of the deposits.

2.5.2 Acidity

Rainfastness of agrochemicals can also be influenced additionally by other factors such as pH of rainwater. Van Bruggen *et al.* (1986) verified that wash off triphenyltin hydroxide and copper hydroxide from potato leaves was higher by acidic rain (pH 2.8), regardless of formulation or potato cultivar. The same authors observed that removal of maneb, mancozeb and chlorothalonil was not affected by reduced pH. Troiano and Butterfield (1984) also studied increased loss of cupric hydroxide and triphenyltin hydroxide due to acidic rain, whereas rainfastness of chlorothalonil was not affected. Researches like these show that experiments using deionised or tap water to simulate rain can underestimate the wash-off magnitude of some pesticides, especially in regions with occurrence of acidic rain.

2.6 Leaf surface characteristics

Some studies have shown that rainfastness of a given active ingredient varies among plant species or cultivars (Kudsk *et al.*, 1991; Bruhn and Fry, 1982; Neely, 1971). This is attributed to differences in surface characteristics, such as presence of trichomes, hairs, and structured wax deposits (Spanoghe *et al.*, 2005; Neely, 1970). Actually, surface characteristics were mainly investigated in relation to deposit formation and biological activity of agrochemicals. Hairs and trichomes can impair pesticide adhesion to surface by intercepting spray drops before they reach the epidermal cells. Likewise, they can impair the impact of rain droplets, reducing pesticide displacement (Neely, 1971). However, studies on the influence of surface structures on rainfastness of pesticides are missing.

Plant waxes consist of mixtures of long-chain hydrocarbons, alcohols, ketones, esters and acids (Baker, 1982; Fernandes *et al.*, 1964). Wax amount, composition and homologue distribution patterns vary considerably between and within plant species and cultivars (Belding *et al.*, 1998; Percy *et al.*, 1994; Baker, 1982). Some pesticides have high affinity to surface waxes (Häuser-Hahn *et al.*, 2003) or are able to diffuse into wax layers (Andrieu *et al.*, 2000). On the other hand, a highly structured epicuticular wax reduces contact between spray droplet and cuticle surface (Price, 1982). Cabras *et al.* (2001) observed that mancozeb has been more easily washed-off from grapes than from grape leaves, and believe that these discrepancies are conditioned by differences in composition of epicuticular wax. In the case of systemic compounds, epicuticular wax is the most significant barrier to absorption of water soluble herbicides (Hess and Foy, 2000). Here, lipophilic compounds penetrate waxy, hydrophobic plant leaves more readily than hydrophilic compounds (Mashaya, 1993). Nevertheless, systematic studies on influence of amount and composition of surface wax on rainfastness of agrochemicals were not conducted, yet.

3 Objective of our studies

An overview on the major factors influencing rainfastness and rain-induced wash-off of foliar-applied agrochemicals is given in Table 3 and Figure 1.