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# Pesticide reclamation and cleaning of direct nozzle injection systems

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## Abstract

Direct injection systems are considered a promising technology to apply pesticides site specifically in the future. Possible benefits of direct injection systems include improved cost efficiency, operator safety, and environmental protection compared with conventional sprayers. Over the past years research has focused mainly on the injection process including, response times, metering accuracy, and the mixing of the chemical and the carrier. However, with the proper cleaning of conventional sprayers becoming more and more important, it is crucial that studies on direct injection systems not only restrict themselves to dosing behaviour and accuracy, but also identify strategies to clean these systems. This includes the reclamation of the residual concentrated pesticide from the injection pipe and rinsing of the contaminated parts of the hydraulic system.

In this study a direct injection system that injects pesticides locally at all nozzles on a boom was assembled and investigated under laboratory conditions with regards to its ability to be cleaned. The system was contaminated with a safe-to-use polyvinylpyrrolidone-water solution as a test pesticide before cleaning. The cleaning process was divided into two steps: 1) reclamation of the simulated pesticide by pushing it back into the pesticide tank using pressurised air (pre-cleaning) and 2) rinsing the contaminated part of the hydraulic system with water. Using gravimetrical and conductivity measurements, the cleaning process was investigated systematically to ascertain the initial dynamics of reclamation and rinsing, as well as the cleaning success. Evaluations included variation of pre-cleaning time and air pressure as well as water inlet positions. Measurements for a 3 m test section showed that the concentration of the simulated pesticide in the rinsing water could initially be as high as 30%. As the pre-cleaning time was extended, the initial concentration was reduced by one third. Changing the water inlet position reduced the initial concentration of the simulated pesticide in the rinsing water to 5%. These concentrations were much higher than in most common spray solutions. This means that if an active pesticide was used, further dilution of the pesticide concentration in the rinsing water would be required for it to be sprayed on a crop. In some cases it took more than 10 min to dilute simulated pesticide residues in a 3 m test section down to 0%.

Measurements also showed that the contaminated rinsing water has to be homogenized in order to be able to uniformly control the dosing valves when applying the contaminated rinsing water to the crop. The test bench experiments were verified on a wide boom DIS sprayer. A method that included homogenization of the contaminated rinsing water was tested and proved to be suitable for future cleaning in the field after operation.

## Kurzfassung

Direkteinspeisungssysteme (DES) gelten als viel versprechende Technologien um Pflanzenschutzmittel (PSM) zukünftig teilschlagspezifisch zu applizieren. Der mögliche Nutzen von DES im Vergleich zu konventionellen Spritzgeräten liegt in besserer Kosteneffizienz, Anwendersicherheit, sowie im Umweltschutz. Die Forschung hat sich bisher hauptsächlich auf den Einspeisevorgang konzentriert, inklusive Verzögerungszeiten, Dosiergenauigkeit und dem Mischen von PSM und Trägerflüssigkeit. Da bei konventionellen Spritzgeräten die richtige Reinigung immer wichtiger wird ist es notwendig, dass sich die Forschung nicht nur auf Dosierverhalten und -genauigkeit beschränkt, sondern auch Strategien zur Reinigung dieser Systeme identifiziert. Das schließt die Rückgewinnung des PSM aus der Injektionsleitung ebenso ein wie das Spülen kontaminierter Teile des hydraulischen Systems.

In der vorliegenden Arbeit wurde ein DES mit Einspeisung an der Düse aufgebaut und unter Laborbedingungen hinsichtlich seiner Reinigbarkeit untersucht. Das System wurde vor der Reinigung kontrolliert mit einer gesundheitlich unbedenklichen wässrigen Polyvinylpyrrolidon Lösung als simuliertes PSM beschmutzt. Die Reinigung wurde in zwei Schritte unterteilt: 1) Rückgewinnung des simulierten PSM durch Zurückdrücken in den Ausgangsbehälter mittels Druckluft (Vorreinigung) und 2) Spülen des kontaminierten Teils des hydraulischen Systems mit Wasser. Der Reinigungsvorgang wurde systematisch hinsichtlich Dynamik und Reinigungserfolg untersucht. Dabei kamen gravimetrische sowie Leitfähigkeitsmessungen zum Einsatz. Für die Bewertung wurde neben der Vorreinigungszeit und dem Luftdruck auch die Position des Wassereinlasses variiert. Messungen an einer 3 m langen Teststrecke ergaben Anfangskonzentrationen des simulierten PSM im Spülwasser von bis zu 30%. Eine verlängerte Vorreinigungszeit reduzierte diese Anfangskonzentration um ein Drittel. Eine Veränderung der Wassereinlassposition reduzierte die Anfangskonzentration auf 5%. Diese Konzentrationen waren höher als in den üblichen konventionellen Spritzbrühen. Bei Verwendung eines echten PSM wäre also eine Verdünnung des mit PSM kontaminierten Spülwassers vor seiner Applikation auf dem Feld notwendig. Mitunter dauerte es mehr als 10 min bis die Konzentration des simulierten PSM im Spülwasser 0% erreicht hatte.

Die Messungen zeigten zudem, dass das kontaminierte Spülwasser homogenisiert werden muss, damit bei seiner Ausbringung alle Dosierventile gleich angesteuert werden können. Die Prüfstandversuche wurden an einer Feldspritze mit Direkteinspeisung an der Düse verifiziert. Eine Methode zur Homogenisierung des kontaminierten Spülwassers wurde getestet und erwies sich als geeignet für zukünftige Feldeinsätze.

# Contents

## A List of abbreviations and symbols

| Abbreviation or symbol | Unit | Denotation |
|---|---|---|
| $A$ | m² | Cross-sectional area of the pipe |
| $A_1$, $A_2$, $A_3$ | - | Parameters of the ExpDec3 curve fit model |
| ADR | - | Accord européen relatif au transport international des marchandises dangereuses par route |
| AG | - | Aktiengesellschaft |
| ANOVA | - | Analysis of variance |
| AOEL | µg day$^{-1}$ | Acceptable operator exposure limit |
| $B_1$, $B_2$ | - | Parameters of the polynomial fit model |
| BBA | - | Biologische Bundesanstalt für Land- und Forstwirtschaft (since 2008: JKI) |
| BLE | - | Bundesanstalt für Landwirtschaft und Ernährung (Federal Office for Agriculture and Food) |
| BMELV | - | Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (Federal Ministry of Food, Agriculture and Consumer Protection) |
| BMPs | - | Best Management Practices |
| BVL | - | Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (Federal Office of Consumer Protection and Food Safety) |
| $c$ | % | Concentration of simulated pesticide in rinsing water |
| $c_0$ | % | Parameter of the ExpDec3 curve fit model |
| Co. | - | Corporation |
| CV | - | Coefficient of Variation |
| $\Delta$ | - | delta (= difference) |
| $D$ | m | Pipe diameter |
| DC | % | Desired concentration |
| DES | - | Direkteinspeisungssystem |

| | | |
|---|---|---|
| DIS | - | Direct injection system |
| DNIS | - | Direct nozzle injection system |
| $\eta$ | kg $m^{-1}$ $s^{-1}$,<br>Pa s | Dynamic viscosity |
| EC | - | Emulsifiable concentrate |
| ECPA | - | European Crop Protection Association |
| e. g. | - | exempli gratia (= for example) |
| EHEDG | - | European Hygienic Equipment Design Group |
| EN | - | European Norm |
| ENTAM | - | European Network for Testing of Agricultural Machines |
| EVA | - | Ethylene vinyl acetate |
| ExDec | - | Exponential decay |
| $f$ | - | Friction factor |
| Fig. | - | Figure |
| $\gamma$ | $s^{-1}$ | Shear rate |
| GmbH & Co. KG | - | Gesellschaft mit beschränkter Haftung & Compagnie Kommanditgesellschaft |
| GPS | - | Global Positioning System |
| HDPE | - | High density polyethylene |
| ID | mm | Inner diameter |
| IDK | - | Luft Injektordüse Kompakt |
| i. e. | - | id est (= that is to say) |
| ISO | - | International Organization for Standardization |
| JKI | - | Julius Kühn-Institut - Bundesforschungsinstitut für Kulturpflanzen (Federal Research Institute for Cultivated Plants) |
| $\kappa$ | mS $cm^{-1}$ | Conductivity value |
| $L$ | m | Pipe length |
| $\lambda$ | - | Basic friction factor |

| | | |
|---|---|---|
| LfU | - | Bavarian Environment Agency |
| $M_L$ | g mol$^{-1}$ | Molar mass of air |
| n | - | Number of replications |
| $n$ | mol | Amount of substance |
| $n_{LA}$ | mol | Amount of substance of air in the air tank before valve opening |
| $n_{LE}$ | mol | Amount of substance of air in the air tank when valve was closed again |
| $\Delta n_L$ | mol | Amount of substance of air streamed out of the air tank between valve opening and valve closing |
| NaCl | - | Sodium chloride |
| $P$ | kPa | Pressure |
| $\Delta P$ | kg m$^{-1}$ s$^{-2}$ | Pressure gradient |
| $P_{LA}$ | kPa | Pressure in the air tank before valve was opened |
| $P_{LE}$ | kPa | Pressure in the air tank after valve was closed again |
| $P_S$ | kPa | Static pressure |
| $P_T$ | kPa | Total pressure |
| PA | - | Precision Agriculture |
| PC | - | Polycarbonate |
| PE | - | Polyethylene |
| $\pi$ | - | Constant pi |
| POM | - | Polyoxymethylene |
| POPs | - | Persistent Organic Pollutants |
| PP | - | Polypropylene |
| PSM | - | Pflanzenschutzmittel |
| PTFE | - | Polytetrafluoroethylene |
| PVC | - | Polyvinyl chloride |
| PVP | - | Polyvinylpyrrolidone |
| PWM | - | Pulse width modulation |
| $Q$ | m³ s$^{-1}$ | Volumetric flow rate |

| | | |
|---|---|---|
| $R$ | J mol$^{-1}$ K$^{-1}$ | Gas constant |
| R² | - | Coefficient of determination |
| Re | - | Reynolds number |
| $\rho$ | g l$^{-1}$ | Density of the fluid |
| $\rho_L$ | g l$^{-1}$ | Density of air |
| RRV® | - | Rapid Reaction Valve |
| SC | - | Suspension concentrate |
| $t_1$ , $t_2$ , $t_3$ | - | Parameters of the ExpDec3 curve fit model |
| $T$ | K | Temperature |
| $\tau$ | N m$^{-2}$ | Wall shear stress |
| Tab. | - | Table |
| TOPPS | - | Train the Operators to Prevent Water Pollution from Point Sources |
| $U$ | V | Voltage |
| $U_W$ | V | Voltage a sensor measured for tap water |
| $v$ | m s$^{-1}$ | Flow velocity |
| $V$ | m³ | Volume |
| $V_B$ | m³ | Capacity of the air tank |
| $V_L$ | l | Air volume streamed out of the air tank between valve opening and valve closing |
| VI | - | Virtual instrument |
| vs. | - | versus (= against) |
| $y_0$ | V | Voltage continuously measured by conductivity sensor |
| $y_1$ | - | Normalized voltage value |

# B List of figures

# C List of tables

# 1 Introduction and objective

In agriculture crop protection is necessary in order to protect the crop from diseases, pests, and weeds that would otherwise impair crop growth. Thus, crop protection is one of the methods that help the farmer achieve high and reliable yields. Among the different possible crop protection strategies pesticide-based approaches (e. g. application of herbicides using field sprayers) play a central role (TISCHNER & KLEIN, 2006). Nowadays, most farmers spray herbicides uniformly on the field as they lack the technology for automatic weed sampling and site specific application technology (GERHARDS & OEBEL, 2006).

Various studies have pointed out that direct injection systems (DIS) could benefit both farmers and the environment as they are suitable for site-specific pesticide application and could therefore (amongst other things) help reduce the pesticide load applied to agricultural crops (GEBHARDT et al., 1984, TOMPKINS et al., 1990, LANDERS, 1992). DIS inject concentrated pesticide into a carrier (usually water), either centrally into the sprayer boom (FROST, 1990, PAICE et al., 1995) or at individual nozzles (MILLER & SMITH, 1992, VONDRICKA, 2008, GILES & BROCK, 2008).

In either case, a part of the hydraulic system (the injection pipe) carries pure concentrated pesticide that has to be removed after operation. Depending on the application rate of the product and the design of the injection system, the residual volume of pesticide in the injection pipe could be enough to treat several hectares of arable land. It could also pose a risk to the environment if not handled properly. What is more, the financial value of the residual pesticide could be saved by the farmer if unused residual pesticide could be reused in an upcoming application. These are good reasons for developing a cleaning strategy for DIS that includes the reclamation of the residual pesticide in order to keep it for future use. Once the pesticide has been reclaimed from the injection pipe there will still be residual pesticide on the pipe walls that cannot be reclaimed. It will have to be rinsed out of the system by using an appropriate rinsing fluid.

Studies on DIS that have been published over the past years took different approaches to engineering DIS, but mainly focused on the injection process. That is to say its dynamics, accuracy, and transient times, as well as the mixing of the pesticide and its carrier (FROST, 1990, PAICE et al., 1995, PAICE et al., 1996, VONDRICKA, 2008). So far, no studies on possible strategies to clean DIS after field use have been conducted, although cleaning is an essential part of the application process. However, TOMKINS et al. (1990) stated that with DIS formation of access spray mixture is eliminated while LANDERS (1992) assumed a

DIS sprayer is easy to flush. Cleanability will be one criterion for commercial success and future use of DIS under field conditions. The amount of inner surfaces becoming contaminated is likely to vary among different types of DIS. Direct nozzle injection systems (DNIS) can be expected to be the most difficult to clean as the injection pipe supplies each single nozzle of the boom with concentrated pesticide. With boom injection systems the injection pipe only makes up a small part of the hydraulic system which is why it might be easier to clean.

Although plenty of research has been done on the cleaning of conventional field sprayers (e. g. GANZELMEIER, 1998, WEHMANN, 2008, ROETTELE et al., 2010), results from these studies are not necessarily transferable to DIS. The reason for this is that the properties of the products that have to be removed from the injection pipe of DIS differ significantly from the properties of conventional spray mixtures as they are more concentrated and therefore more viscous. It is known that the cleaning of conventional sprayers can cause severe damage to both the environment and the crop if not carried out correctly, that is, if Best Management Practices (BMPs) are disregarded by the operator (ROETTELE et al., 2010). Improper sprayer cleaning can lead to crop damage due to contamination of susceptible crops (WEHMANN, 2006) as well as to contamination of ground and surface waters (WENNEKER et al., 2010). As a result of this, research on the cleaning of conventional sprayers has been reinforced at a European level over the past years (COOPER & TAYLOR, 2008, ROETTELE, 2008, ANDERSEN et al, 2010). Against this background it is crucial that the development of DIS wide boom sprayers designated for field use is accompanied by research that identifies and investigates strategies to thoroughly clean the parts that get contaminated with concentrated pesticide, particularly the injection pipe and the injection units. This includes the reclamation of the concentrated pesticide from the injection pipe after operation and the removal of remaining residual pesticide through proper rinsing.

***Objective***

The study presented herein was part of a 3-year project aimed at developing and investigating a wide boom DIS field sprayer that is suitable for pesticide application in the field. The objective of this study was to investigate the two essential steps that make up the cleaning process of DIS: 1) Reclamation of the concentrated pesticide from the injection pipe and 2) rinsing the contaminated part of the hydraulic system. This included:

- Development of a test bench and methods that allow systematic ascertainment of pesticide reclamation and rinsing of DIS.
- Identification and investigation of parameters affecting pesticide reclamation and the rinsing of DIS.
- Identification of strategies for reclamation and rinsing.
- Ascertainment of initial dynamics as well as quantification of the cleaning success of different reclamation and rinsing strategies.
- Drawing conclusions from test bench experiments with a view to wide boom DIS sprayers.
- Application of the results gained from test bench experiments through comparative experiments on a wide boom DIS sprayer and development of a cleaning procedure that is suitable for future field use.

# 2 State of the art

## 2.1 Pesticide risk reduction

EU plant protection policy has been characterized by the aim of risk reduction and sustainability. Therefore, in 2009 the EU Directive 2009/128/EC of the European Parliament and of the Council (ANONYMUS, 2009) established a framework for community action to achieve the sustainable use of pesticides. In Article 4 of this “Sustainable Use Directive” member states were called upon to work out so called National Action Plans. These set up quantitative objectives, measures and timetables to reduce risks and impacts of pesticide use on human health and the environment as well as to encourage the development and introduction of integrated pest management and of alternative approaches or techniques in order to reduce dependency on the use of pesticides (ANONYMOUS, 2009a). Already in 2008 the German Federal Ministry of Food, Agriculture and Consumer Protection (BMELV) responded to the expected future plant protection legislation of the European Union by publishing a National Action Plan on Sustainable Use of Plant Protection Products (BMELV, 2008). The goals mentioned in this National Action Plan are reduction of

- risks associated with the use of plant protection products by 25% until 2020,
- the use of plant protection products to the “necessary minimum”, and
- health-impairing residues of plant protection products in food.

One of the measures intended to achieve risk reduction and sustainability is advancing plant protection equipment and introducing these new technologies into everyday practice. The National Action Plan (BMELV, 2008) states that although there have already been a number of technological approaches to reducing pesticide quantities (for example by developing site specific pesticide application techniques) there is still a lack of practicable solutions in many instances (BMELV, 2008). This implies that direct injection systems (DIS) are seen to be a promising future tool for the sustainable use of pesticides but also that substantial research is needed to develop DIS that are viable enough to assist the farmer in sustainable low-risk pesticide application.

## 2.2 Pesticide application as part of precision farming

Pesticide application is an important tool that assists farmers in obtaining stable and reliable yields. Usually, pesticides are applied through mounted, trailed, or self propelled field crop sprayers (ESTLER, 1998, BÖRNSEN, 1999). The operator mixes concentrated pesticide and water in the sprayer's main tank, typically via induction hopper, to create the spray mixture which is then uniformly applied to the target area without accounting for the differing individual requirement in individual parts of the field. Fig. 2-1 provides a simplified illustration of a conventional field crop sprayer.

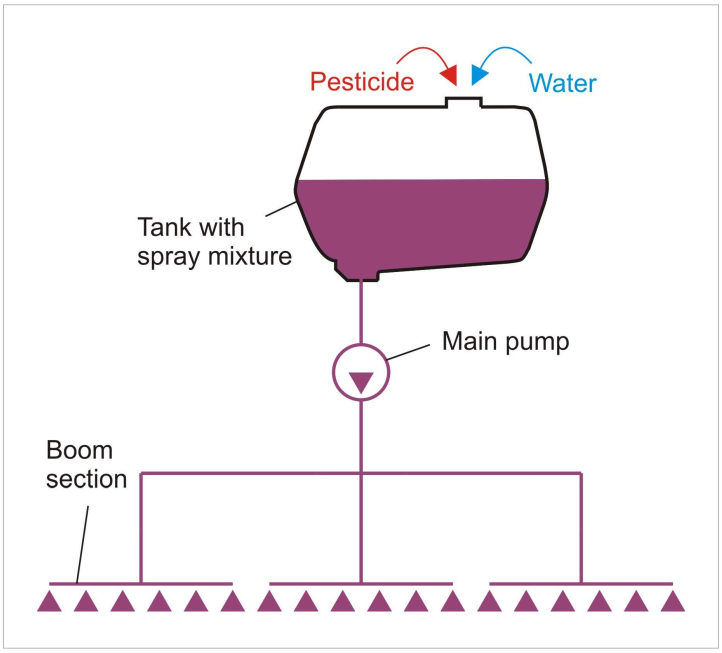


Fig. 2-1: Simplified illustration of a conventional field crop sprayer.

However, since the mid 1980s scientists have been incorporating new technologies into agriculture to create what is today known as precision agriculture (PA) (ROBERT, 2002). According to OLSON (1998), precision agriculture can be defined as “the application of a holistic management strategy that uses information technology to bring data from multiple sources to bear on decisions associated with agricultural production, marketing, finance and personnel”. SRINIVASAN (2006) stated that PA consists of the following five consecutive steps: data collection, diagnostics, analysis, precision field operations, and evaluation with site specific pesticide application being one example for precision field operations.

GERHARDS & OEBEL (2006) stated that through site specific herbicide application chemical use could be reduced in winter cereals by 6 - 81% for herbicides against broad leaved weeds and 20 - 79% for grass weed herbicides. The authors say that their system for site specific weed control included online weed detection using digital image analysis, computer-based decision making, and Global Positioning System (GPS)-controlled patch spraying. This enabled them to accurately apply chemicals according to the individual needs of each weed infested location. The application technique used by GERHARDS & OEBEL (2006) was a multiple sprayer with three separated hydraulic circuits. The herbicide mixture was varied by switching each of the hydraulic circuits individually. The application rate was varied by changing the pressures in the hydraulic systems. According to the authors each of the sprayer's three hydraulic circles was similar to that of a conventional sprayer. Fig. 2-2 is a simplified illustration of the multiple sprayer concept (compare Fig. 2-1).

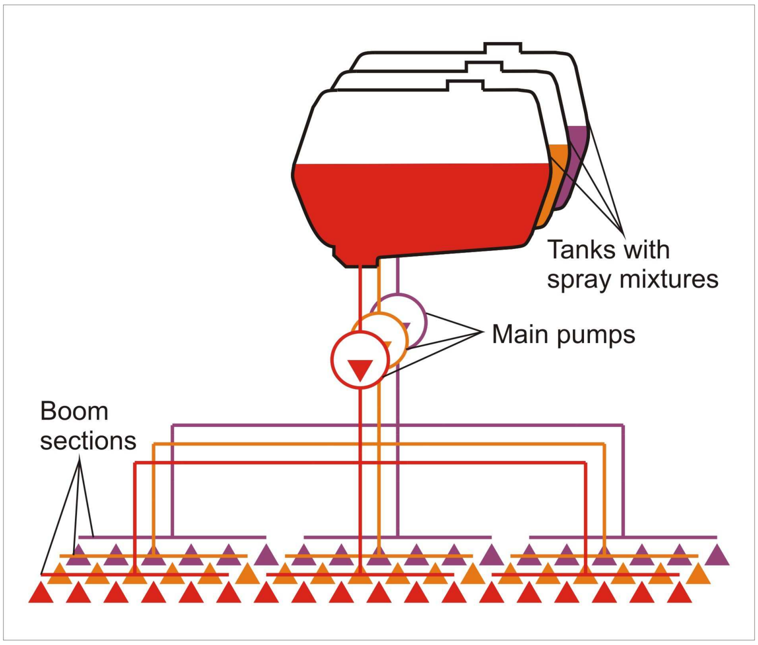


Fig. 2-2: Simplified illustration of the multiple sprayer concept developed by GERHARDS & OEBEL (2006) who equipped a field crop sprayer with three hydraulic systems, each carrying a different spray mixture.

An alternative approach that allows site specific pesticide application is the development of direct injection systems (DIS) which keep the pesticide and the carrier (usually water) separate while metering and mixing them on demand within the pipeline before entering the nozzle (e. g. ROCKWELL & AYERS, 1996), as will be described in the following sections.

## 2.3 Direct injection systems (DIS)

### 2.3.1 Types of DIS

DIS are often characterized by the location where the chemical is injected into the carrier as the distance between the injection point and the nozzle outlet determines the system's transient time. According to Tomkins et al. (1990) transient time is the time from initiation of injection to achievement of uniform pesticide concentration at all nozzles. Some DIS inject pesticides centrally into the sprayer boom (e. g. Frost, 1990, Paice et al., 1995), while others inject the chemical locally into individual boom sections (Hloben, 2007), or are equipped with one injection unit at each nozzle (direct nozzle injection system (DNIS), Miller & Smith, 1992, Vondricka, 2008a, Giles & Brock, 2008). Fig. 2-3 illustrates these different DIS concepts.

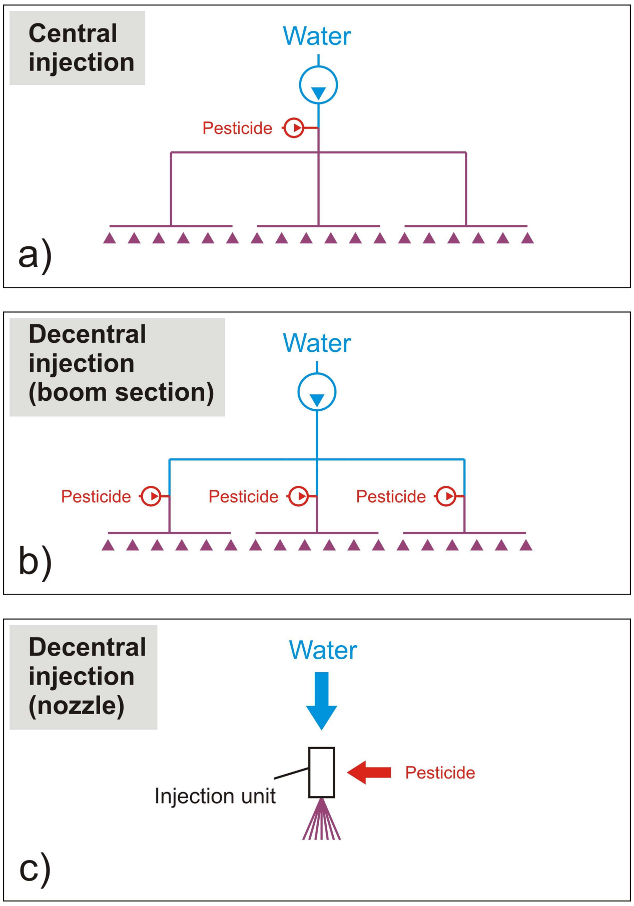


Fig. 2-3: Different DIS concepts: a) pesticide injection centrally into the sprayer boom, b) decentral injection of the pesticide into each boom section, and c) injection of the pesticide locally at individual nozzles.

In discussing central DIS LANDERS (1993) explained that some DIS inject pesticide into the pressure water line after the main water pump using a mechanical pump (Fig. 2-3a). Alternatively, it is also possible to meter pesticide into the suction side of the water pump. This means low pressure injection pumps can be used to obtain a good mixing of the carrier and the pesticide as the pesticide-water-mixture passes through the main pump (LANDERS, 1993).

### 2.3.2 Advantages and disadvantages of DIS

***Advantages of DIS over conventional sprayers***

Potential benefits of DIS were discussed by several authors, especially in the 1990s. TOMKINS et al. (1990) listed the following benefits associated with the direct injection concept:

- Improved personal safety as a result of reduced operator exposure to pesticides during measuring, mixing, and loading into the tank.
- Cost efficiency through avoidance of over- and under application.
- Environmental protection as a result of the reduced formation of excess spray mixture and, therefore, reduced risks through questionable residue disposal methods which could lead to contamination of surface and underground water supplies.

Moreover, FROST (1990) mentioned the following advantages of DIS over conventional sprayers:

- Instead of relating nozzle pressure to forward speed in order to achieve a uniform dose rate of chemical per unit area of field (which is done with conventional sprayers) a DIS can vary the injection rate (and with it the concentration of the diluted spray) while keeping the nozzle pressure constant so that the drop size spectrum and distribution pattern of the spray are not affected by changes in forward speed. According to ROCKWELL & AYERS, (1996) the reason for this is that with DIS pressure at the nozzles changes very little with large changes in active ingredient flow rate since the flow rate of active ingredient is typically at least an order of magnitude smaller than that of the carrier.
- Logistical advantages since the chemical is not diluted until it is required. Any surplus chemical at the end of a spraying operation can be taken back from the machine and kept for future use. The problem of disposing of unwanted diluted chemicals is therefore removed.

In addition to this, LANDERS (1992) stated the following benefits:

- The operator can change dose rates quickly and accurately. With a view to this advantage, PAICE et al. (1993) explain that errors in concentration introduced when formulations are mixed in the tank manually and errors in the volume rate no longer affect the pesticide dose rate.
- Only clean water is used in the main sprayer tank which reduces the risk of pesticide carry-over to non cropped areas or the following crop being accidentally sprayed.
- The DIS sprayer is easy to clean since (with central DIS) only a small part of the piping system gets contaminated with concentrates pesticide.
- The injection system (if it is a kit) is easily fitted to conventional sprayers.
- Water can be withdrawn from a natural watercourse without fear of suck-back of pesticide since only water is used in the main tank.

PAICE et al. (1993) noted that foam generation in the tank can be reduced since little or no tank agitation is required.

***Disadvantages of DIS compared with conventional sprayers***

Although PAICE et al. (1993) acknowledge the potential benefits of DIS they also describe some potential disadvantages of DIS compared with common sprayers:

- DIS have a reduced range of operation. It is difficult for one single injection metering system to achieve the flow rates required at all possible values of speed and boom width.
- Greater complexity and more difficult operation. It is very likely that the cost of sprayers with DIS is considerably higher than that of conventional systems. In addition, more operator training is necessary.
- Time delay in pipes. A change in flow rate leads to a concentration front moving through the pipes between the injection point and the nozzles which causes delay.

AMSDEN & SOUTHCOMBE (1977) stressed that certain materials used in the construction of field crop sprayers can be susceptible to chemical attack, physico-chemical attack or mechanical damage through certain pesticide mixtures. The authors note that some materials are resistant to one type of solvent but susceptible to another. Their experiments showed that the relative levels of attack stayed the same when the solvents were diluted in the sprayer. However, while the degree of attack fell when the solvents were diluted with water over a period of time the cumulative effect could be just as devastating (AMSDEN & SOUTHCOMBE, 1977). This implies that materials used in the construction of DIS could be subjected to even worse attacks through chemicals as some parts of the hydraulic systems carry undiluted, concentrated pesticides.

With a view to the different types of DIS, ROCKWELL & AYERS (1996) noted that DNIS have the following advantages and disadvantages compared with boom injection systems.

***Advantages of DNIS over boom injection systems***

- Direct nozzle injection significantly reduces transport lag

The aforementioned transient times of the different types of DIS have been evaluated by several researchers. TOMKINS et al. (1990) measured transient times from 12 s to 26 s with central chemical injection while HLOBEN et al. (2006) reported transient times of between 1.8 s and 7.5 s when the chemical is injected into individual boom sections. Significantly shorter transient times were measured by VONDRICKA et al. (2007) who evaluated the performance of a DNIS. Each injection unit included a fast reacting ball valve which was placed only a few centimetres upstream of the nozzle and a mixing chamber, including a static mixer. The shortest injection times the authors measured under laboratory conditions were between 40 and 80 ms, depending on the injected volume and the carrier flow rate.

***Disadvantages of DNIS compared with boom injection systems***

- In DNIS, time for mixing is very short before the spray mix is discharged out of the spray nozzles.
- There are concerns with the even distribution of the active ingredient to all nozzles since particularly at the small flow rates used.
- Direct nozzle injection is more expensive than boom injection due to the additional plumbing required to deliver the active ingredient to the nozzle

The last of these three points mentioned by the ROCKWELL & AYERS (1996) implies that with DNIS long runs of pipe work hold the concentrated pesticide whereas in boom injection systems only a comparatively short part of the pipe system gets contaminated. This could be an important disadvantage regarding the cleanability of DIS.

### 2.3.3 Application strategies for DIS

DIS are considered a possible future tool for site specific pesticide application. However, due to their long transport lags, boom injection systems could only be used for site specific pesticide application if the creation of the weed map and the control of the sprayer with this map were two consecutive work steps. This is often referred to as off-line application (see Fig. 2-4a) and is, according to MILLER & LUTMAN (2008), one of two possible application strategies for patch spraying. The alternative strategy would be mapping and spraying in one operation. In other words: real-time treatment or on-line application (Fig. 2-4b). MILLER & LUTMAN (2008) stated that real-time treatment is only used in industrial weed control, but not in arable agriculture as automated detection is not yet fully commercially viable and users have difficulty assessing how much product is needed. In contrast, according to the authors, the off-line strategy has been applied to arable crops because the time between both work steps allows the farmer to consider treatment before operation, accurately calculate pesticide use, and appropriately load the sprayer while the required computing power is less than what is needed for online application. MILLER & LUTMAN (2008) also reported that farmers would prefer the fully automated online system as it would avoid extra visits to the field to create weed maps.

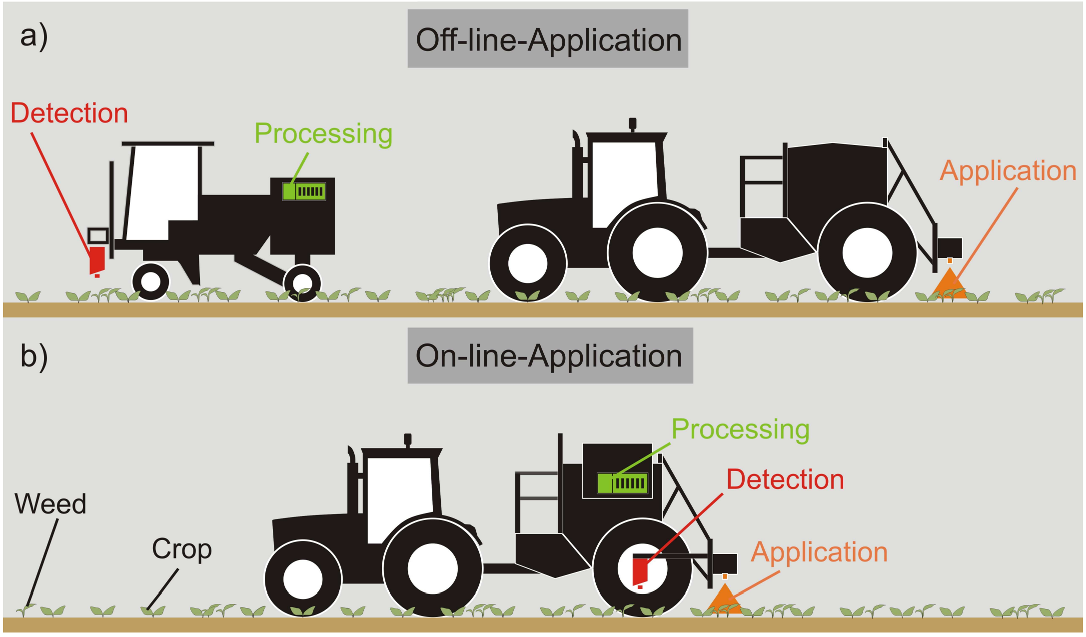


Fig. 2-4: Site specific pesticide application according to the a) off-line and b) online concept.

## 2.4 Cleaning of plant protection equipment

### 2.4.1 Cleaning of conventional sprayers

***Environmental impact***

In the 1980s and 1990s it was recognized and discussed that pesticides pose a major risk to ground and surface waters in Europe. As a result of advances in organic trace analysis during the past decades a very low drinking water contamination limit for any individual pesticide (0.0001 mg $l^{-1}$) and for the sum of all individual pesticides (0.0005 mg $l^{-1}$) detected and quantified was implemented through the European Directive 80/778/EEC and the revised Directive 98/83/EEC (ANONYMOUS, 1998a). However, for some compounds (which were outlawed at the Stockholm Convention on Persistent Organic Pollutants (POPs)) the thresholds are even lower (0.030 µl $l^{-1}$ = 0.00003ppm) (ANONYMOUS, 1998a, ANONYMOUS 2010). GANZELMEIER (1998) illustrated the risk of drinking water contamination by the fact that one droplet of pesticide may, in terms of the aforementioned contamination limit, be enough to pollute about 250 m³ of drinking water.

When the contamination level of 0.0001 mg $l^{-1}$ was established back in 1980 this figure was in fact a surrogate for zero since at that time this was the detection limit for almost all active ingredients (CARTER, 2000). The contamination limits were, according to WOHLRAB et al. (1992) and ISENBECK-SCHRÖTER et al. (1998), in the first instance designed to show that these synthetic substances are unwanted in drinking water, independent of the respective risks of each individual chemical. Apparently, this move was not based on toxicological risk estimate but was mainly politically motivated. Introducing Best Management Practices (BMPs) and getting the operators involved in preventive measures soon seemed to be an appropriate measure to reduce both the use of pesticides and associated risks (ISENBECK-SCHRÖTER et al., 1998). Pesticide manufacturers tried to reduce the amount of active ingredient applied to the crop by developing highly active formulations such as sulfonyl-urea herbicides which can be applied at considerably lower application rates (ca. 10 g $ha^{-1}$) (ISENBECK-SCHRÖTER et al., 1998).

According to SEEL et al. (1995) and the Bavarian Environment Agency (LfU, 2008) there are the following routes of entry by which pesticides used in agriculture can enter the environment (including ground or surface waters):

- Runoff from pesticide treated areas
- Volatilisation of active ingredients can lead to chemicals getting into the atmosphere which is seen as a major cause of their global distribution
- Pesticide loss through tile drainages

- Interflow of pesticides
- Unintended treatment of surface waters with pesticides through spray drift
- Percolating water that carries pesticides into the ground water
- Discharging farmyard waste water into receiving waters over the canalization
- Improper disposal of pesticide residues and waste

According to ROETTELE (2008), water contaminations resulting from the movement of pesticides from the field of application to water resources (such as spray drift, runoff, leaching and drain flow) are referred to as diffuse source pollution. Inappropriate handling of plant protection products during plant protection activities in the farmyard such as sprayer filling, loading and mixing of pesticides, washing spray equipment and improper pesticide waste disposal can lead to so called point source pollutions (ROETTELE, 2008). SEEL et al. (1995) added that these routes of entry apply not only to agricultural use of pesticides but also to other pesticide users, for example in railway weed control or municipal weed management. However, it is clear that insufficient cleaning of plant protection equipment can contribute to severe ground and surface water pollution (BEERNAERTS et al., 1999, CARTER, 2000). According to the LfU (2008), improper disposal of pesticide residues and waste can account for up to 90% of a water body's pesticide load with small bodies of water being more likely to show increased concentrations even after very little waste water has been discharged. HERBST & GANZELMEIER (2002) noted that in 1993 sprayer cleaning in agricultural settings caused an influx of roughly 7 to 22 t of active ingredients in Germany which for some regions was even more than 90% of the total pesticide load in surface waters. The authors also stated that sprayer cleaning on the field dramatically reduces the introduction of chemicals to waste water systems and surface water.

***Typical cleaning procedures***

Different cleaning methods have been evaluated by several authors with regards to the internal and external cleanability of commercial agricultural field sprayers. Investigations into the internal rinsing process gained in importance when low dose formulations such as sulfonyl-urea herbicides became widely used, triggering fears of crop damage by even small amounts of residues in subsequent applications (TAYLOR & COOPER, 1998). The authors described double rinsing as being the typical farmer practice and the use of a cleansing agent as a recommended means to thoroughly clean internal sprayer surfaces after sulfonyl-urea use.

HOLST et al. (2002) noted that a series of up to five smaller clean water volumes removed residues more effectively than one single large quantity. For many years triple rinsing was the cleaning method recommended by agricultural advisory services (ANONYMOUS, 2009b). Despite this, a survey carried out by ROETTELE et al (2010) showed that only 11% of the farmers actually apply triple rinsing to their sprayers while 39% prefer double rinsing and 38% single rinsing. Another 11% of the farmers stated they would not rinse their sprayer at all. Recognising that conventional sprayer cleaning in the field can be very time consuming and inconvenient for farmers, ANDERSEN et al. (2010) and ROETTELE et al. (2010) described an alternative internal rinsing procedure which proved to be highly efficient: continuous rinsing. Continuous rinsing is characterized by a separate pump delivering clean water from the cleaning water tank through the rinsing nozzles into the main tank. The water continuously pushes out and dilutes residual spray mix. According to the authors this one-step rinsing method leads to both water and time savings compared with triple rinsing. The latest approach to more operator friendly sprayer cleaning has been the development of automatic cleaning programs that can, according to the manufacturers, automatically clean the complete sprayer and its components with the use of minimal water (PAULUS, 2011, KIEFER, 2011).

Methods for decontaminating external sprayer surfaces have been investigated in detail by RAMWELL et al. (2010). The authors stated that methods currently used by farmers could be broadly categorized as rinsing at low water pressure (with and without brushes), pressure washing, and steam washing, all either with or without a cleaning agent. RAMWELL et al. (2010) concluded that the extent to which pesticides can be removed from the surface of sprayers was dependent on the active ingredient, the cleaning method used, and the lag time between pesticide deposition and washing (see section 2.5.3).

### *International standards and residue levels*

The international standards EN 12761-2 (2001) and ISO 13440 (1996) offer guidance on determining residue of pre-mixed spray mixture in common field crop sprayers. ISO 13440 (1996) specifies a test method for the determination of the volume of total residual for agricultural sprayers used for crop protection and fertilization. The following definitions are given in this standard:

- Volume of total residual: volume of the spray mixture remaining in the sprayer which cannot be delivered with the intended application rate and/or pressure, equal to the sum of the volume of residual tank and the dead volume

- Volume of residual in the tank; dilutable volume: Part of the total residual that remains in the tank or that can flow back to the tank during normal sprayer operation
- Dead volume; non dilutable volume: Part of the residual volume that cannot flow back to the tank during normal operation of the sprayer.

Fig. 2-5 illustrates both the dilutable and non-dilutable volume of a field crop sprayer.

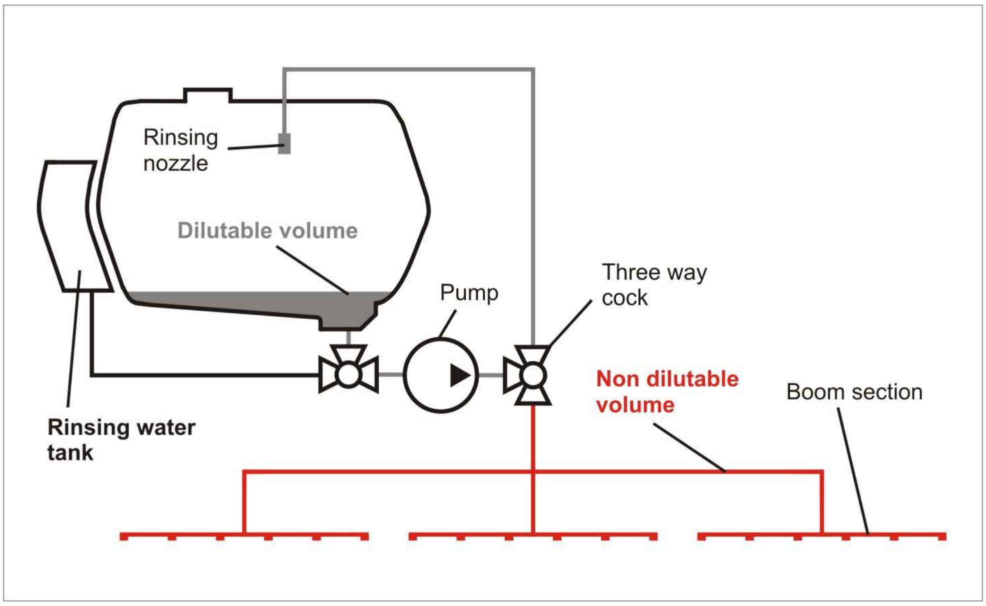


Fig. 2-5: Dilutable and non-dilutable volume of a field crop sprayer (according to DEBAER et al., 2008, modified).

ISO 13440 (1996) states that under the laboratory conditions described in the standard the test liquid (water) shall be discharged through the nozzles until the first pressure drop of 25% for 1 s occurs. The amount of residual shall then be measured either volumetrically or, alternatively, by weighing the sprayer. The volume of residual in the tank and the dead volume shall be measured to an accuracy of 0.1% of the nominal tank volume.

EN 12761-2 (2001) defines minimum requirements for design and performance of field crop sprayers with respect to minimizing the risk of environmental contamination. According to specifications given in EN 12761-2 (2001) the volume of total residual as defined in section 2.1 of ISO 13440 (1996) shall not exceed 0.5% of the nominal tank volume plus 2 l per meter of the boom. Additionally, the sprayer shall be equipped with a rinsing water tank which shall not be combined with the cleaning water tank for the operator's use. It shall have a volume of at least 10% of the nominal tank volume or at least 10 times the volume of residual which can be diluted (EN 12761-2, 2001).

DEBAER et al. (2008) compared the maximum volume of residual stated in EN 12761-2 (2001) with the actual volume of total residual of 163 sprayers. In order to gain data on the actual volume of total residue of these sprayers the authors analysed test reports from the European Network for Testing of Agricultural Machines (ENTAM). DEBAER et al. (2008) stated that, according to the ENTAM test reports, all tested sprayers complied with the requirements in EN 12761-2 (2001). In many cases the sprayer's total residual volume was even less than 50% of the threshold mentioned in EN 12761-2 (2001) (0.5% of the nominal tank plus 2 l per meter of the boom). DEBAER et al. (2008) therefore suggested that the requirements in this standard should be tightened to achieve a reliable dilution of residual volume with an economically acceptable rinsing tank volume. Further reasons for minimising residue levels are, according to the authors, on-farm clean up systems such as bio-purification systems, which can only deal with a limited hydraulic and chemical load, as well as cleaning procedures in the field (DEBAER et al., 2008).

So far, there are no international standards on dilution thresholds which the operator could use to decide whether the sprayer is actually clean, probably due to the broad range of pesticide compounds, toxicities and formulations. Despite this, France and Denmark introduced thresholds that require the operator to dilute the spray mix down to 1 - 2% of the original tank mix concentration before draining the residual volume in the field (ROETTELE et al., 2010). Investigating the effectiveness of decontamination methods on residues of amidosulfurone, a low dose sulfonyl-urea herbicide, READ & TAYLOR (1998) found that the lower residue level at which no damage occurred to sensitive crops such as sugar beets was 0.4ppm of the concentrated chemical.

In a comprehensive report on external cleaning of agricultural sprayers RAMWELL et al. (2010) defined an acceptable level of residues on the sprayer according to the precautionary principle. The critical level of residues was derived from the acceptable operator exposure limit (AOEL), dermal sorption, and the operator body weight. According to the authors the operator (70 kg bodyweight) could be exposed to a pesticide mass of 700 µg $day^{-1}$ without exceeding the AOEL.

The only concentration threshold indicating that the sprayer is absolutely clean (which will barely be the case in practice) would be the contamination limit given by the aforementioned Drinking Water Directive (ANONYMOUS 1998a). However, in the literature a contamination limit as low as this has not been applied to assess the cleanability of plant protection equipment.

***Best plant protection practices***

Legislation in Germany does not quantify the degree of cleanliness to which the sprayer operator is required to decontaminate crop protection equipment. However, there are basic guidelines known as Best Plant Protection Practices which all users of plant protection equipment have to comply with according to section 2a of the German Plant Protection Act (ANONYMOUS, 1998b). These guidelines are therefore legally binding. The instructions given in the German guidelines cover planning, filling and mixing, field management, sprayer maintenance and use, storage and transport of crop protection equipment. The following principles mentioned in the guidelines directly refer to the internal or external cleaning of plant protection equipment or to residue disposal (BMELV, 2010).

- Plant protection product cans must be rinsed out after emptying and draining. Recommended are chemical induction hoppers equipped with a rinsing nozzle. The rinsing water must be added to the spray mixture. The cleaned empty cans should be returned to the manufacturers as they guarantee container take-back at no charge.
- In order to prevent excess spray, the required amount of spray mixture must be estimated prior to operation. With regards to the last tank filling it is recommended to accurately calculate the required volume and to fill a little less than that in the main tank.
- Depending on the pesticide being used, small amounts of diluted residual spray may remain in the sprayer and be applied during the next operation.
- External cleaning, filling, care, and maintenance of the sprayer shall be carried out in the field. If the farm yard provides installations for waste water treatment and disposal these activities can take place in the farm yard. The paved area must eliminate percolation into the ground as well as uncontrolled drainage into canalization or water bodies. Contaminated sprayers must be parked after operation in such a way that adherent spray mixture cannot be washed off the sprayer surfaces by precipitation.
- When applying residual spray it has to be taken into account that residues between armature and nozzles cannot be diluted which leads to the operator spraying fully concentrated spray mixture at the very beginning of the cleaning

process. Fresh water should be directed into the main tank via the inside rinsing nozzles to decontaminate internal tank surfaces from pesticide residues.
- Residual spray mixes and washings must be diluted adequately and applied to the targeted cultivated area. Residue disposal via the farm yard draining system or canalization violates the guidelines given in the Best Plant Protection Practices.

Cleaning the sprayer after operation is widely regarded by farmers as an inconvenient and time consuming operation and can result in sprayers not being cleaned according to Best Management Practices (ROETTELE et al., 2010). At the same time there is a growing public environmental awareness which leads to some countries defining to which degree the residual spray has to be diluted before the operator is allowed to drain the main tank in the field in order to make sure that no spray mix gets into ground and surface waters. At the European level significant efforts have been made to increase awareness of potential risks arising from the use of pesticides and to identify solutions and guidelines which could lead to a more responsible and risk reducing way of using pesticides in agriculture. One example is the Train the Operators to Prevent Water Pollution from Point Sources (TOPPS)-Project which was funded by the European Commission's Life program and by the European Crop Protection Association (ECPA) from 2005 to 2008. TOPPS involved a number of European countries and intended, according to its website (www.topps-life.org), to create awareness on six critical processes of pesticide use: storage, transport, the phases before, during, and after spraying, and residue disposal management at a larger coordinated scale in Europe in order reduce pesticide spills into ground and surface water. One outcome of TOPPS was the definition of Best Management Practices (BMPs) similar to the German guidelines to help change operator behavior.

### 2.4.2 Cleaning of DIS

Researchers have so far focused on control requirements and the system's hydraulic behaviour, for example, response time or the mixing process when evaluating DIS (FROST, 1990; PAICE et al., 1995; PAICE et al., 1996; VONDRICKA, 2008a). However, DIS concepts have rarely been assessed with regards to their cleanability, although cleaning could, just as with any common commercial sprayer, possibly cause environmental and safety problems if not carried out properly. Despite this, some authors assume that the fact that DIS keep the pesticide and the carrier separate could eliminate some of the problems the operator has to deal with when cleaning his (conventional) sprayer. GANZELMEIER (1998) pointed out that avoiding residual spray is the best way of waste disposal. This is in accordance with TOMKINS et al. (1990) who in discussing DIS assumed these systems might lead to increased operator safety because one advantage of DIS is the elimination of excess spray mixture. MATTHEWS (2008) noted that sprayer cleaning might be less of a problem if DIS were used, but also stated that the broad range of formulation types available (described in detail by KNOWLES, 2008) are one reason why DIS development had not been very significant. FROST (1990) pointed out that in central DIS the chemical is not diluted until it is required. Any surplus chemical at the end of a spraying operation could therefore be taken from the machine and kept for future use. Thus, the problem of unwanted diluted chemicals could be removed. However, when discussing the cleaning of DIS it must be taken into account that the hydraulic system of DIS partly carries pure pesticides that differ from spray mixes in both the concentration of active ingredient and in flow properties. According to ZHU et al. (1998), dynamic viscosities of additives vary from below 1 mPa s to about 1000 mPa s with viscosities of most common liquid pesticides being below 100 mPa s. According to FRIESSLEBEN (2011) the viscosities of the most important approved pesticides in Germany range from 1 mPa s to 700 mPa s. 75% of the products listed by FRIESSLEBEN (2011) are less viscous than 100 mPa s.

In boom injection systems the part of the hydraulic system that gets contaminated with concentrated pesticide can be kept short. However, this is not necessarily the case with DNIS where the pesticide pipe supplies every single injection unit with concentrated pesticide. This leads to a significant amount of inner pipe surfaces becoming contaminated with concentrated pesticide. The unused volume of concentrated pesticide would have to be reclaimed before residues could be rinsed out. Just like excess spray mixture, these pure pesticides have to be removed from inner pipe surfaces once the application is finished or the operator decides to switch pesticides. High viscosities and very effective active ingredients (like sulfonyl-ureas) could lead to DIS having even more difficulties than common sprayers in achieving a degree of cleanness that conforms to guidelines and best management practices.

## 2.5 Assessing cleanability

### 2.5.1 Residue measurements

In discussing the cleaning behaviour of dead end pockets in piping systems, GRASSHOFF (1983) reported that a cleaning procedure can be assessed by applying a test soil to a test surface and analysing residues after cleaning. According to the author, a test soil should meet the following criteria:

- The test soil properties should be close to the real-life product
- In a cleaning procedure, which should be close to the real-life cleaning procedure, the test soiling should be tenacious enough to be detectable after cleaning
- Residues should be both easily detectable and quantifiable
- Residue analysis should be non-destructive

AMSDEN & SOUTHCOMBE (1977) noted that it can be appropriate to use a test rig that simulates the real-life machine as closely as possible if the researcher is unable to use a real device (e. g. the sprayer) due to, for instance, the difficult disposal of large quantities of diluted chemicals. GRASSHOFF (1983) further listed the following four detection methods which may be suitable for residue detection:

1) Gravimetrical methods
2) Chemical-analytical methods
3) Methods using radioactive isotope tracers
4) Microbiological methods

GRASSHOFF (1983) described the above methods as follows:

***Gravimetrical methods***

The object being tested is weighed prior to cleaning and after cleaning. Weighing is the fundamental, most direct method of detecting residues. However, disadvantages to this method are that scales might not be accurate enough to detect traces, and it is only suitable to weigh small objects.

***Microbiological methods***

Microbiological methods are the methods most commonly used in food science (e. g. European Hygienic Equipment Design Group (EHEDG), 2007) as cleaning problems are very often closely related to hygiene requirements in food processing industries. The objects being tested (e. g. pipes) are contaminated with a suspension of bacterial spores in skimmed milk which is then activated by heat. After cleaning, the pipes are dried, coated with culture medium, and incubated. Spores that survived the cleaning procedure will germinate and their colonies can subsequently be made visible with a dye and then counted.

***Radioactive isotope tracers***

According to GRASSHOFF (1983), using radioactive isotope tracers is the most elegant method to detect residues as it allows the researcher to track soil removal and to subsequently detect remaining residues on the cleaned surface. On the one hand, this method provides the opportunity to use real-life products as test soils, but on the other hand the equipment required means it takes great efforts to realize several repetitions. Another disadvantage is the disposal of the rinsing fluid used and safety measures necessary when working with radioactivity.

***Chemical-analytical methods***

After cleaning the remaining test soil (or an aliquot of it) is removed by a suitable solvent and its quantity determined.

Tab. 2-1 compares the advantages and disadvantages of the test methods described by GRASSHOFF (1983). It considers the reported accuracy of each method as well as the information the researcher gets with regards to the special, temporal, and quantitative allocation of residues. It also accounts for the fact that, in this study, not all possible detection methods were feasible.

Tab. 2-1: Advantages and disadvantages of reported methods of determining cleanability as derived from GRASSHOFF (1983).

| Method | Accuracy | Allocation of residues | | | Feasibility |
|---|---|---|---|---|---|
| | | spacial | temporal | quantitative | |
| gravimetrical | - | - | - | + | + + |
| microbiological | - | + | - | - | - |
| radioactive isotopes | + + | + | + | + | - - |
| chemical-analytical | + | - | + | + | + |

In addition to the methods mentioned in Tab. 2-1 PLETT & GRASSHOFF (2007) listed visual and optical methods to determine the presence of soil. Visual methods can be used to determine the wettability of surfaces or adherence of gas bubbles. Detection of remaining soil through optical methods includes adsorption and reflectance measurements.

According to PLETT & GRASSHOFF (2007), a clean surface is a surface free from residual film or soil and, in addition, free of cleaning agents. The authors reported that the removal of contaminants is of logarithmic nature. That is to say it is impossible to remove 100% of the remaining soil in finite time. The decision of whether the surface being tested is clean enough therefore depends on the sensitivity of the corresponding technical measurement procedure (PLETT & GRASSHOFF, 2007). RAMWELL et al. (2008) stated that sampling methodology can also affect the quantity of residues detected. To give an example, the authors mention two common techniques for investigating the external cleaning of sprayers: the use of methanol swabs to remove residues from defined parts of the sprayer, and, as an alternative, the analysis of the washings after the sprayer has been cleaned. Comparing the outcome of several studies, they concluded that methanol-swabbing the surface of a sprayer is likely to over-estimate the quantity of pesticide residue that is removed by cleaning.

### 2.5.2 Simulating pesticides

What makes the experimental cleaning of field crop sprayers difficult is the fact that there are many different formulation types available. CropLife International, an international federation of agricultural biotechnology companies, provided a catalogue of pesticide formulation types and international coding system (ANONYMUS, 2008) with more than 60 different formulation types of conventional agrochemicals. According to KNOWLES (2008), the most common liquid formulations (only those can be applied with DIS without pre-mixing) are still soluble concentrates for water-soluble chemicals, emulsifiable concentrates for oil-soluble chemicals, and suspension concentrates for insoluble solids. Tab. 2-2 lists the concentration of active ingredient in some of the most important common types of conventional liquid formulations of agrochemicals according to KNOWLES (2008).

Tab. 2-2: Concentration of active ingredient in most common types of conventional liquid formulations of agrochemicals, according to KNOWLES (2008).

| Formulation type | Concentration of active ingredient (%) |
|---|---|
| Solution concentrates | 20 - 50 |
| Emulsifiable concentrates | 20 - 70 |
| Suspension concentrates | 20 - 50 |

The figures in Tab. 2-2 illustrate that the most common liquid formulations can consist of up to 70% active ingredient. This means that if the researcher leaves out the active ingredient in an attempt to create a non-toxic solution that simulates pesticides for experimental reasons, he or she will be ignoring a major part of the pesticide. The same is true for other ingredients of pesticide formulations such as solvents and dispersing agents as they can be toxic as well and therefore cannot always be included in the formulation of the non-toxic simulated pesticide.

In the literature two approaches to experimental cleaning of crop protection equipment can be found. Researchers either use a selection of real pesticides to examine the cleaning process or identify suitable reference products. An example where real pesticides were used in cleaning experiments is GANZELMEIER (1998) who placed contaminated sprayers in a catchment pool and analysed the amount of 17 active substances in the wash water. RAMWELL et al. (2010) used five pesticide products of differing formulations to investigate different decontamination methods on external tank surfaces. Residues from external surfaces were determined using either liquid chromatography or gas chromatography. The use of real pesticides allows conclusions to be drawn from experiments about the real situation on farms, the impact of different formations on the cleaning result and the possible environmental threat that improper cleaning of plant protection equipment poses to the environment (RAMWELL et al. 2008).

However, many scientists prefer reference products over real pesticides when evaluating the cleanability of plant protection equipment. Reasons for this include the relatively high costs involved in both the analysis of residues and the subsequent disposal of the pesticides. In addition, researchers conducting the experiments are at risk from exposure to pesticides (RAMWELL et al., 2008).

Some reference products used are listed in International Standards, notably ISO 22368 (1. internal cleaning of complete sprayers, 2. external cleaning of sprayers, 3. internal cleaning of tank) and EN 12761-2 which describes a test method for cleaning crop protection product cans. EN 12761-2 mentions a mixture of water, polysaccharide, and methyl cellulose and other ingredients which, according to BALSARI (2004), results in a sticky solution. Thus, it is suitable for simulating pure pesticides, but the large number of ingredients makes the mixture both expensive and time-consuming to prepare. ISO 22368-2 lists copper oxychloride as a test compound. According to WEHMANN (2008) cleaning tests for complete sprayers are performed using a 1% suspension of this powder to represent common spray mixes. It is (like many pesticides) toxic and therefore requires safety measures when used. Additionally, several scientists have identified alternative reference products, which, although not standardized, seemed to be more suitable for representing real pesticides than those listed by EN or ISO Standards. BALSARI et al. (2008) used Luvitec® K90, a polyvinylpyrrolidone (PVP) powder, which, when dissolved in water, creates a tenacious transparent solution, and blue dye as a tracer. The authors used the product for simulating a pure pesticide when testing internal washing systems of induction hoppers. Luvitec® is also a registered additive in real pesticides in Germany according to the Federal Office of Consumer Protection and Food Safety (BVL, 2011). However, not all reference products mentioned in the literature derive from the ingredients of plant protection products. To give an example, the simulated pesticide created by COOPER & TAYLOR (2004) was a mixture of heavy duty wallpaper paste mixed to give the maximum recommended strength and blue food colouring as a tracer dye. The viscous simulated pesticide was used to contaminate a 10 l pesticide container which was then cleaned by sprayer operators in a survey aimed to highlight the technique that gave the best cleaning results. COOPER et al. (2006) conducted experiments to quantify the effectiveness of washing systems at removing dried chemical deposits from external surfaces of field crop sprayers. Using the commercial formulation Coolglass® (shade paint for glasshouses) mixed with water, the authors created a pesticide-like suspension which was applied to the surface being tested with a brush. Residue detection in the above mentioned examples was done by either colorimetry or spectrophotometry. Although some of the above mentioned simulated pesticides represent pure viscous pesticides, none of them was employed when DIS were investigated with regards to their dosing properties or control requirements.

Both HLOBEN (2007) and VONDRICKA (2008a) opted for a mixture of glycerine, water, and (as a tracer) food colouring or alternatively sodium chloride (NaCl) to determine the dynamics of the DIS dosing behaviour at varying viscosities, either through transmission or conductivity measurements. In other cases authors deployed solutions of pure water and different water soluble tracers to investigate DIS. The tracers were fluorescent dye (ROCKWELL & AYERS, 1996), methylene blue (BENNET & BROWN, 1997), Orange G dye or NaCl (PAICE et al., 1995), or potassium bromide (TOMKINS et al., 1990). Residues were determined by fluorometry (ROCKWELL & AYERS, 1996), spectrophotometry (BENNET and BROWN, 1997, PAICE et al., 1995) or by electrical conductivity measurements (PAICE et al., 1995, TOMKINS et al., 1990). ANTUNIASSI & MILLER (1998) described the characteristics of a test liquid formulation for use in metering systems. Just as the reference product mentioned in ISO 12761-2, the test liquid was a mixture of tap water, xanthan, methylcellulose, and dye. As stated earlier, the addition of salt is a common method to increase the test solutions conductivity in order to be able to monitor changes in electrical conductivity on-line using conductivity sensors when evaluating DIS. The authors therefore investigated if the addition of salt (NaCl) could change the liquid's properties (such as density and viscosity) and found out that the addition of 5.85% NaCl increased density by less than 2.5%. The authors assumed this could influence the results of a steady-state accuracy test with a DIS. The viscosity was found to have decreased by less than 7% through the addition of salt.

Some authors accounted for the fact that there are several formulation types with quite diverse flow properties. ZHU et al. (1998) simulated pesticide liquids in order to measure lag times for an inline injection sprayer system. The four products used were water, Prime Oil, Prime Oil II, and Silicon Oil, each with fluorescent dye as a tracer. Viscosities of these reference products ranged from 0.9 to 97.7 mPa s and did not affect lag times of this DIS. However, the cleanability of these reference products was not discussed by the authors.

Most of the reported simulated pesticides were either water soluble or water based formulations. There are no international standards which list non-toxic, safe-to-use simulated pesticides suitable for representing other widely used liquid formulation types such as, for example, suspension concentrates (SCs) or emulsifiable concentrates (ECs). It is known that the water soluble tracers used by the reported authors cannot represent all commercial pesticide formulations of which some may be composed of non water soluble active ingredients or solvents (RAMWELL et al. 2008). Therefore, results gained from cleaning experiments using tracers instead of real pesticides can only provide a rough estimation of what could happen on real farms under practical conditions.

### 2.5.3 Parameters of the cleaning process

The literature shows that cleaning has been more thoroughly investigated for dairy, food and beverage operations than for agricultural sprayers. Parameters of the cleaning process have been investigated for years in order to improve cleaning of long runs of pipe work (TIMPERLEY, 1981). According to LIND (1990), the four main factors that influence the cleaning performance of milking installations are 1) detergent concentration, 2) cleaning temperature, 3) the time the cleaning solution is in contact with contaminated surfaces, and 4) mechanical forces. The pie chart in Fig. 2-6 illustrates these factors in a variation of what is known as “The Sinner Circle” (WILDBRETT, 2006) which is also commonly applied to domestic laundering (e. g. BURKINSHAW & NEGROU, 2011).

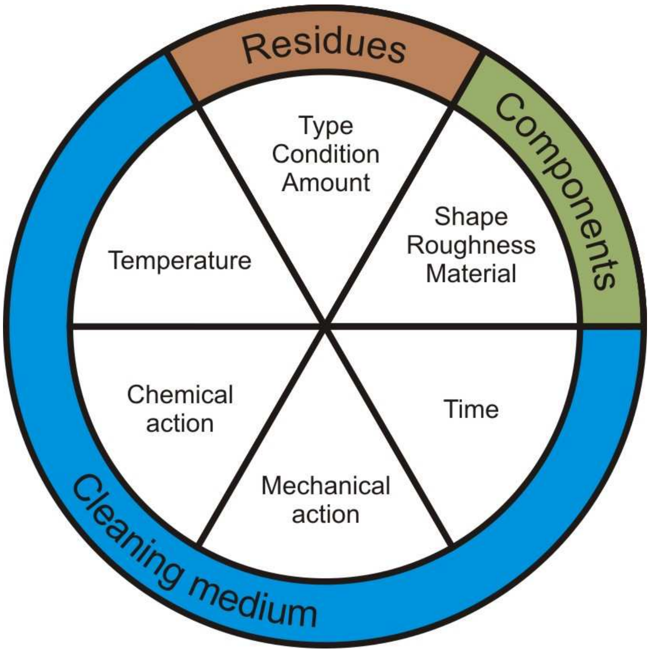


Fig. 2-6: Factors influencing the cleaning process (WILDBRETT, 2006, modified).

Here this concept was modified to represent all parameters that influence the cleaning of plant protection equipment, including DIS. The illustration in Fig. 2-6 shows that the factors of chemical action, mechanical action, temperature, and time take effect mainly through the rinsing medium e. g. water. According to PACKMAN et al. (2008) the different parameters can substitute for each other within certain limits or restrictions that stem from the nature of the product that has to be cleaned.

***Residues***

As stated in section 2.5.2, many researchers investigating the cleaning of plant protection equipment did not use real pesticides, but reverted to simulated pesticides instead. However, those who conducted cleaning experiments using real pesticides observed that the cleanability of the equipment being tested can depend on the formulations used. READ & TAYLOR (1998) for instance noted that mixtures of amidosulfuron and propiconazole proved to be more tenacious and more difficult to remove from 1.5 l tanks of domestic compression sprayers than amidosulfuron alone, whereas no detergents were necessary to thoroughly remove a mixture of fenoxaprop-p-ethyl and amidosulfuron. GANZELMEIER (1998) carried out about 50 on-farm cleaning trials using different plant protection products and different sprayers. The results showed that the absolute amount of active substance removed from the sprayer by the rising water could vary significantly. For instance, ca. 1000 mg of Tribenuron (Tribenuron is a short persistence sulfonylurea herbicide for the control of broad-leaved weeds in cereals) were removed by the rinsing water which would, according to the authors, still be sufficient to treat ca. 850 m² of arable land. In a cleaning test with Anilazine (an active ingredient e. g. in fungicides for turf grass) internal cleaning removed a total of ca. 9000 mg from the sprayer which would theoretically be enough to treat only ca. 100 m². This shows that beyond the mere amount of residual the pesticide’s effectiveness (application rate) is an important factor when describing the degree of a sprayer’s cleanness.

***Temperature***

PLETT & GRASSHOFF (2007) noted that raising the detergent solution temperature would generally enhance the cleaning rates up to a point where other reactions cause heat alterations that will cause difficult cleaning. KULKARNIE et al. (1975) simulated soiling and cleaning in a model high-temperature short-time pasteurizer, and examined (among other things) the effect of temperature on the cleaning result for different dairy products (skim/whole milk or cream). While rinsing water at 75 to 80°C was slightly more efficient in removing lipoidal material than water at 10 to 15°C there was no difference in the removal of proteinaceous soil. LLOYD (2008) reports that if the product is thick and fatty, warm temperatures of 40°C will be sufficient to “melt” the fat and increase cleaning efficiency through savings of detergent and time.

***Chemical effects***

Tests by KULKARNIE et al. (1975) indicated that alkaline cleaner (1% NaOH) was more efficient in removing both lipoidal and proteinaceous material from the equipment than acid cleaner (Dicoloid-FF). In discussing various studies by several researchers on the effect of the detergent concentration on the cleaning rate PLETT & GRASSHOFF (2007) concluded that initially a raise in detergent concentration leads to an almost linear increase of cleaning rates. Then the cleaning rate peaks. The authors also noted that in some cases decline in cleaning rates could be observed when the detergent concentration was too high. With a view to the external cleaning of sprayers RAMWELL et al. (2010) reported that the total pesticide amount removed from external sprayer surfaces was more than 20% higher when a pressure washer with detergent was used compared with a pressure washer without application of detergent. READ & TAYLOR (1998) conducted experiments on the effectiveness of different decontamination methods applied to polyethylene tanks that are commonly used on conventional sprayers. The authors state that a sulfonyl-urea spray mixture could be removed more effectively when detergents such as ammonia soak or even household bleach were included in the decontamination procedure whereas a double water rinse failed to completely remove all residues of this mix. Further evaluations of different decontamination methods were conducted by TAYLOR & COOPER (1998) using an 800 l sprayer contaminated with an aminosulfuron mixture. Results confirmed that appropriate detergents can help clean the sprayer more effectively since no residues were detectible while double water rinsing still lead to 0.4 ppm active ingredient in the refilled 800 l sprayer tank.

Detergents widely known amongst the farming community in Germany and recommended by German agricultural advisory services are for instance All Clear® Extra (Du Pont de Nemours (Deutschland) GmbH), Agroclean® (Spiess-Urania Chemicals GmbH), and Agroquick® (Feinchemie Schwebda GmbH). These detergents are particularly recommended after use of sulfonyl-urea herbicides in cereals if the subsequent application is destined for sugar beet, rapeseed, or legumes (ANONYMOUS, 2011).

***Mechanical effects***

PLETT & GRASSHOFF (2007) stated that besides chemical action and heat, mechanical action is the third form of energy input into the system that is being cleaned. The authors argued that the mechanical action is provided by either shear forces acting on the residue layer or by the turbulent burst action of circulating cleaning solutions or, in the case of out of place cleaning, through a bristle brush. In discussing methods for tank cleaning, PACKMAN et al. (2008) noted that the mechanical forces involved in the cleaning process are primarily a function of the total flow of the cleaning liquid, and of the means by which it is applied to the tank walls and internal structures. GRASSHOFF & REINEMANN (1993) noted that flooding the pipeline of a milking installation (ID 76 mm or larger) and applying continuous flow at 1 - 2 m $s^{-1}$ results in Reynolds numbers of between 100 000 and 500 000 which, according to the authors, indicates highly turbulent flow. The authors stated that introducing air at frequent intervals into the cleaning circuit can further increase flow velocity and turbulence within the piping system and provide a more intense cleaning effect at the air/water boundary.

According to LEWIS (2008) there are two possible types of flow when a fluid flows through a pipe: Streamline and turbulent flow. The flow is streamline if the Reynolds number is less than 2000 and turbulent if it is greater than 4100. The author also stated that for cleaning operations turbulent flow is usually required (LEWIS, 2008). REINEMANN (1996) improved the cleaning result in a milking system by creating a two-phase (air/water) slug flow through cycled air admission. According to the author this can reduce the amount of water required for circulation and increase flow velocities, thus enhancing mechanical cleaning action.

RAMWELL et al. (2010) compared methods for external cleaning of sprayers such as using a hose with or without a brush (under mains pressure), and pressure washing. The test surfaces were pure water tanks which had been contaminated with test solutions of selected pesticide products of different formulations. Using a pressure washer at 15000 kPa with a wide spray angle of 25° was not more effective than a simple garden hose under mains pressure which was attached to a variable nozzle set at a jet spray (spray angle: 0°). The authors therefore assumed that the water pressure hitting the surface was more similar between cleaning methods than expected and that a narrow angled nozzle could enhance removal rates. A second factor that the authors believed may have contributed to this result was the water flow rate, which was 14 l $min^{-1}$ for the hose but only 9 l $min^{-1}$ for the pressure washer. The authors assumed that in this case the extra water had increased the potential to remove residues.

***Components***

The properties of the components that need to be cleaned (e. g. the injection pipe and dosing valves of a DIS) can have an impact on the sprayer's cleanability as well. Just as described by GRASSHOFF (1980), GRASSHOFF (1992), and PLETT & GRASSHOFF (2007), for piping systems in the food processing industry, some parts of the DIS might be more difficult to clean than others due to design and construction parameters including the nature of the surface, finishing, and condition of the surface and equipment design. With a view to food processing equipment, HASTING (2008) mentioned the following general hygienic design principles which apply to plant protection equipment as well:

- Materials of construction should be resistant to the product and cleaning materials under the conditions of use e. g temperature, pressure, and concentration. They should also be non-toxic, smooth, non-porous, and free from crevices.
- Equipment geometry and fabrication should be self-emptying and draining, and avoid creation of stagnant areas where the product can accumulate. Sharp corners and metal-to-metal contact should be avoided. The equipment should also protect product from external contamination.
- Equipment should be easily dismantled for cleaning and surfaces should be visible for inspection.

However, HASTING (2008) added that a design with excellent hygienic characteristics, but unable to meet its functional requirements, will be of little or no value in a practical environment. In discussing equipment construction materials in food processing industry LEWAN (2003) stated that austenitic stainless steels are the automatic choice as materials of construction for food processing plants and equipment. Their popularity derives from their general resistance to corrosion by food products and to the recommended cleaning regimes, as well as from the ease with which they can be cleaned and sterilised (LEWAN, 2003). With conventional sprayers the pipeline through which the spray mixture is delivered to the nozzles is also made of stainless steel (PAULUS, 2011). The following plastics are further examples for easy-to-clean materials and are, therefore, also used in hygienic design (LEWAN, 2003):

- Polypropylene (PP)
- Polyvinyl chloride (PVC) unplasticized
- Acetal copolymer (Polyoxymethylene, POM)
- Polycarbonate (PC)
- High density polyethylene (HDPE)

According to HASTING (2008), polytetrafluoroethylene (PTFE) is often considered a potentially attractive material because of its high chemical resistance. LEWAN (2003) pointed out that PTFE could be difficult to clean because it can be porous and is also not resilient enough to provide a permanently tight seal.

According to DÖHNERT (1998) the most commonly used primary packaging material for agrochemicals is polyethylene (PE). Plastics used for packaging and transport of agrochemicals must comply with the requirements mentioned in the European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR, 2010), one part of which is a permeability test for plastics. Just as with pesticide packaging, PE is also a very common construction material for sprayer tanks designed to hold diluted spray mixture during application (READ & TAYLOR, 1998).

AMSDEN & SOUTHCOMBE (1977) noted that not all engineering materials used in the construction of field crop sprayers are resistant to common formulation types. The authors compared combinations of plastics and elastomer materials (polyvinyl chloride (PVC), ethylene vinyl acetate (EVA), nitrile, and Viton) and commonly used solvents (Xylene, Naphta, Isophorone and Cyclohexanone) for relative levels of chemical attack. The results showed that susceptibility of materials to chemical attack strongly depended on the combination of solvent and the material the solvent was in contact with. Whereas Viton proved to be resistant to Xylene and Naphta solvents it was highly susceptible to chemical attacks through Isophorne and Cyclohexanone. The same was true for PVC which, as the authors point out, can absorb enough of certain solvents to increase its weight by 150% in 7 h. EVA proved to be resistant to Isophorone and Cyclohexanone whereas all other combinations showed a medium susceptibility to chemical attack. AMSDEN & SOUTHCOMBE (1977) also stated that PE is apparently resistant to organic solvents and to surfactants, the proximity of certain chemicals induces a state of stress in the material which may cause it to develop cracks and eventually to disintegrate. Of course this implies that materials which absorb pesticides that they are in contact with or that are subjected to chemical attack by the pesticide will never be completely clean once they have been contaminated. AMSDEN & SOUTHCOMBE (1977) observed that the limiting factor is the range of materials usefully available to the engineer. Although, according to the authors, the use of titanium and PTFE might possibly be the answer, they also added that its manufacture and repair would defy normal methods and its costs would be prohibitive.

# 3 Materials and methods

Some of the materials and methods presented in this section were published by DOERPMUND et al (2011). The cleaning process was divided into two steps:

1. Reclaiming the simulated pesticide by returning it to the pesticide tank using pressurised air ( i.e. pre-cleaning)
2. Rinsing the contaminated part of the hydraulic system with water

## 3.1 Test bench

The concept for the DIS used in this study originated from the work of SÖKEFELD et al. (2004) and VONDRICKA & SCHULZE LAMMERS (2009). The core of the direct injection unit was a rapid response dosing valve and a static mixer (see section 3.1.1). The test bench used in this study is illustrated in Fig. 3-1.

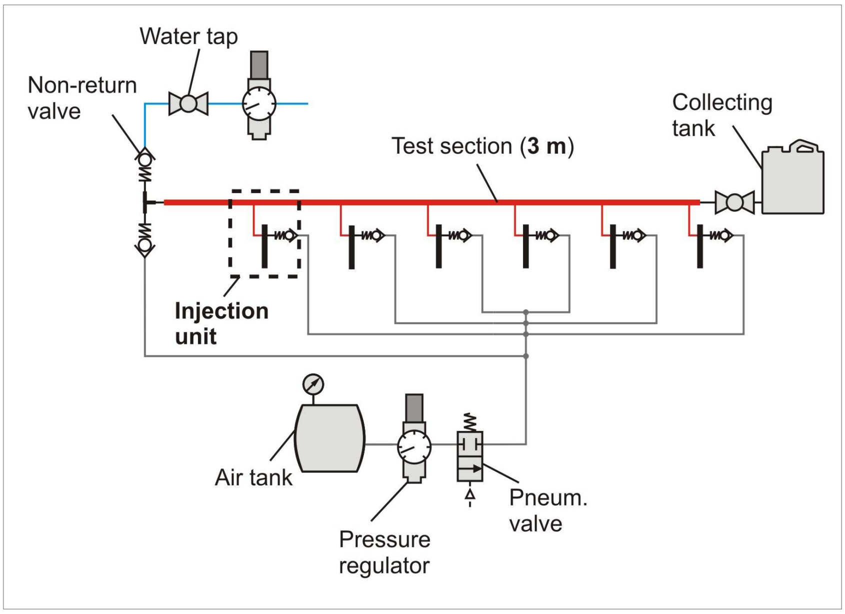


Fig. 3-1: Schematic of the test bench representing a boom section at the end of a sprayer boom.

The assembly in Fig. 3-1 represents a boom section at the end of a sprayer boom where air enters the pesticide pipe through a main air inlet (inner diameter (ID): 10 mm) located at the end of the boom and also through ancillary inlets (ID: 4 mm) at the injection units. The test bench was made up of a support frame carrying six injection units spaced 500 mm apart and a stainless steel pipe (ID: 10 mm) with adapters and 50 mm long PTFE hoses (ID: 4 mm) supplying these units with simulated pesticide. The pipe (including adapters and hoses) represented the test section which was contaminated and cleaned under laboratory conditions. A supply line for the carrier (water) into which the pesticide is normally injected during application was not included in the set-up since the aim of the tests was to detect residues in the rinsing water without further dilution. Fig. 3-2 illustrates the flow direction of air and water on this test bench as well as the nozzle designation by location.

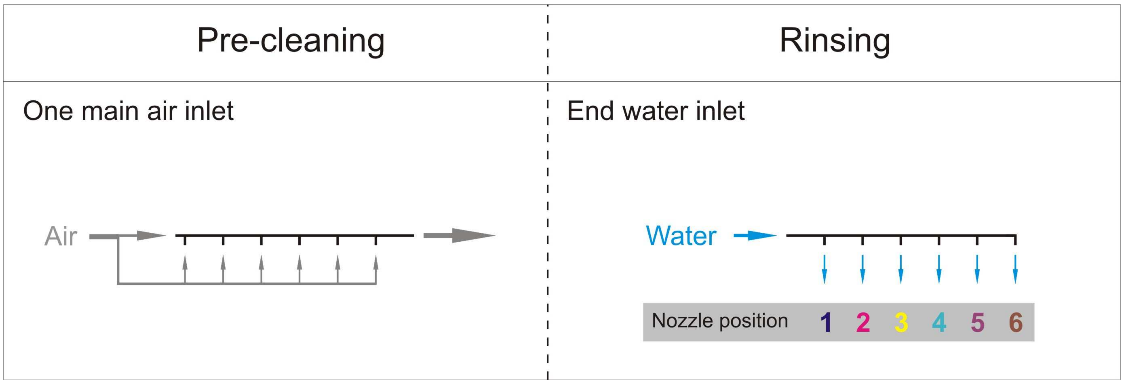


Fig. 3-2: Flow direction of air and water and nozzle designation by location on the test bench illustrated in Fig. 3-1.

### 3.1.1 Injection units

Fig. 3-3 is a detailed representation of Fig. 3-1 (dashed frame) illustrating one of the injection units that were part of the test bench.

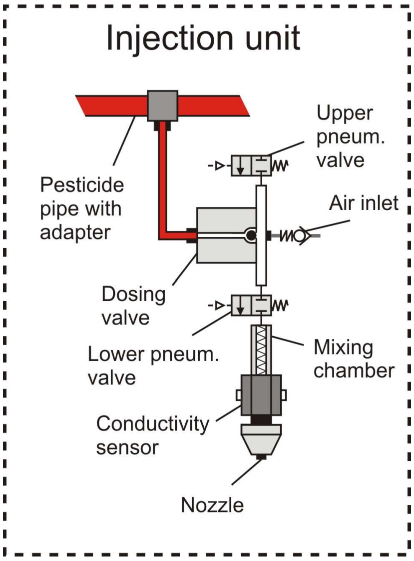


Fig. 3-3: Illustration of a direct injection unit as developed by VONDRICKA (2008a). The conductivity sensor was included for the measurements but will not be part of the injection units once they are ready for field use.

The core of each injection unit was the injection valve (an early version was described by VONDRICKA, 2008a), a so called Rapid Reaction Valve® (RRV®, GSR Ventiltechnik GmbH & Co. KG, Vlotho-Exter, Germany). According to information from GSR, RRV®s are highly precise dosing valves designed to meter a broad range of fluids of different viscosities (VONDRICKA, 2008b). What is more, the response times of these valves are in the range of a few milliseconds. These properties combined make the RRV®s suitable for online application of pesticides in precision plant protection and were the reason why there were included in the experimental set-up. The valves consist of a valve seat (ID: 2 mm) and a magnetizable ball (ID: ca. 5 mm) which is surrounded by a coil (see Fig. 3-3). As current runs through the coil the ball gets pulled off the valve seat, which opens the valve. Once the current stops the medium inside the valve pushes the ball back onto the valve seat and thus closes the RRV®. In order to achieve a large dosing range the current in the coil is controlled via pulse width modulation (PWM) which leads to the ball being pulled off and pressed onto the valve seat many times a second, depending on the desired flow rate of the dosing medium. For the cleaning experiments conducted in this study the RRV®s were not opened through PWM signals but instead through constant current so that the ball was constantly pulled off the valve seat, making way for either air during the push-back or the water during rinsing. Above and below the RRV® of each injection unit there was a pneumatic shut-off valve (Lechler GmbH, Germany). The upper shut-off valve was primarily to switch off the carrier (which was not used in this study) while the lower shut-off valve was installed as a security valve. Apart from that, both valves were necessary for returning the pesticide back to the pesticide tank as will be described in section 3.3. The mixing chamber, which was also part of each injection unit, was placed below the lower shut-off valve and consisted of a custom-made polyoxymethylene (POM) housing with a QUADRO® static mixer (Sulzer Chemtech Ltd, Switzerland) which has been described and tested with regards to its suitability in DIS by VONDRICKA (2008a). The injection unit was fixed to the injection pipe with a standard single nozzle holder (Lechler GmbH, Germany). The nozzle below the conductivity sensor was a standard IDK 120-03 flat fan nozzle (Lechler GmbH, Germany).

### 3.1.2 Pressure measurements

A pressure sensor (CTE8016GY0, Sensortechnics GmbH, Puchheim, Germany) was used to derive the amount of air used for the push-back from the pressure drop in the air tank. Voltage signals from the sensor ranged from 0 to 10 V at a measuring range from 0 to 1600 kPa. The pressure was thus derived from

$$P = 160U \qquad (3\text{-}1)$$

where $U$ was the voltage signal from the sensor in V and $P$ the pressure in kPa. In addition, six pressure sensors similar to the one described above were used to describe the dynamics of the reclaiming process (see section 3.4.2).

### 3.1.3 Conductivity measurements

#### ***Conductivity measuring cells***

Six conductivity measuring cells (described in detail by HLOBEN, 2007 and VONDRICKA, 2008a) were used to simultaneously determine the concentration of the simulated pesticide in the effluent of each nozzle. The sensors were calibrated with a concentration vs. voltage calibration equation derived from measurements of simulated pesticide solutions at known concentrations where the pure simulated pesticide was 100% and pure tap water was 0%. The set-up used for the calibration is shown in Fig. 3-4.

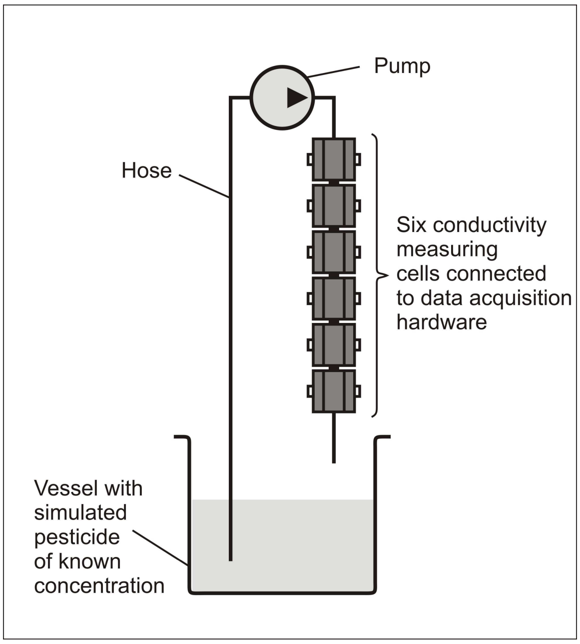


Fig. 3-4: Set-up for calibrating the six conductivity measuring cells.

All six sensors were screwed together to form a pipe as shown in Fig. 3-4. The voltage signals from the six sensors were continuously measured using LabVIEW 8.6 while 500 g of simulated pesticide (see section 3.2) at concentrations of between 0.025% and 100% were pumped round in circles to make sure that it was thoroughly mixed and the voltage signals were stable. The signals generally became stable within the first seconds of circulation. However, it was noticed that excessive circulation (e. g for more than 3 min) led to lower voltage signals, probably because the pump heated up, thus heating the circulating test solution. After the signal was stable the average voltage during 10 s was calculated and used as independent variable in the non linear exponential decay curve fit model ExpDec3 (Origin® 8.0). This was then used to create the calibration curves. For each concentration three solutions of simulated pesticide were prepared and measured one by one. Between the replications the pump, attached hoses, and conductivity sensors were thoroughly cleaned by circulating tap water until the voltage signals from the sensors were equal to the voltage signals of tap water. The latter had been determined prior to the experiment.

The equation of the calibration was

$$c = A_1 \exp(-U t_1^{-1}) + A_2 \exp(-U t_2^{-1}) + A_3 \exp(-x U t_3^{-1}) + c_0 \qquad (3\text{-}2)$$

where $c$ was the concentration of the simulated pesticide in % and $U$ the voltage signal from the respective sensor in V. $A_n$, $t_n$, $c_0$ were parameters of the ExpDec3 curve fit model. Fig. 3-5 shows the calibration curve of one of the six sensors.

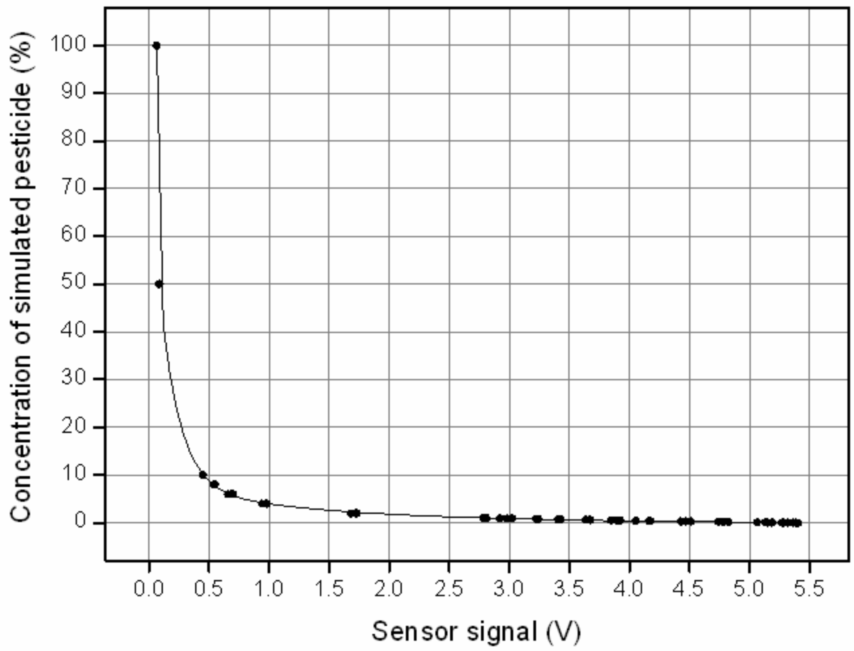


Fig. 3-5: Voltage vs. concentration calibration curve for one of the six conductivity measuring cells (R² = 0.99). The curve was calculated using an ExpDec3 model in Origin® 8.0.

The exponential shape of the calibration curve implies that the calibration equation will translate a given voltage difference into different concentration differences, depending on whether the voltage level is high or low. Fig. 3-6 shows an idealized voltage vs. concentration calibration curve where the two slope triangles illustrate that the same voltage difference ($\Delta U_1 = \Delta U_2$) leads to varying calculated concentration differences ($\Delta c_1 > \Delta c_2$) at different concentration levels.

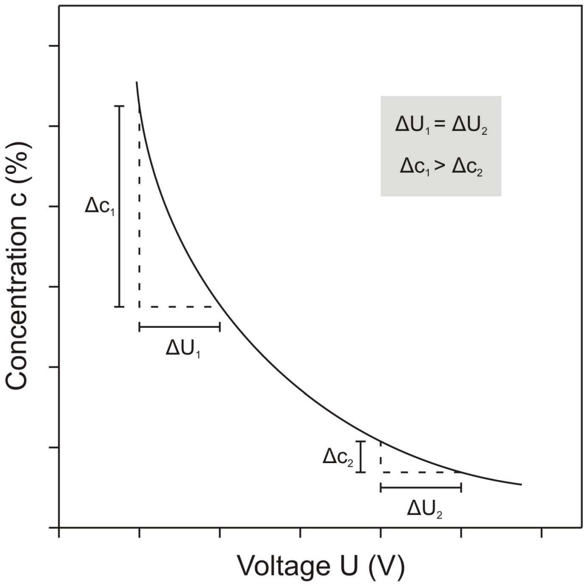


Fig. 3-6: Idealized voltage vs. concentration calibration curve illustrating the effect of voltage changes (ΔU) on the calculated changes in concentration (Δc) at different concentration levels.

In order to exemplify this effect Fig. 3-7 shows both the original signals from one of the six conductivity measuring cells measured during calibration (Fig. 3-7a) and the concentrations of the simulated pesticides that were then derived from the voltage signals using the corresponding calibration equation (Fig. 3-7b). For clarity, only data for desired concentrations (DC) of 1, 2, 4, 6, 8, and 10% are shown in Fig. 3-7, although, as mentioned earlier, the calibration covered a wider range of concentrations.

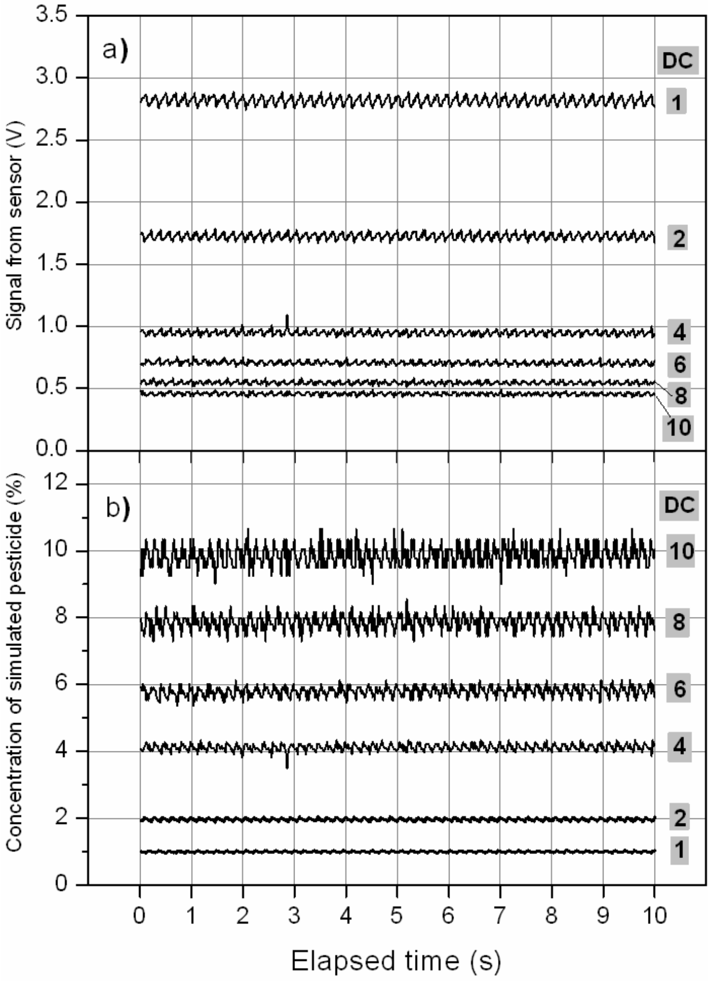


Fig. 3-7: a) Voltage signals from one of the six conductivity measuring cells at different desired concentrations (DC) of the simulated pesticide (%) as a function of time and b) concentration of the respective simulated pesticide derived from the above signals using the calibration equation.

As can be seen from Fig. 3-7a the signal noise slightly decreased with increasing concentration of the simulated pesticide. The reason for this was that not only the voltage signal dropped as conductivity increased, but also the voltage noise. The signal-to-noise ratio remained nearly constant. However, the signal noise was amplified through the calibration equation so that concentration curves in Fig. 3-7b appear noisier at high concentrations than at low concentrations.

Another effect of the calibration equation was that the sensors were only reliable at concentrations of simulated pesticide from 0.2% to 100%. At lower concentrations, the calibration curve runs almost parallel to the x-axis, making a further decline in concentration hardly detectable (Fig. 3-5). The sensors were therefore used to describe the initial dynamics of the rinsing process within the first 1 - 2 min where, as pre-tests had shown, concentrations were unlikely to exceed this range of concentrations.

***Hand-held conductivity meter***

A hand-held conductivity meter (pH/Cond 340i, WTW GmbH & Co. KG, Weilheim, Germany) was used to determine concentrations beyond the reliability of the conductivity measuring cells. Since the device required samples of ca. 20 ml to be drawn manually it was not suitable for simultaneous measurements at all nozzles. It was calibrated with a concentration vs. conductivity calibration equation.

For calibration 200 g of each calibration solution at concentrations of between 0.02% and 75% were prepared in three replicates. For 0% (pure tap water) and 100% (pure simulated pesticide) only one 200 g sample was measured. The 0% sample was drawn from running tap water while the 100% sample was taken from the vessel containing the supply of pure simulated pesticide.

In order to derive the calibration curve from the data, the polynomial regression tool for polynomial fitting of curves in Origin® 8.0 was used. The general equation of this polynomial fit was

$$c = B_2\kappa^2 + B_1\kappa + \mathit{intercept} \qquad (3\text{-}3)$$

where $c$ was the concentration of the simulated pesticide in %, $\kappa$ the conductivity value measured in mS cm$^{-1}$, and $B_1$, $B_2$, and *intercept* parameters of the polynomial fit model.

Fig. 3-8 shows the calibration curve which was measured prior to the experiments. The calibration equation of this graph was

$$c = 0.02178\kappa^2 + 1.6773\kappa - 0.63202 \qquad (3\text{-}4)$$

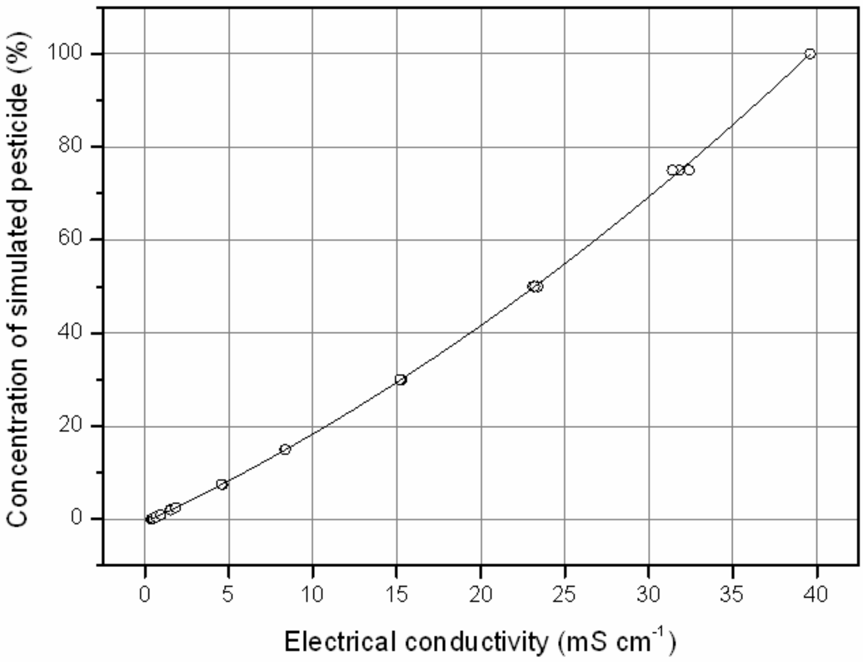


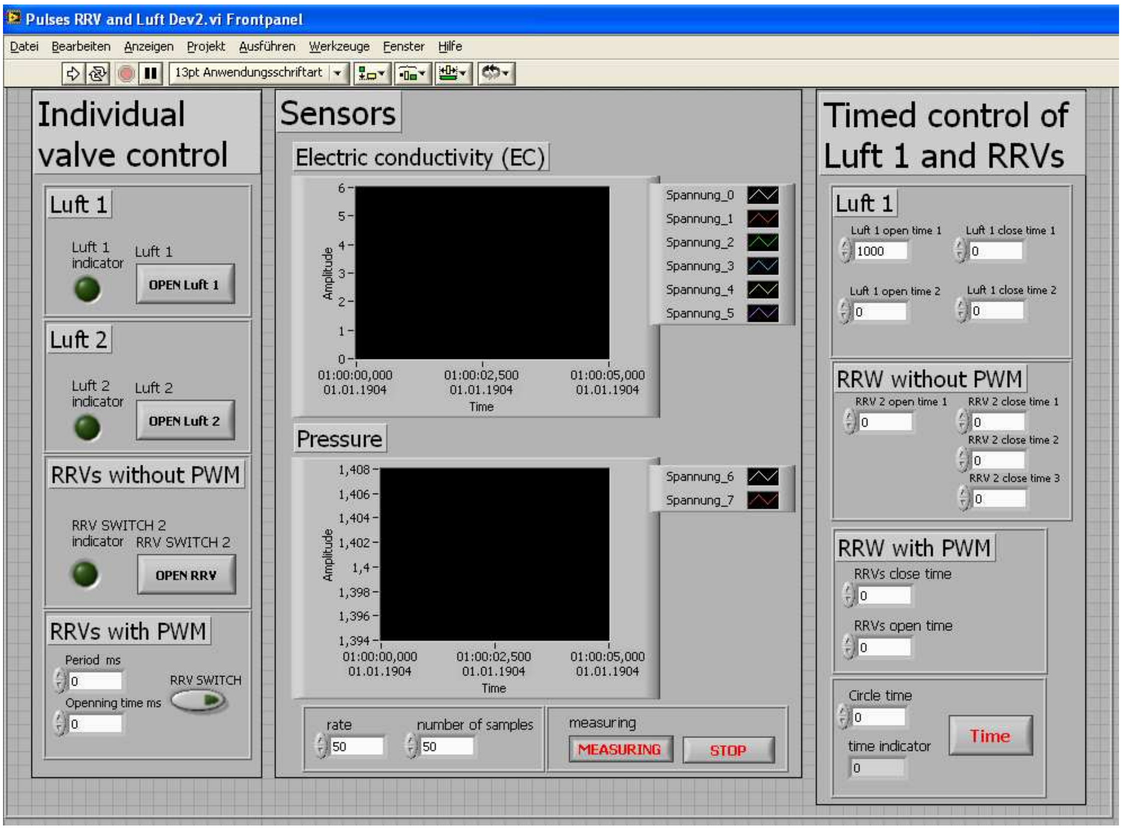
Fig. 3-8: Calibration curve for the pH/Cond 340i conductivity meter derived from conductivities of solutions of simulated pesticide at known concentrations ($R^2 = 0.99$).

As it turned out, the electrical conductivity of the tap water used was not constant throughout the study but instead ranged from 0.310 to 0.376 mS cm$^{-1}$, although it was obtained from the same water tap. This explains why the conductivity meter had to be recalibrated prior to each experiment in order to avoid incorrect calculated concentration values. Due to time constraints the recalibration was at first simplified by using only three concentrations of the simulated pesticide (0, 50 and 100%) and applying the aforementioned fitting model to the data.

Due to the device's decreasing resolution at increased conductivities there was, independent of the tap water conductivity, no change in conductivity detectable in both the 50% and the 100% solutions. As a consequence of this, the recalibration was further simplified by exclusively updating the conductivity of the 0% sample (pure tap water) in the calibration data and recalculating the calibration curve.

### 3.1.4 Data acquisition system

In order to read voltage signals from both pressure and conductivity sensors and to control the various valves on the test bench a USB-6008 data acquisition box (National Instruments, USA) and custom designed software developed in LabVIEW 8.6 (National Instruments, USA) were used. Fig. 3-9 shows the front panel of the Virtual Instrument (VI) designed for the experiments.



Period ms 0
Openning time ms 0
rate 50
number of samples 50
Luft 1 open time 1 1000
Luft 1 close time 1 0
Luft 1 open time 2 0
Luft 1 close time 2 0
RRV 2 open time 1 0
RRV 2 close time 1 0
RRV 2 close time 2 0
RRV 2 close time 3 0
RRVs close time 0
RRVs open time 0
Circle time 0
time indicator 0

Fig. 3-9: LabVIEW front panel used for data acquisition and controlling of six RRV®s and two standard valves.

It controlled the opening times of the valves and was used to monitor the voltage signals from the sensors in a running experiment as the data was saved to txt-files. The VI controlled two electric valves on the test bench. One of them (GSR K0510105) released the lower pneumatic shut-off valves of the injection units (all at once). The other (GSR 0511805) released a pressure controlled valve which in turn opened or closed the air tank. Data from the txt-files were subsequently processed in Excel® 2003 and Origin® 8.0.

## 3.2 Simulated pesticide

The simulated pesticide was made from 5%, 10% or 15% polyvinylpyrrolidone (PVP) powder (Luvitec® K90, BASF, Köln, Germany), 3% salt (NaCl), and water. The reason for not using a higher NaCl concentration was that changes in voltage signals from the conductivity measuring cells (see section 3.1.3) would have been hardly distinguishable since at higher concentrations they all would have been near zero.

According to the manufacturer Luvitec® powder is hygroscopic and water soluble. In crop protection it is used to increase adhesion of the active ingredients to the plant. The reason for not using one of the reference products mentioned in ISO 22368 or EN 12761 (see section 2.5.2) was that the PVP-salt-water mixture was non-toxic and easier to prepare. What is more, Luvitec® is a registered additive in real pesticides in Germany (Federal Office of Consumer Protection and Food Safety, BVL, 2008) and was thus considered suitable for creating a preferably pesticide-like solution. Moreover, this compound had been used by other researchers as well, e. g. by representatives from the German Julius Kühn-Institut (JKI) (STIEG, 2009) and BALSARI et al. (2008). The PVP powder and salt were dissolved in warm water with continuous stirring. The amount prepared for the experiments ranged from 1000 g for small scale experiments to 5000 g for experiments that were carried out on a boom section. It took approximately 24 h for the powder to completely dissolve in the water. Although most of the powder generally dissolved within the first six hours after the ingredients had been mixed, there would still be white flakes visible which would only disappear several hours later. The NaCl was added after the PVP powder had dissolved completely, that is, after all flakes had disappeared. The bucket containing the simulated pesticide was covered with foil in order to prevent the water from evaporating. As pointed out by ANTUNIASSI & MILLER (1998), knowing the physical properties of the simulated pesticide used (such as density and viscosity) is essential for reliable and repeatable results when working with DIS. Therefore, density, dynamic viscosity and surface tension were measured in the course of this study.

### *Density*

Densities of aqueous PVP solutions of different concentrations of PVP powder (5, 10, and 15%, each with 0% or 3% NaCl) were determined using a DMA 55 density meter (Anton Paar GmbH, Graz, Austria). Prior to the measurements the device had been calibrated according to the manual. For each of the aforementioned PVP concentrations with 0% NaCl 1 kg of simulated pesticide was prepared in three replications and stored in wide mouth bottles. For the 3% NaCl solutions only one bottle for each PVP concentration was prepared. From each bottle a sample of approximately 10 ml was drawn with a disposable syringe and injected into the density meter's measuring chamber. For each sample a clean, unused syringe was used. After each measurement the measuring chamber was cleaned by pressing distilled water through the measuring chamber using another clean and unused syringe. All measurements were carried out at a sample temperature of 20°C.

***Dynamic viscosity***

In order to determine viscosities of aqueous PVP solutions at different concentrations a Bohlin Gemini 150 cone and plate rheometer (Malven Instruments, Malvern, UK) was used. For this experiment, solutions of the same PVP and NaCl concentrations as for the density measurements were prepared. However, at the beginning of the study in 2009 solutions without NaCl were prepared in three replications using powder from the new, sealed PVP container. One year later in 2010 a second batch of test solutions was prepared, this time with and without addition of 3% NaCl. At that time the resealed container had been stored in the department's experimental hall for almost one year. Due to time constraints the viscosities of the solutions prepared in 2010 were only measured once while the PVP solutions prepared in 2009 were measured in three replications. The rheometer measured shear stress ($\tau$) at shear rates ($\dot{\gamma}$) from 0.05 to 100 $s^{-1}$ at 25°C. Since the simulated pesticide behaved, according to its shear stress vs. shear rate curve, almost like a Newtonian fluid (i. e. viscosity remained constant for all shear rates) the following equation was applied for calculating the dynamic viscosity of each solution (LEWIS, 2008):

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad (3\text{-}5)$$

where

$\dot{\gamma}$ : Shear rate ($s^{-1}$)

$\tau$ : Shear stress (mPa)

$\eta$ : Dynamic viscosity (mPa s)

In order to apply the above-mentioned formula the shear stress and shear rate raw data from the rheometer was copied into an Excel® 2003 spreadsheet. The data was plotted in a chart with shear stress being the dependent variable and shear rate the independent variable. Then a trend line through origin was applied to the graphed raw data. The slope of the trend line was then the calculated dynamic viscosity $\eta$ of the respective test solution.

Experiments on the 3 m test bench were conducted using a simulated pesticide at 250 mPa s. With small scale cleaning experiments where the test section was significantly shorter (total length ca. 500 mm) the viscosity of the simulated pesticide was increased to 500 mPa s in order to highlight differences between treatments more clearly.

In order to determine the effect of temperature on the viscosity of the simulated pesticide the rheometer was equipped with parallel plate geometry. The reason for using the parallel plate geometry was the larger gap between the two surfaces (500 µm) compared with the cone and plate geometry (30 µm). The solutions' expansion at higher temperatures could have led to it running out of the rheometer gap while being sheared if a cone and plate system had been used. Temperatures ranged from 10 to 40°C at a heating rate of 3°C $\text{min}^{-1}$ and a constant shear rate of 50 $\text{s}^{-1}$. The simulated pesticide used for this purpose was a 10% PVP solution. Due to time restrictions only one sample of this solution was measured.

***Surface Tension***

Surface tension was determined for the aforementioned solutions of 2010 with and without NaCl using a Drop Shape Analysis System DSA30 (Krüss GmbH, Hamburg, Germany). From each solution ten droplets were analysed for surface tension.

***Diffusion of the tracer***

As mentioned earlier the simulated pesticide contained NaCl as a tracer. RAMWELL et al (2008) noted that there might be discrepancies between the removal of the pesticide and the tracer used for tracking this product. In order to avoid possible data interpretation errors due to tracer diffusion from the simulated pesticide into the rinsing water a static diffusion test was carried out. Beakers (250 ml capacity) were filled with 150 ml of distilled water which were then carefully underlayed with 50 ml of the simulated pesticide. For this experiment distilled water was preferred over tap water because it was available in the quantities needed and allowed smaller changes in concentration to be detected.

A clean and unused 10 ml syringe with a thin needle was installed with the tip of the needle 0.5 cm, 2.5 cm or 4.5 cm above the interface between the simulated pesticide and the distilled water.

Fig. 3-10 illustrates the experimental setup for determining the diffusion of the simulated pesticide into the layer of distilled water. An experimental setup similar to that applied here has been used by HOFMANN (2007) who described diffusion from a whey protein layer into water.

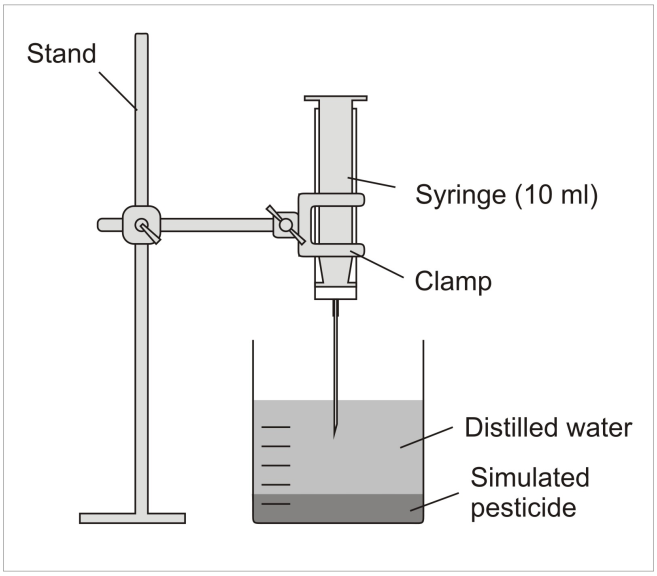


Fig. 3-10: Setup for determining diffusion of the simulated pesticide into a layer of distilled water.

At defined times (after 0 h, 1 h, 6 h, and 18 h) samples of 10 ml were drawn with the syringe and their conductivity measured using the hand-held conductivity meter. The samples taken after 0 h and 18 h were additionally analysed for dynamic viscosity using the cone-and-plate rheometer. This was done in order to ascertain if the conductivity truly reflected the concentration of the simulated pesticide or if it was possibly caused by the tracer diffusing out of the PVP-solution into the distilled water. This would be the case if there was an increase in the solution's conductivity while its dynamic viscosity changed significantly less.

## 3.3 Cleaning procedure

The general cleaning procedure at the test bench was conducted as follows:

1. The clean detached test section was filled with test simulated pesticide, using a small gear pump (Tuthill Co., Derbyshire, UK).
2. The filled test section was attached to the direct injection units, the air and water supply and the collecting tank (Fig. 3-11a). Then pre-cleaning was started through LabVIEW. The air tank and the dosing valves were opened while both upper and lower shut-off-valves remained closed (Fig. 3-11b).

3. The simulated pesticide was pressed into the collecting tank until LabVIEW automatically stopped pre-cleaning after a defined time by closing the air tank and the dosing valves (Fig. 3-11c)
4. All lower shut-off valves and dosing valves were opened through the VI while the upper shut-off valves remained closed. Then the water tap was opened manually to rinse the pre-cleaned test section at a given water pressure (Fig. 3-11d).
5. After each replication the test section was, if necessary, rinsed with additional water until the conductivity of the rinsing water was equal to the conductivity of pure tap water. Water samples from all nozzles were drawn and measured by the hand-held conductivity meter. The test section was then detached from the test bench and residual water was blown out with a blow gun. After that, the test section was considered clean and ready for the next replication.

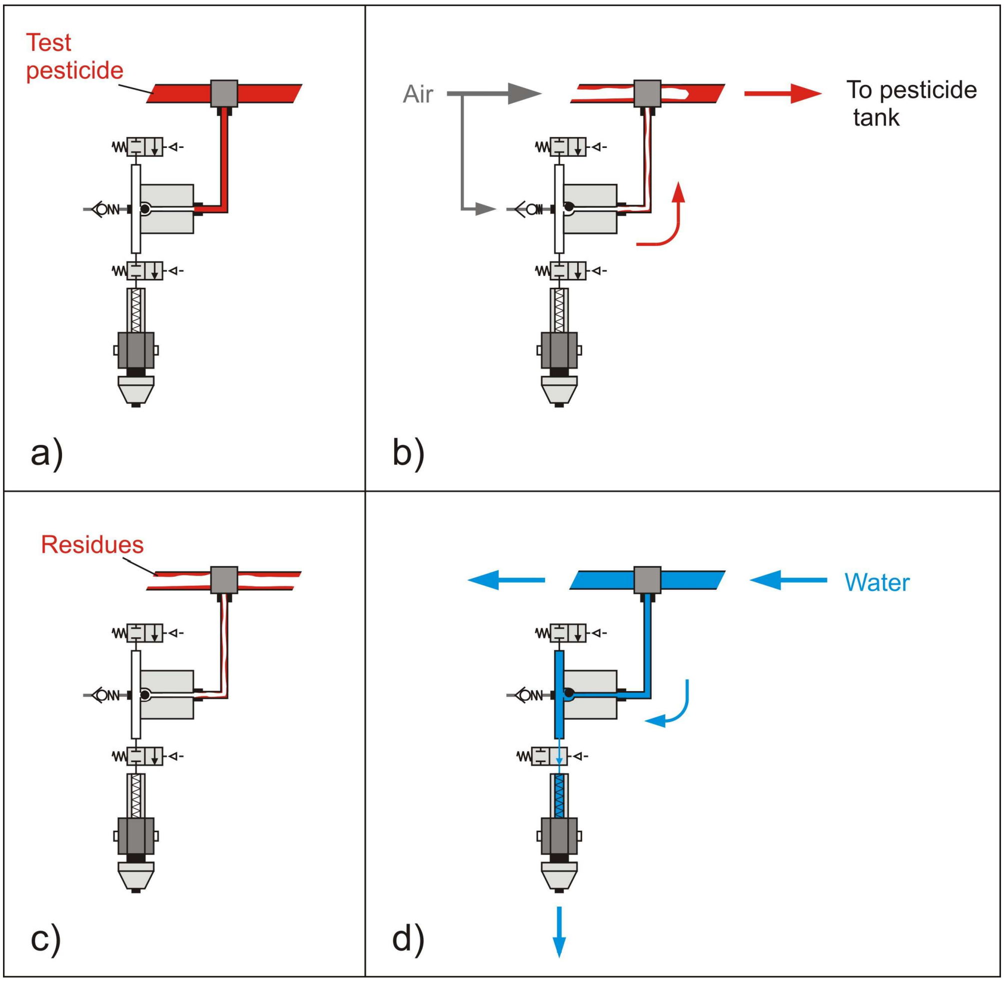


Fig. 3-11: Injection unit a) before, b) during, and c) after reclamation of the simulated pesticide with pressurized air. d) illustrates subsequent rinsing with water.

## 3.4 Reclaiming the simulated pesticide (pre-cleaning)

### 3.4.1 Calculation of the amount of air used for reclaiming

Prior to all experiments it was made sure that the pressure in the air tank was 1000 kPa. Thus the amount of air available for the reclamation of the simulated pesticide was the same in all trials. The pressure drop in the air tank was used to calculate the amount of air that had streamed out of the tank based on (3-6), the ideal gas law (STÖCKER, 2010)

$$PV = nRT \tag{3-6}$$

where

$P$: Pressure (kPa)
$V$: Volume (m³)
$n$: Amount of substance (mol)
$R$: Gas constant (J $\text{mol}^{-1}$ $\text{K}^{-1}$)
$T$: Temperature (K)

The equation was transformed to (3-7), (3-8) and (3-9) respectively to estimate the amount of substance of the air whereas (3-10) was used for calculating the air volume

$$n_{LA} = P_{LA}V_B(RT)^{-1} \tag{3-7}$$

$$n_{LE} = P_{LE}V_B(RT)^{-1} \tag{3-8}$$

$$\Delta n_L = n_{LA} - n_{LE} = (P_{LA} - P_{LE})V_B(RT)^{-1} \tag{3-9}$$

$$V_L = \Delta n_L M_L \rho_L^{-1} \tag{3-10}$$

where

$n_{LA}$: Amount of substance of air in the air tank before valve opening (mol)
$n_{LE}$: Amount of substance of air in the air tank when valve was closed again (mol)
$\Delta n_L$: Amount of substance of air streamed out of the air tank between valve opening and valve closing (mol)
$R$: Gas constant, 8.31 J $\text{K}^{-1}$ $\text{mol}^{-1}$
$T$: Temperature, 293.15 K (20°C)

$V_B$ : Capacity of the air tank, 0.055 m³ (55 l)

$P_{LA}$ : Pressure in the air tank before valve was opened

$P_{LE}$ : Pressure in the air tank after valve was closed again (kPa)

$M_L$ : Molar mass of air (28.96 g mol$^{-1}$)

$\rho_L$ : Density of air (1.2 g l$^{-1}$,derived from LIDE, 2003)

$V_L$ : Air volume streamed out of the air tank between valve opening and closing (l)

### 3.4.2 Effect of air pressure

In order to describe the effect of air pressure on the initial dynamics of the reclaiming process a simplified version of the test bench shown in Fig. 3-1 was set up (Fig. 3-12).

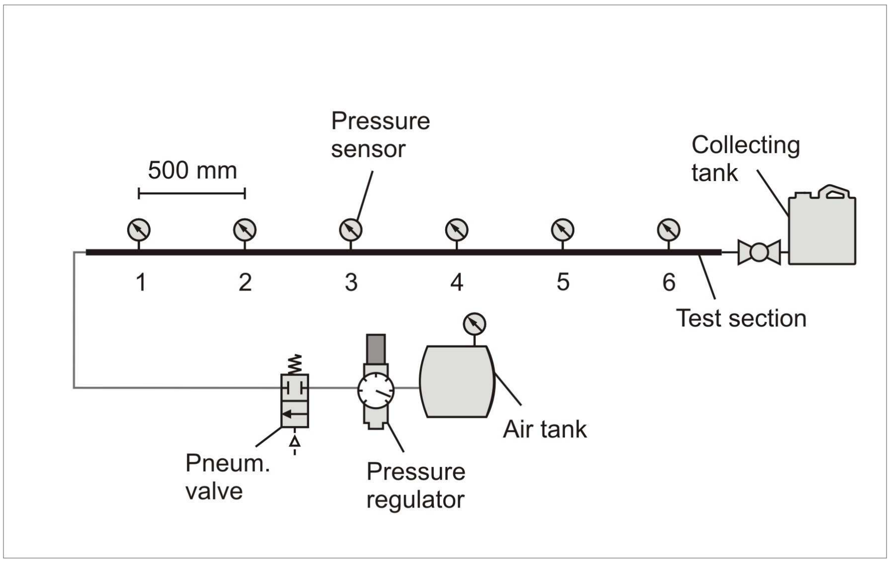


Fig. 3-12: Set-up for determining the initial dynamics of the reclaiming process. The numbers indicate the sensor positions.

The 3 m test section was not connected to the DIS units. Instead, pressure sensors were plugged into the adapters for the hoses leading to the injection units. The air inlet was placed at the end of the test section, taking into account the possible flow direction of pressured air in the real DIS sprayer. The capacity of the tank installed to collect the simulated pesticide during the push-back was approximately 10 l. The tank, which was empty before the push-back started, allowed the air to escape through an opening on top of the tank. Pressure sensors continuously measured the static pressure in the test section at the adapter positions while the simulated pesticide was being pushed into the collecting tank. According to Bernoulli's equation (STÖCKER, 2010) the static pressure can be expressed as in (3-11) when changes in elevation are insignificant.

$$P_S = P_T - 0.5\rho v^2 \tag{3-11}$$

with:

$P_S$ : Static pressure (kPa)
$P_T$ : Total pressure (kPa)
$v$ : Flow velocity (m $s^{-1}$)
$\rho$ : Density of the fluid (kg $m^{-3}$)

By using the set-up in Fig. 3-12 it was possible to describe both the static pressure inside the test section at different adapter positions and the time taken for the air to push the simulated pesticide out of the test section. In these trials, total air pressure for reclaiming was either 300 kPa or 500 kPa. Pressure measurements were carried out using either an empty and clean test section or a test section filled with simulated pesticide.

The pressure measurements were also supposed to highlight potential pressure losses caused by the narrow injection pipe and the large distance between air inlet and pesticide tank. This is particularly important with a view to wide boom DIS sprayers with long injection pipes. Frictional loss in a smooth circular pipe can be described through the following equation (SCHADE & KUNZ, 2007):

$$\frac{\Delta P}{\rho} = \lambda \frac{L}{D} \frac{v^2}{2} \tag{3-12}$$

where

$\Delta P$ : Pressure gradient (kg $m^{-1}$ $s^{-2}$)
$\rho$ : Density of the fluid (kg $m^{-3}$)
$D$ : Pipe Diameter (m)
$L$ : Pipe length (m)
$v$ : Average flow velocity (m $s^{-1}$)
$\lambda$ : Basic friction factor (dimensionless)

### 3.4.3 Effect of air inlet position and pre-cleaning time

In order to quantify how air inlet position and pre-cleaning time affects the amount of simulated pesticide reclaimed through pressured air and residue distribution along the test section a test bench as shown in Fig. 3-13 was set up. The 3 m long test section was made of six 500 mm long screwed together pipe sections (stainless steel, ID: 10 mm) including compression fittings. The test section, with an inner diameter of 10 mm, was attached to the air handling components so that air entered the test section either through one air inlet (Fig. 3-13a) or two air inlets (Fig. 3-13b). Pre-cleaning times were 10, 20 or 30 s each at 300, 400 or 500 kPa when only one air inlet was used. With two air inlets, pre-cleaning times were halved to 5, 10 or 15 s each at 300, 400 or 500 kPa. The order of the pipe sections was changed before each of the four replications. The amount of air used for pre-cleaning was derived from the pressure drop in the air tank as described in section 3.4.1. Residual in each of the six pipe sections was determined gravimetrically. The short T-junction, shown in Fig. 3-13b between pipe sections 3 and 4, was not included in the interpretation of the data because dismantling the test section after cleaning could lead to a disproportionately high amount of residues at the middle end of the T-junction.

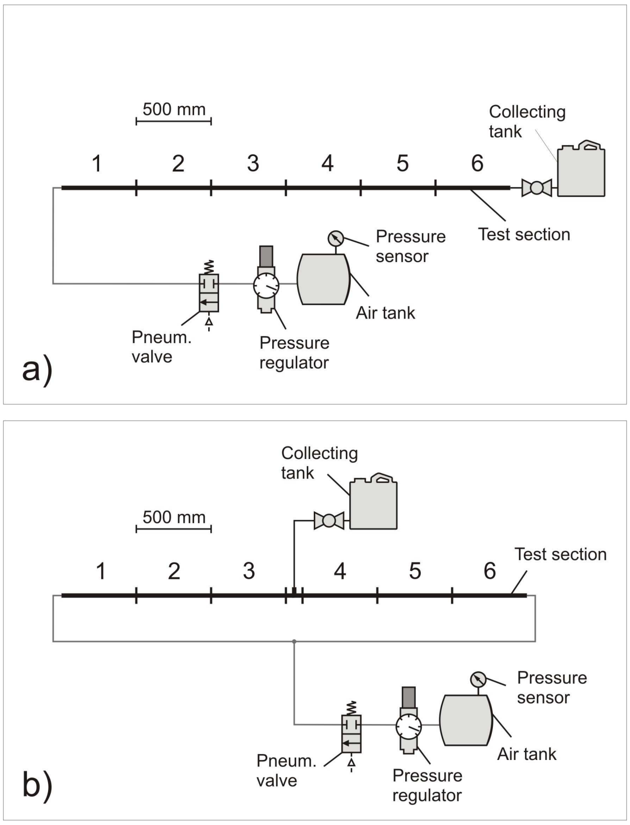


Fig. 3-13: Set-up for examining the distribution of residual along the test section after reclamation.

### 3.4.4 Effect of piping material

As described in section 3.1 the injection pipe on the test bench was a stainless steel pipe with smaller PTFE hoses which supplied the dosing valves with simulated pesticide. In order in to quantify the cleanability of these materials and to compare them with others a test bench as shown in Fig. 3-14 was set up.

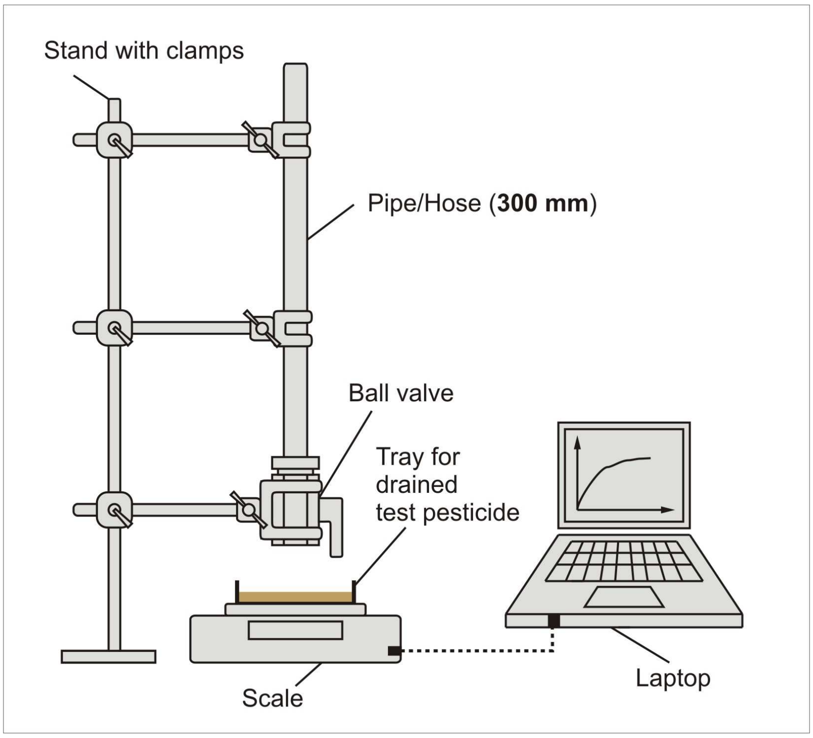


Fig. 3-14: Set-up for testing the cleanability of pipes made of different materials.

Pipes (300 mm long, ID: 10 mm) made of the following materials were tested with regards to their ability to be cleaned:

- Stainless steel as a common pipe material for field sprayers. It is broadly available and easy to machine
- Polyvinyl chloride (PVC), since some pesticide hoses are made of PVC
- Glass as a reference material since many applications in chemistry revert to glass
- Polytetrafluoroethylene (PTFE) as it is known for its non-stick properties and has a reputation of being an easy-to-clean material.

Each pipe was screwed into a closed ball valve and then filled with 20 g of simulated pesticide. The filled pipe was fixed to a stand and the ball valve was opened so that the simulated pesticide could run out. A flat tray was used to catch the liquid, while a scale (Sartorius 1518, Sartorius AG, Göttingen, Germany) connected to a laptop automatically weighed the liquid running out of the pipe at a sampling rate of 4 Hz. The LabVIEW software that was used for data acquisition was provided by Sartorius AG, and was specifically designed to control and read this type of scale.

The viscosity of the simulated pesticide, as determined by the cone and plate rheometer (see section 3.2) was 529.3 mPa s. This viscosity was higher than in most real pesticides. It was chosen because it was expected to highlight possible differences between the materials more clearly than lower viscosities.

In addition to the above-mentioned test, another small scale experiment was carried out to find out whether the differences occurring during the drain out test would still be visible after pre-cleaning with pressurized air. Therefore the two materials that showed the largest differences in the drain out experiment (stainless steel and PTFE) were subjected to another test. Pipes made of these materials (500 mm long, ID: 10 mm) with a ball tap at each end were filled to capacity with simulated pesticide and the ball taps were closed. Then the respective pipe was attached to the air handling components and a collecting tank as shown in Fig. 3-15.

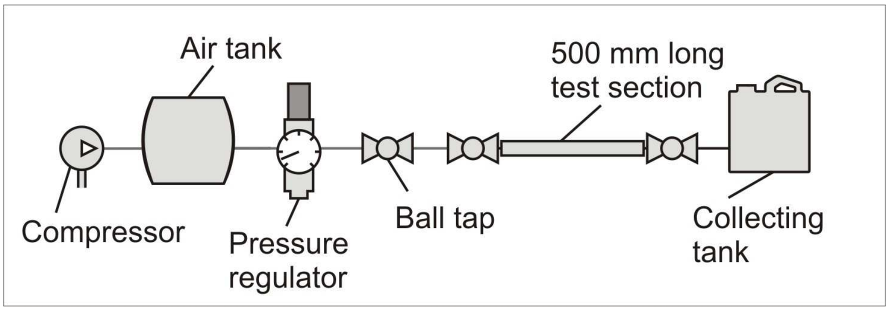


Fig. 3-15: Set-up for comparing a stainless steel pipe and a PTFE pipe with regards to their cleanability through pressurized air.

The ball taps at both ends of the test section were opened manually before the air tank was opened through another ball tap and kept open for five seconds at 50, 100, 150, 200, 300, 400, and 500 kPa respectively. After the air tank had been closed again the test section was dismantled and weighed on a scale (Sartorius 1518, Sartorius AG, Göttingen, Germany) in order to determine the residual of the simulated pesticide in the test section. At all pressures six replications were carried out to account for any inaccuracies due to the manual operation of the taps. The elapsed time was measured with a stopwatch.

### 3.4.5 Effect of viscosity

A set-up similar to the one depicted in Fig. 3-14 was carried out to assess a possible impact of the simulated pesticide's viscosity on the amount of residues remaining on inner pipe surfaces. Viscosities of the simulated pesticides were 58.9 mPa s, 529.3 mPa s and 1485.4 mPa s. The test pipes used here were the same as in section 3.4.4.

## 3.5 Rinsing of the hydraulic system

### 3.5.1 Effect of pre-cleaning time

The cleaning procedure was carried out as described in section 3.3. In order to ascertain the effect of pre-cleaning time on rinsing curve progression the test bench depicted in Fig. 3-1 was used. The test section had been pre-cleaned for either 10 s, 20 s or 30 s when rinsing started.

Average flow velocities and Reynolds Numbers were calculated according to (3-13) and (3-14) (LEWIS, 2008)

$$v = \frac{Q}{A} = \frac{4Q}{\pi D^2} \tag{3-13}$$

$$\mathrm{Re} = \frac{v \rho D}{\eta} \tag{3-14}$$

with

$Q$: Volumetric flow rate ($m^3$ $s^{-1}$)

$A$: Cross-section area of the pipe ($m^2$)

$D$: Pipe diameter (m)

$\pi$: Constant pi (ca. 3.14)

$\mathrm{Re}$: Reynold number (dimensionless)

$v$: Flow velocity (m $s^{-1}$)

$\eta$: Dynamic viscosity (kg $m^{-1}$ $s^{-1}$)

$\rho$: Density of the fluid (kg $m^{-3}$)

### 3.5.2 Effect of water inlet position

In order to ascertain the effect of different water inlet positions on the cleaning performance of the DIS the test bench that has already been described in section 3.1 was used and also modified. Fig. 3-16 illustrates the modified set-up.

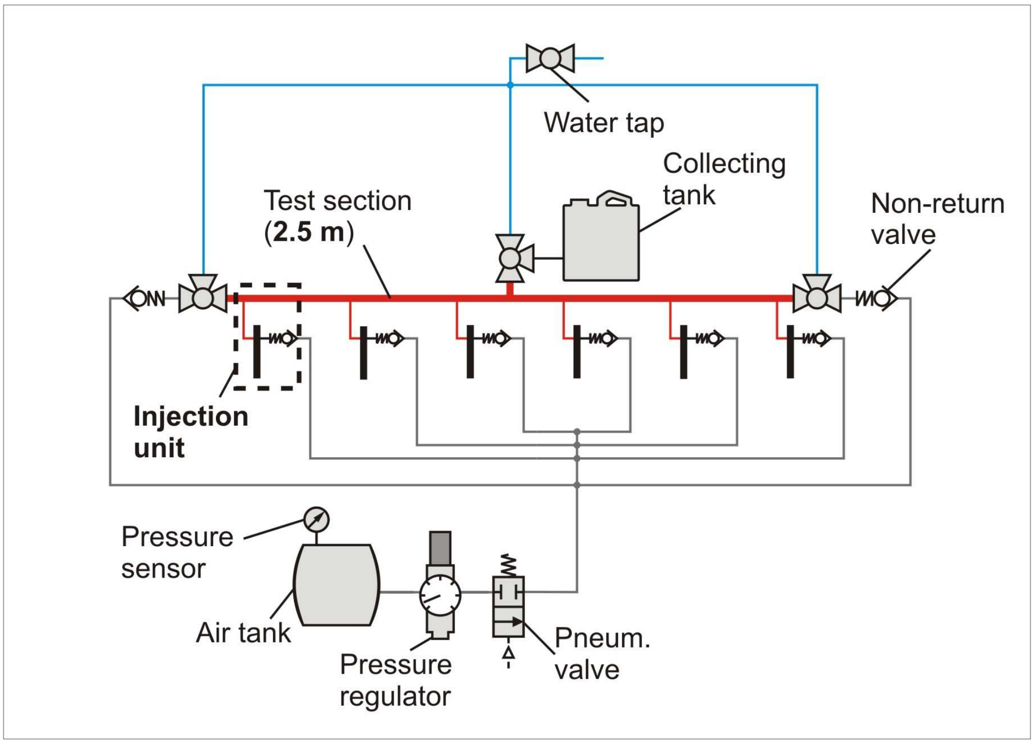


Fig. 3-16: Modified test bench for examining the effect of water inlet position on the cleaning result.

The modified assembly represents a boom section in the middle of a sprayer boom where air enters the injection pipe through two main air inlets (ID: 10 mm) located at the end of the boom and also through ancillary inlets (ID: 4 mm) at the injection units. The injection pipe (i. e. the test section) was shortened from 3 m to 2.5 m to keep dead legs as short as possible. Water inlets were placed at both ends and in the middle of the test section. The air handling components were the same as in section 3.1. Fig. 3-17 and Fig. 3-2 (see section 3.1) illustrate the flow direction of air and water as well as the nozzle designation by location. The amount of air was determined as described in section 3.4.1. Pre-cleaning times were either 10 s (one main air inlet) or 5 s (two main air inlets).

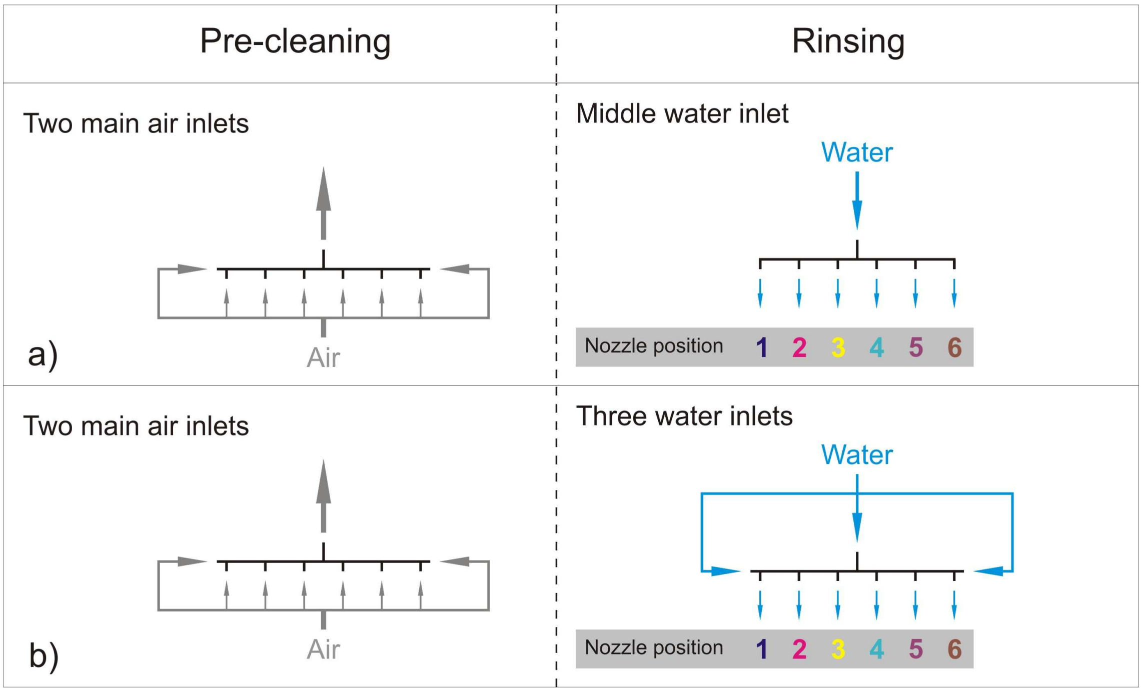


Fig. 3-17: Flow direction of air and water and nozzle designation by location on the test bench illustrated in Fig. 3-16. a) one middle water inlet, b) two end water inlets and one middle water inlet.

### 3.5.3 Effect of water pressure

With agricultural sprayers adjusting the water pressure is a common procedure to achieve a desired volumetric flow rate and flow velocity (compare section 3.5.1). This in turn could affect cleaning efficiency. In order to ascertain the impact of the rinsing water pressure on the cleaning performance of the investigated DIS cleaning regimes at different water pressures were conducted on the test bench shown in Fig. 3-1. Before rinsing started, the test section had been pre-cleaned for 20 s with pressurized air at 300 kPa. The rinsing water pressure was set to either 200 kPa, 300 kPa or 400 kPa and concentrations of simulated pesticide in the rinsing water were then measured using the conductivity measuring cells described in section 3.1.3. The time taken for the concentrations in the effluents of nozzles 1 through 6 to reach 0.25% was determined by filtering the data in an Excel 2003 spreadsheet. The rinsing water flow rate was determined gravimetrically using a Kern 752 scale (Kern und Sohn GmbH, Balingen-Frommern, Germany). The amount of water that had been consumed until then was calculated by multiplying the rinsing water flow rate by the time taken for the concentration to reach 0.25%. The reason for defining a concentration of 0.25% as a threshold was that the conductivity measuring cells were not reliable at concentrations much lower than that.

### 3.5.4 Effect of residence time

This experiment aimed at finding out whether increased residence time of the rising water in the test section led to time and water savings. The set-up used was the same as illustrated in Fig. 3-1. The test section was filled to capacity with simulated pesticide and then pre-cleaned with pressurized air for 20 s at 300 kPa. Subsequently the test section was filled with rinsing water to compare the following treatments:

1) The injection pipe was rinsed continuously.
2) The rinsing water was not rinsed out immediately, but instead remained in the injection pipe for 5 min.
3) Residence time of the rinsing water in the injection pipe was 30 min.

Concentrations of simulated pesticide in the rinsing water were measured using the conductivity measuring cells (see section 3.1.3). The rinsing curves derived from the data of all nozzle positions were compared with regards to initial concentration and shape. Sensor data were analysed to determine the time it took for the concentration of the simulated pesticide to reach 0.25%.

### 3.5.5 Effect of pulsed water-air flow

The test bench shown in Fig. 3-1 was used to examine the effect of pulsed water flow. The test section was pre-cleaned at 300 kPa for 30 s and the injection units were disconnected from the air supply. The air pressure was then set to 500 kPa and the water pressure to 400 kPa. Software developed in LabVIEW 8.6 for controlling the valves on the test bench was started with the water tap already open. The following treatments were carried out:

1) The air tank was alternately open for 1 s and closed for 1 s. The air/water pressure difference of 100 kPa led to air streaming through the inlet when the air tank was open whereas otherwise water entered the test section (“1-1 treatment”).
2) The air tank was alternately open for 10 s and closed for 1 s (“10-1 treatment”).
3) Continuous water flow without air injection.

The RRV®s were opened completely as soon as the air valve was released for the first time.

### *Amount of water*

Before the software for controlling the pulsed flow treatments was started the water tap of the rinsing water supply had to be opened manually. Since the RRV®s were leak-proof when water was used but not air tight there was already rinsing water in the test section before the actual pulsed flow treatments were started. This water was pushed out of the test section as the first air pulses moved through the injection line and attached injection units. As a result, the first air pulses pushed more water per time unit out of the nozzle than those which only entered the test section after the initial water core had already been pressed out.

Apart from that it was volitional that water entered the test section first since otherwise air could have pushed pure simulated pesticide through the attached injection units and conductivity measuring cells which would have contaminated the sensors and led to unusable signals from the sensors.

Since one aim of this experiment was to correlate the remaining concentration of the simulated pesticide in the rinsing water with the amount of water the water flow rate had to be determined circle-wise (one circle = one air pulse followed by one water pulse) for each of the pulsed treatments. Otherwise, the water flow rate of the pulsed flow treatments would have been underestimated, especially at the very beginning of each pulsed-flow treatment. However, the average water flow rate of those treatments was considered constant throughout the test section as soon as the initial water core had been pressed out of the test section and the air reached the nozzle most distant from the water inlet (nozzle 6). For the volume metering of the pulsed flow treatments the software was preset to allow only a defined number of circles before it stopped automatically. The amount of water that had flowed through each nozzle was determined gravimetrically.

### *Dynamics of the pulsed water-air flow*

In order to describe the dynamics of the pulsed water-air flow the pulsed treatments were applied to a clean test section, using clean tap water and air. Sensors measured 9 V when only air was streaming through the sensors and, depending on the sensor, voltages of between 3 and 6 V for tap water. The voltages from the conductivity sensors were converted to values between 0 (only tap water in the sensor) and 1 (only air in the sensor) using equation (3-15)

$$y_1 = (y_0 - U_W)(9 - U_W)^{-1} \qquad \text{(3-15)}$$

where $y_0$ was the voltage continuously measured by the respective sensor in V, $U_W$ the voltage this sensor measured for tap water in V, and $y_1$, the normalized value. Fig. 3-18 gives an example of the normalization of data from the conductivity sensor at nozzle 1 when the air tank was alternately open for 5 s and closed for 5 s.

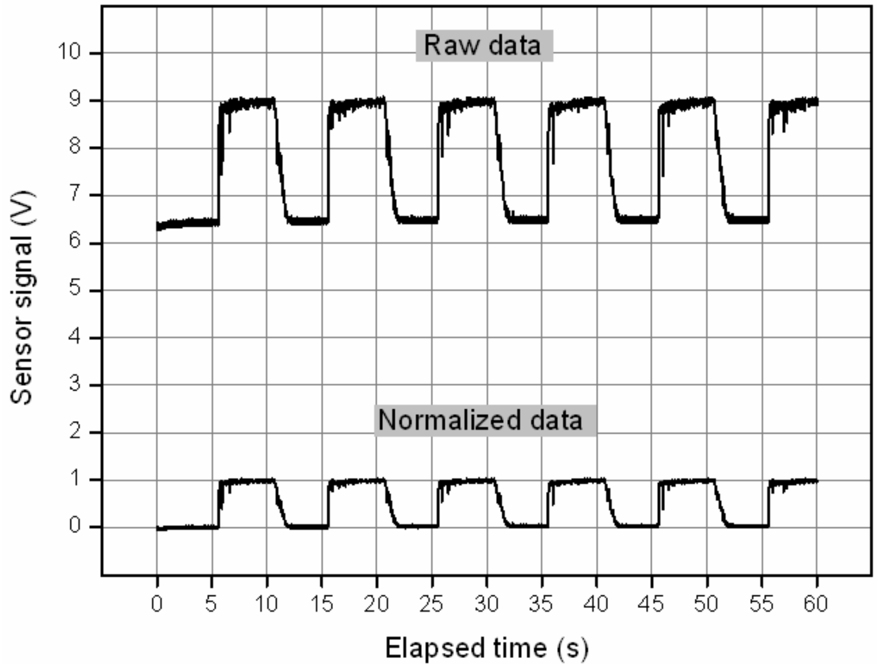


Fig. 3-18: Original voltage signal from the conductivity sensor at nozzle 1 during pulsed water-air flow and the normalized data derived from this signal using equation (3-15). The air tank was alternately open for 5 s and closed for 5 s.

***Cleaning effect***

The data from the aforementioned online measurements were used to calculate flow velocities, Reynolds Numbers and wall shear rates using (3-13), (3-14) (see section 3.5.1), and the following formulas mentioned by GRASSHOFF & REINEMANN (1993):

$$\tau = \frac{f \rho v^2}{8} \tag{3-16}$$

and

$$f = 0.0056 + \mathrm{Re}^{-0.32} \tag{3-17}$$

with

$\tau$ : shear stress at the wall (N $m^{-2}$)

$\rho$ : density of the fluid (kg $m^{-3}$)

$f$ : friction factor (dimensionless)

$v$ : average fluid velocity (m $s^{-1}$)

$\mathrm{Re}$ : Reynolds Number (dimensionless)

While rinsing the pre-cleaned system samples of ca. 20 ml were drawn from nozzle 6 at intervals of 5 s (1-1 treatment) and 11 s (10-1 treatment). With continuous rinsing the sampling interval was 5 s for the first 30 s and afterwards 30 s. The concentration of simulated pesticide in the rinsing water was measured by the hand-held conductivity meter. The water flow rate was derived from the known sampling times and aforementioned water vs. time calibration curves.

### 3.5.6 Effect of temperature

A 500 mm long pipe made of either stainless steel or PTFE was filled to capacity with simulated pesticide (viscosity: ca. 500 mPa s) and then attached horizontally to the test bench shown in Fig. 3-19.

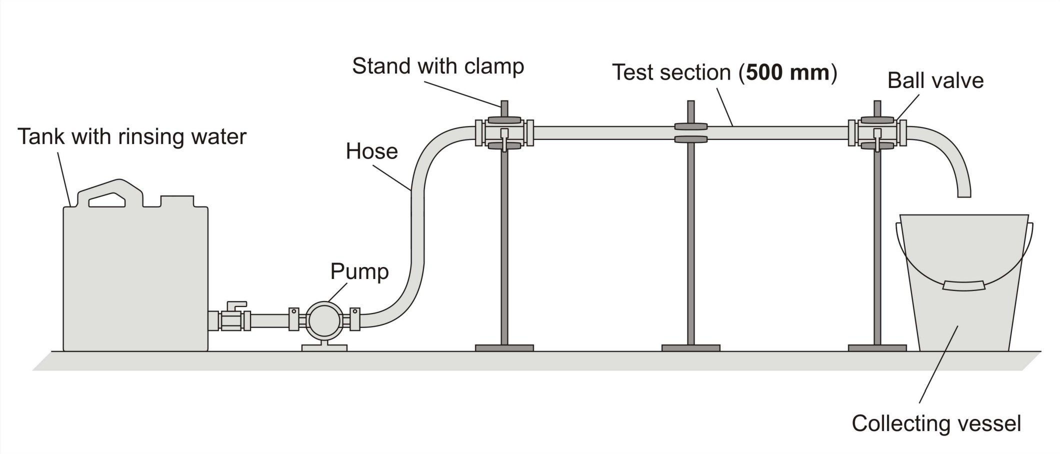


Fig. 3-19: Set-up for determining the effect of cleaning water temperature on the cleaning result.

The water tank contained rinsing water at either 4°C, 22°C or 55°C. In order to ascertain the effect of rinsing water temperature only, the test pipe was not pre-cleaned with air. Instead the rinsing water pushed the simulated pesticide out of the pipe into a collecting vessel once the pump was switched on. The flow rate of the rinsing water was ca. 1 l $min^{-1}$

which was within the range of possible rinsing flow rates in the injection pipe of a real DIS. After either 10, 20, 30, 60, or 90 s the pump was stopped and residual rinsing water was carefully drained out of the pipe before its inner surface was cleaned by pushing small pieces of absorptive paper through it. The amount of residual was then derived from the dried paper mass and the known dry matter content of the simulated pesticide.

## 3.6 Cleaning of an experimental wide boom DIS sprayer

Conclusive laboratory experiments were conducted on an experimental wide boom DIS sprayer. The sprayer was assembled at the Department of Agricultural Engineering in Bonn based on a commercial Ikarus A38 sprayer (Kverneland Group, Nieuw Vennep, Netherlands). Fig. 3-20 illustrates the experimental setup.

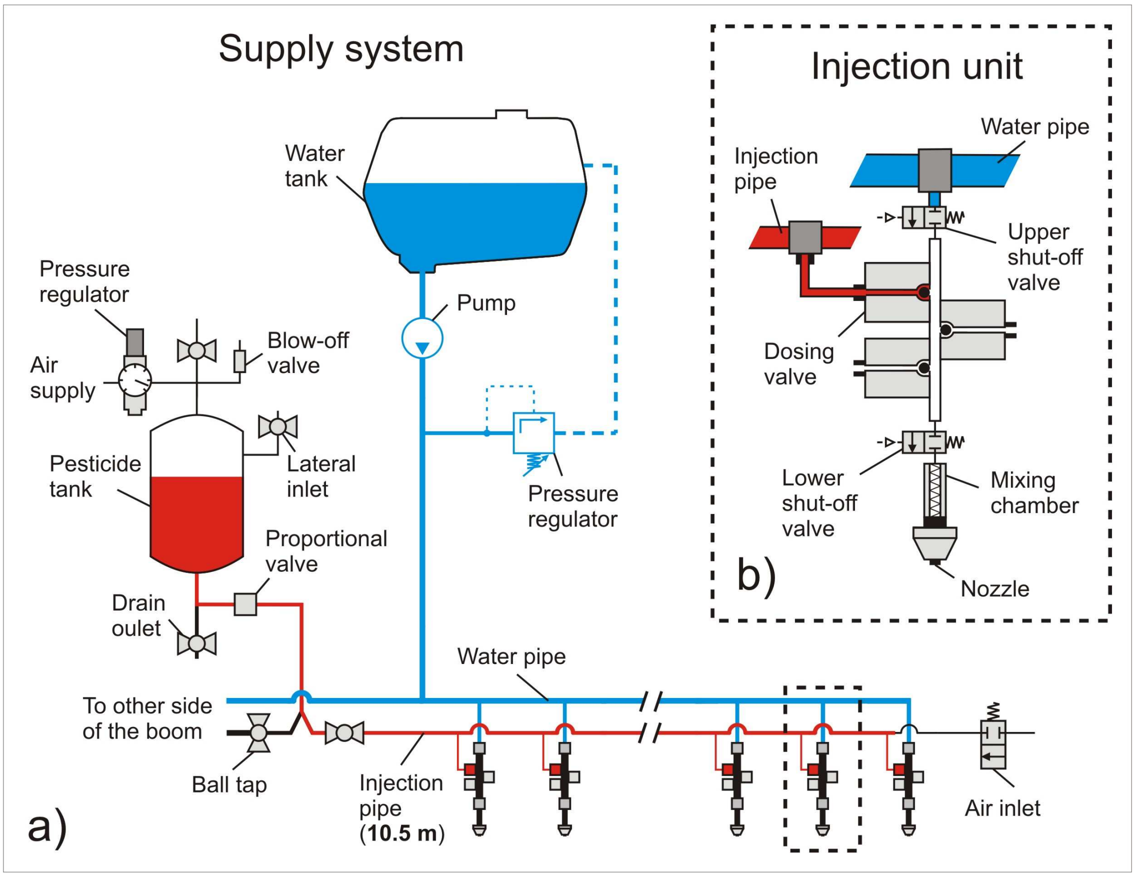


Fig. 3-20: a) Experimental setup for verifying the test bench results on the experimental DIS field sprayer and b) detail of one of the injection units.

As opposed to the test bench, the injection pipe of the DIS field sprayer was (for experimental reasons) a glass fibre coated Viton hose (Lézaud & Co. GmbH, Marpingen, Germany) (ID: 10 mm) that was attached to the dosing valves through stainless steel swaged sockets. This led to significantly shorter ancillary inlets, which is why there were no further air inlets at the injection units. What is more, the air inlet at the end of the sprayer boom (ID: 1/8“) was smaller than the one on the test bench (ID: 10 mm). Compared with the RRV®s on the test bench the DIS sprayer’s dosing valves had optimized valve seats and coils with regards to power consumption and dosing behaviour.

For practical reasons the tests were carried out on one side of the 21 m wide sprayer boom. Thus the test section was 10.5 m long including 21 injection units. A pressure tank (capacity: 30 l) attached to the sprayer lift supplied the injection pipe and the RRV®s with simulated pesticide. The pressure tank also caught the simulated pesticide during the push-back. It was equipped with a centre outlet at the bottom, a lateral inlet at the top and a pressure regulator including blow-off valve (Fig. 3-20). The outlet at the bottom led to a proportional valve which was controlled via software developed in LabVIEW. The pipe was then divided into two branches each of which supplied one side of the sprayer boom with simulated pesticide. Ball taps, which were mounted between the injection pipe and the pressure tank, allowed using one side of the injection pipe while excluding the other side from the experiment.

To begin with, 2 kg of simulated pesticide (10% PVP, ca. 250 mPa s, see section 3.2) were filled in the pressure tank through the lateral inlet at the top. Then the pressure in the pressure tank was increased to 300 kPa and the proportional valve at the bottom of the pressure tank was opened to fill the injection line. The filling status of the injection pipe was monitored through a short transparent hose mounted between the end of the injection pipe and the air inlet. Once the injection line was filled the proportional valve was closed again and the remaining simulated pesticide in the tank was drained and subsequently weighed. Then the simulated pesticide was pushed back into the depressurized pressure tank for 30 s at 800 kPa. The reclaimed simulated pesticide was drained and its weight used to calculate the amount of simulated pesticide that had remained in the injection pipe after the push-back.

Once the recovery of the simulated pesticide had been completed, one of the following two cleaning methods was applied to the DIS field sprayer: 1) Continuous rinsing method or 2) Homogenization method.

***1) Continuous rinsing method***

30 l of water were manually filled in the pressure tank and the air pressure was set to 800 kPa. Then the rinsing water was pressed through the injection pipe with the proportional valve, the RRV®s and the lower shut-off valves of the injections units completely open. Samples of ca. 20 ml were taken every 10 s for ca. 4 min from the effluent of the nozzle most distant from the pressure tank. The concentration of the simulated pesticide in the rinsing water was determined with the hand-held conductivity meter (see section 3.1.3).

***2) Homogenization method***

In order to homogenize the residual of the simulated pesticide in the injection pipe water from the sprayer's main tank was directed into the pressure tank after pre-cleaning had been completed. This was done by keeping the upper shut-off valves, the RRV®s and the proportional valve open while the lower shut-off valves remained closed and the main pump was running. The pressure was adjusted with the sprayer's regulation system to 240 kPa (256 l $ha^{-1}$). After 2 min all valves were closed and the pump was stopped. The remaining water in the injection pipe was subsequently pressed into the depressurized pesticide tank for a period of 30 s for thorough homogenization. Just as with continuous rinsing the water that was then in the pressure tank (ca. 4 l) was pressed out through the nozzles at 800 kPa. Once air started coming out of the nozzles the proportional valve was closed and another 10 l of fresh water were manually filled in the pesticide tank. This volume was subsequently continuously pressed out of the nozzles. Samples of the rising water were taken and analysed as described with the continuous rinsing method.

# 4 Results and discussion

Some of the results presented herein were published by DOERPMUND et al. (2011).

## 4.1 Simulated pesticide

***Density***

Fig. 4-1 illustrates the densities of aqueous PVP solutions at different concentrations that were used as simulated pesticide.

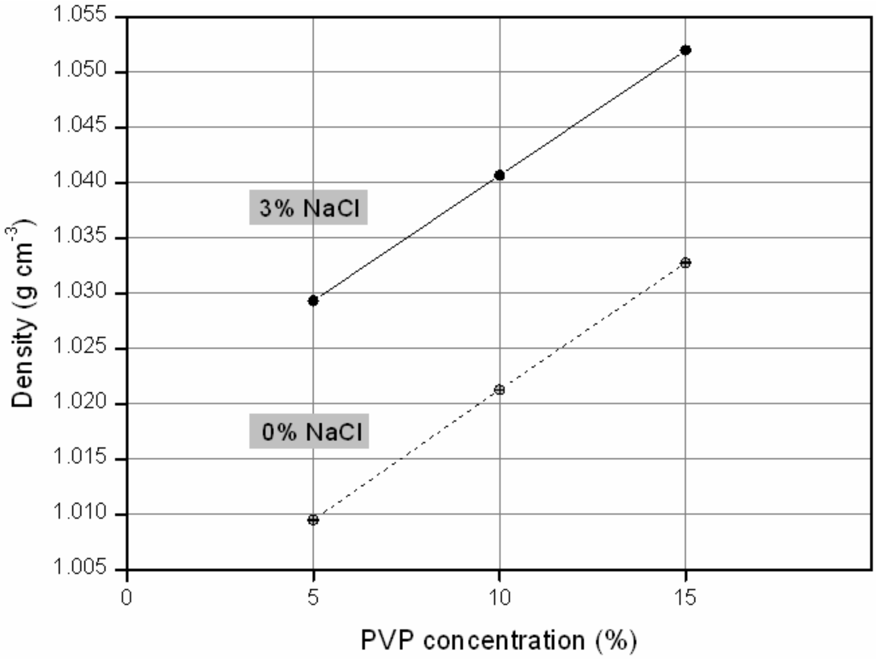


Fig. 4-1: Densities of aqueous PVP solutions at different PVP concentrations. Solutions were prepared either with 3% NaCl (n = 1) or with 0% NaCl (n = 3). Error bars indicating standard deviations were smaller than symbols for all data points.

Fig. 4-1 shows that the densities increased with increasing concentration by ca. 0.2% for each percent of added PVP and that the relationship between concentration and density was linear within the NaCl and PVP concentrations considered. The seemingly steep rise in density with concentration shown in Fig. 4-1 is merely due to the fact that the y-axis does not start at 0.000 g $cm^{-3}$ but at 1.005 g $cm^{-3}$. It is fair to say that the addition of PVP powder to the solvent (tap water) did not change the solutions' density much. Even at a concentration of 15% densities did not go over 1.035 g $cm^{-3}$, a value which is only 3.7% higher than the density of tap water which was assumed to be 0.998 g $cm^{-3}$ (LIDE, 2003).

Measurements were also in agreement with densities of aqueous PVP K90 solutions reported by MONCALVO & FRIEDEL (2009) who measured densities of 1.007 g cm$^{-3}$, 1.021 g cm$^{-3}$ and 1.0297 g cm$^{-3}$ for PVP solutions of 4, 12 and 16.5%, respectively.

With the PVP solutions containing 3% NaCl the shape of the line did not change. However, the addition of NaCl increased density at all PVP concentrations by ca. 0.02 g cm$^{-3}$, leading to the density line being shifted upwards. According to information from the manufacturer of the PVP powder used (BASF, 2009) the density of a water-based 10% PVP Luvitec® K90 solution (without NaCl) is 1.04 g cm$^{-3}$ which is slightly denser than what was measured in this study (1.02 g cm$^{-3}$). Possible reasons for this are inaccuracies in preparing the PVP solution due to the PVP powder being hygroscopic. Therefore, it may already have contained some water before it was dissolved.

The fact that the addition of NaCl increased density is in accordance with ANTUNIASSI & MILLER (1998) who also stated that the addition of NaCl increased the density of their water-based test formulation. In their study, however, the authors added 5.85% of NaCl, which is almost twice as much as in this study. Despite this, the solution’s density increased by 0.0244 g cm$^{-3}$, which is about as much as in Fig. 4-1 despite the higher NaCl concentration. These differences may be a result of the composition of the test liquid used by ANTUNIASSI & MILLER (1998) being different from what was used in this study as it included xanthan and methyl cellulose instead of PVP-powder.

***Dynamic viscosity***

Fig. 4-2 exemplarily shows the measured shear stress at different shear rates of simulated pesticide at three different PVP concentrations: 5, 10, and 15%. For these measurements no NaCl had been added to the test solutions.

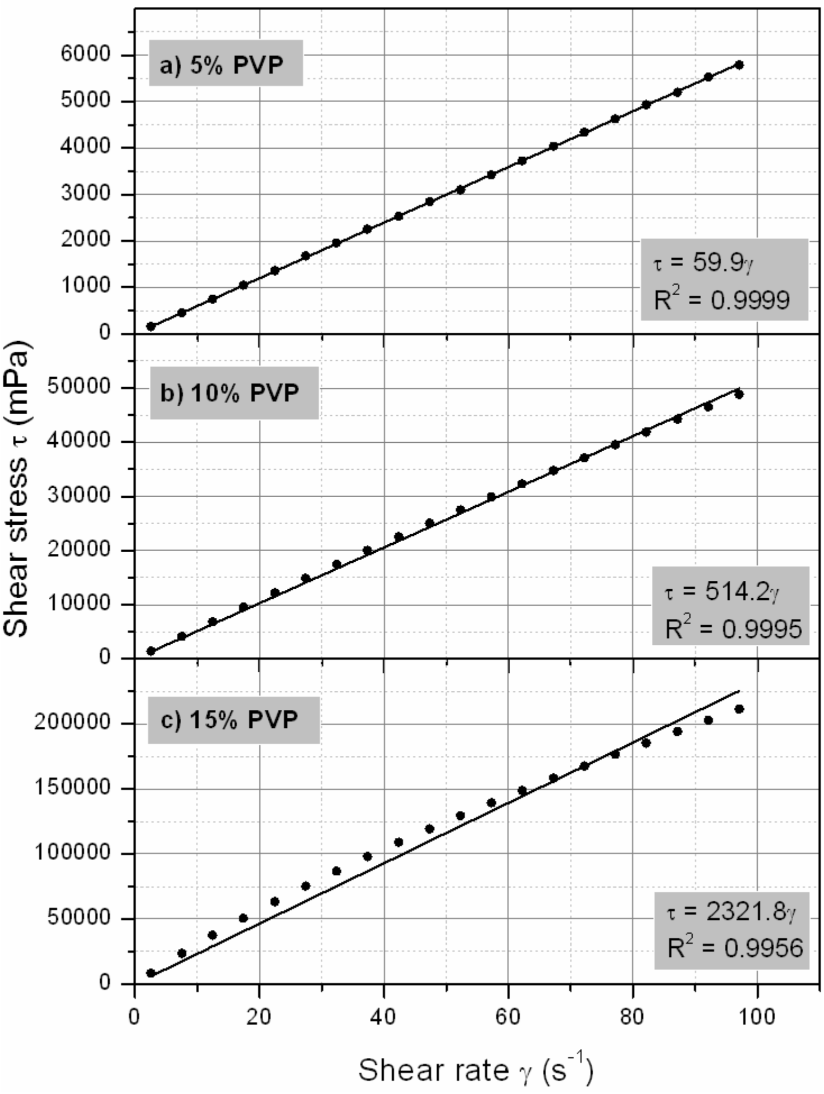


Fig. 4-2: Shear stress of PVP solutions at different shear rates and PVP concentrations of 5, 10, and 15% including trend lines and corresponding coefficients of determination (R²). Temperature: 25°C.

As illustrated in Fig. 4-2 the measured shear stress vs. shear rate curves were lines through the origin for the given range of shear rates. The coefficients of determination (R²) were very close to 1 for all PVP concentrations. This means that the simulated pesticide had almost Newtonian behavior at the given concentration and within the considered range of shear rates. The slope of each trend line is therefore equal to the solution's dynamic viscosity (see section 3.2). In the above example the dynamic viscosities were

59.9, 514.2, and 2321.8 mPa s at 5, 10 and 15% PVP respectively (Fig. 4-2). However, it can also be seen from Fig. 4-2 that the R² values slightly decreased as the PVP concentration increased. Fig. 4-2c (and to a lesser extend Fig. 4-2b) illustrate that solutions of 15% (and 10%) showed slight shear-thinning properties since an increase in shear rate led to a disproportionately smaller increase in shear stress. This is in accordance with MONCALVO & FRIEDEL (2009) who examined dynamic viscosities of three aqueous solutions of PVP K90 (at PVP concentrations of 4, 12, and 16.5%) at shear rates from zero to above 1000 $s^{-1}$. The authors reported that shear-thinning behavior was more pronounced with solutions containing higher percentages of PVP. WANG et al. (2002) who measured the viscosities of 1% PVP solutions in different solvents observed constant viscosities over shear rates from 1 - 100 $s^{-1}$ when water was the solvent. The authors stated that this is typical for polymer solutions without strong intermolecular interactions among the polymer chains. Viscosity measurements with 11% PVP K90 solutions conducted by HOOD et al (2003) showed nearly Newtonian behavior at shear rates of between 0.1 and 10 $s^{-1}$ and shear thinning at higher shear rates. The authors stated that this shear thinning (pseudo plastic) behavior is an indication of the structure within the fluid collapsing under flow (HOOD et al, 2003). According to GEBARDT et al (1984) there are both pesticides which behave as Newtonian fluids and pesticides which behave as non-Newtonian fluids.

With a view to DIS, the part of the cleaning process that could affect the fluid’s viscosity through high shear rates is the push-back of the unused chemical into the pesticide tank through pressurized air. High shear rates could occur during the metering process as well, for instance if a pump (instead of a pressure tank) was used to deliver the pesticide to the injection units. In order to limit costs the same simulated pesticide was reused in experiments where no water was involved (e. g. the push-back). Since all results were repeatable it was assumed that shear thinning caused by shear stress during the experiment was reversible. This would be in agreement with KRASNOU et al. (2008) who, in discussing rheological properties of PVP solutions also assumed that the processes caused by shear stress are reversible.

Fig. 4-3 illustrates the viscosities of aqueous PVP solutions at concentrations of 5, 10, and 15% with and without addition of 3% NaCl as derived from shear stress vs. shear rate curves at 25°C.

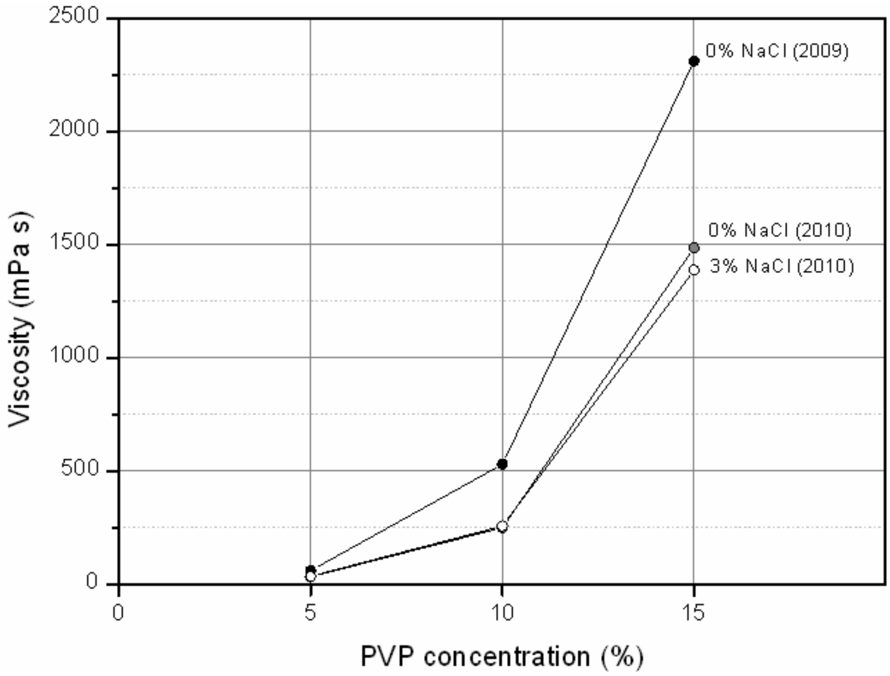


Fig. 4-3: Viscosities of aqueous PVP solutions at different PVP concentrations. Measurements were made using the new PVP powder in 2009 (n = 3) and PVP powder after one-year storage in 2010. In the latter case solutions where prepared adding 3% NaCl (n = 1) or without NaCl (n = 1).

Preparing solutions with powder from a sealed original packaging led to viscosities of ca. 50, 500 and 2300 mPa s at PVP concentrations of 5, 10 and 15% respectively ("0% NaCl (2009)" in Fig. 4-3) which was in accordance with the manufacturer's data (BASF, 2007). However, powder from an opened packaging that had been stored in a sealed container for up to one year resulted in significantly lower viscosities, probably due to the powder's hygroscopy ("0% NaCl (2010)" in Fig. 4-3). Viscosity measurements carried out later on indicated no further decrease in viscosity within the period of this study.

Fig. 4-3 also illustrates that in contrast to ANTUNIASSI & MILLER (1998) the addition of NaCl had little impact on the solutions' viscosity. Although the graphs of the year 2010 indicate a lower viscosity at 15% PVP, this could not be confirmed for the other concentrations where the viscosity of the non-salty solutions could as well be slightly less viscous (249.4 mPa s) than the salty solution (256.7 mPa s). This, however, is hardly recognizable from the graphs in Fig. 4-3.

Fig. 4-4 presents the result of a viscosity vs. temperature measurement of a 10% PVP solution that was prepared in 2009.

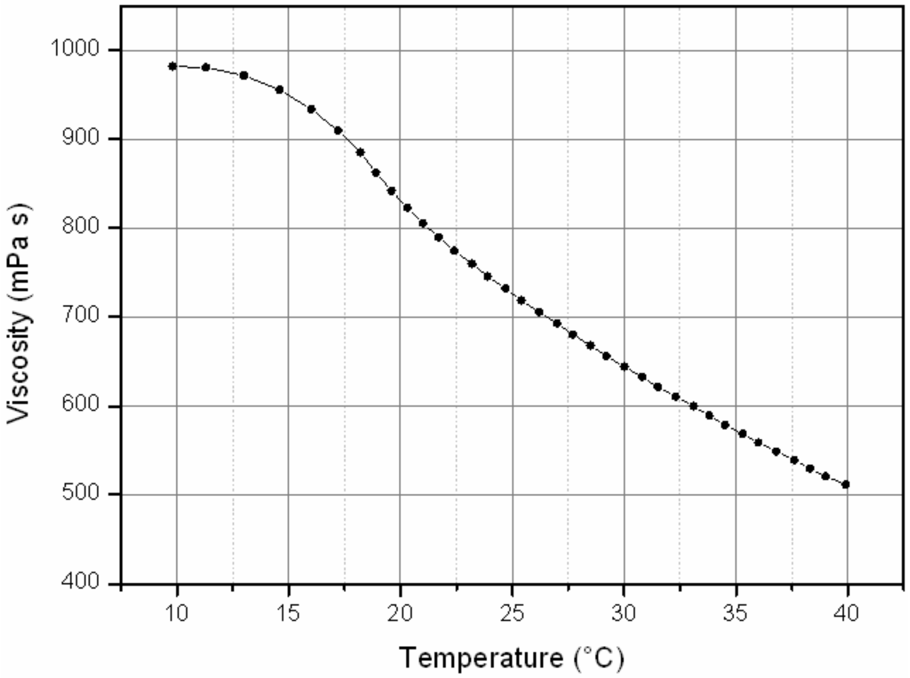


Fig. 4-4: Viscosity of an aqueous 10% PVP solution at different temperatures. Shear rate: 50 $s^{-1}$; heating rate: 3°C $min^{-1}$. Year of preparation: 2009.

There was a significant change in the solution's viscosity with temperature. As the temperature increased from 10°C to 40°C the viscosity was reduced by approximately a half which equals (on average) 1.7% for each degree Celsius. It is important to note that calculated viscosities at 25°C were higher than in Fig. 4-3 ("0% NaCl 2009"). This was because internal formulas of the software used for shear-stress calculation had changed as a result of the different geometry that was applied in this part of the experiment. LEWIS (2008) mentioned that the viscosity of fluids usually decreases with increasing temperature between 2% and 10% for each degree Celsius. MONCALVO & FRIEDEL (2009) measured viscosity vs. temperature curves which indicated that viscosity decreased (on average) by 2.5% for each degree Celsius increase in temperature which is well within the range mentioned by LEWIS (2008). The sensitivity of the simulated pesticide to temperature changes was unlikely to affect the results in this study as all experiments were carried out under laboratory conditions at ambient temperatures of between 20 - 25°C.

### *Surface tension*

Fig. 4-5 illustrates the surface tensions of aqueous PVP solutions at concentrations of 5, 10, and 15% with and without addition of 3% NaCl. Measurements were made using the solutions of 2010 (compare Fig. 4-3).

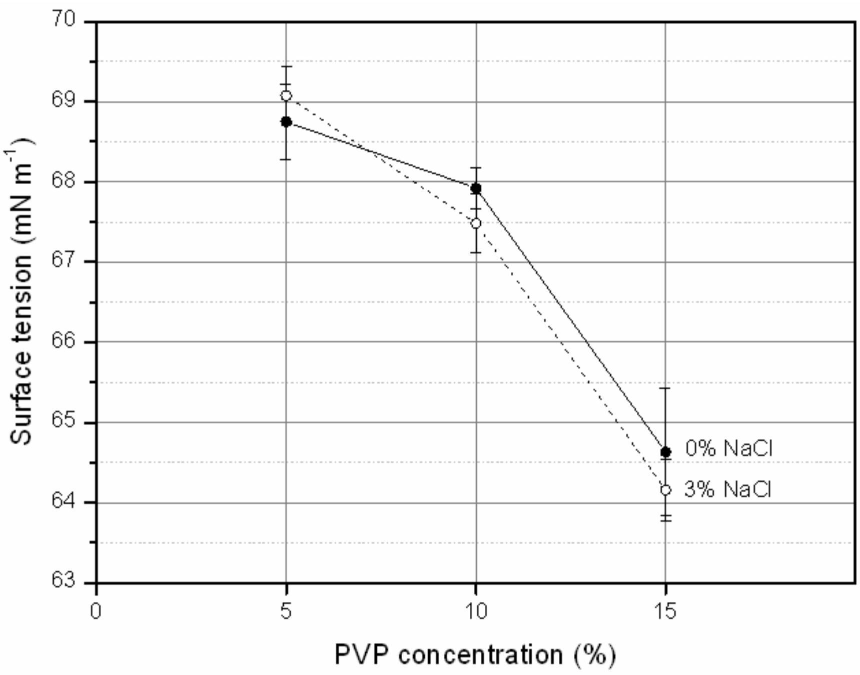


Fig. 4-5: Surface tension of aqueous PVP solutions prepared in 2010 at ambient temperature (24°C). Error bars indicate standard deviations (n = 10).

Surface tensions of the aqueous PVP solutions were lower than the surface tension of water (72.0 mN m$^{-1}$) and decreased with increasing PVP concentration. They deviated from the surface tension of water within 3 mN m$^{-1}$ (5% PVP), 4 mN m$^{-1}$ (10% PVP), and 7.5 mN m$^{-1}$ (15% PVP). The addition of NaCl did not measurably affect the solutions' surface tensions. Surface tensions of aqueous PVP solutions measured by MONCALVO & FRIEDEL (2009) were also lower than the surface tension of water. However, unlike in this study the deviation from the surface tension of water was only 3 mN m$^{-1}$ or less (MONCALVO & FRIEDEL, 2009). According to the safety data sheets of common herbicides for cereals the surface tensions of these products are generally well below the values shown in Fig. 4-5. They usually range from 25 to 40 mN m$^{-1}$. It can therefore be concluded that the wetting of surfaces would have been more pronounced if a real pesticide had been used. Having said that, not all manufacturers include information on surface tension in their safety data sheets and even if they do comparability is often limited since temperatures and dilutions of the pesticides tested are not consistent among safety data sheets.

***Diffusion of the tracer***

Fig. 4-6 illustrates changes in concentration (according to conductivity measurements, Fig. 4-6a) and changes in viscosity (rheometer measurements, Fig. 4-6b) caused by diffusion of the simulated pesticide into an overlying layer of distilled water.

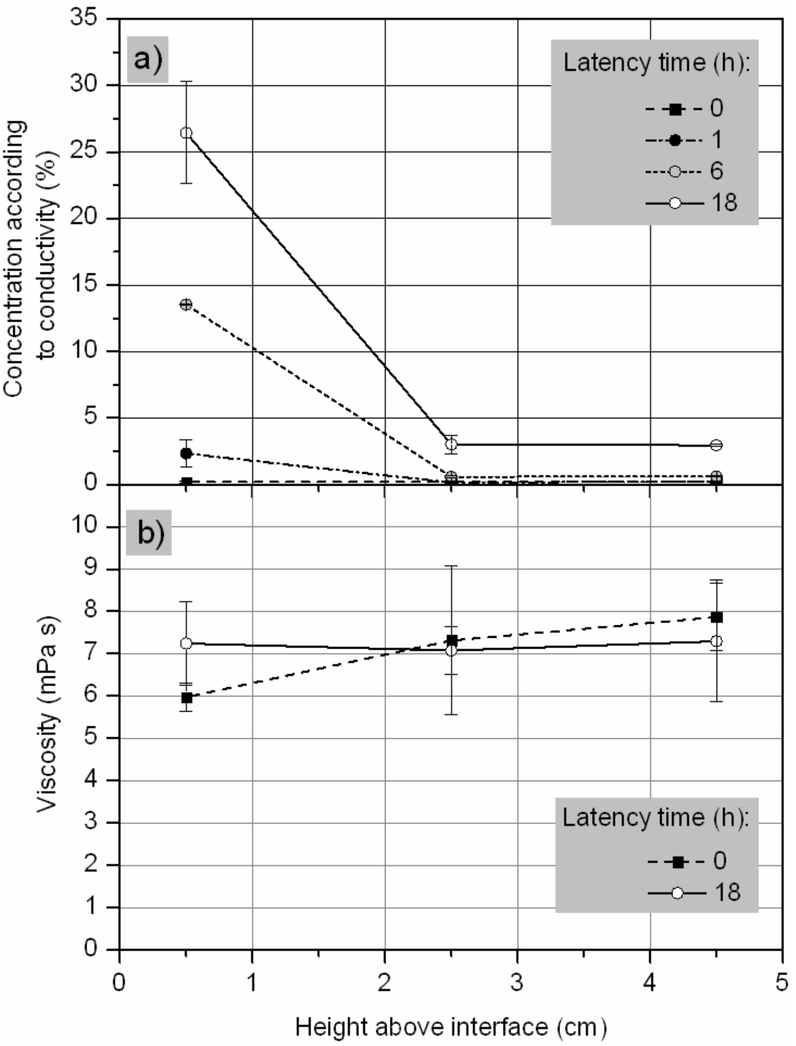


Fig. 4-6: a) Changes in concentration (according to conductivity measurements) and b) changes in viscosity (rheometer measurements) of samples taken 0.5, 2.5, and 4.5 cm above the interface between simulated pesticide and distilled water. Temperature: 20°C. Error bars indicate standard deviations (n = 3).

The graphs depicted in Fig. 4-6a show that a concentration gradient along the first centimetres above the interface formed over time with the concentrations being high close to the interface and decreasing with increasing distance from the interface. It became apparent that within the first hour of the experiment conductivity measurements indicated an increase in concentration 0 cm above the interface to 2.3% of the pure simulated pesticide. After 6 h and 18 h the concentration at this height was 13.5% and 26.5%

respectively. However, at 2.5 cm and 4.5 cm there was an increase to only 0.6% after 6 h and to 3% after 18 h.

Fig. 4-6b illustrates that the variation in concentration at different heights as measured by the hand-held conductivity meter was not reflected by the viscosities of these samples as they did not change significantly within 18 h. According to data shown earlier (Fig. 4-3) the viscosities of ca. 7 mPa s in Fig. 4-6b correspond to a PVP concentration in the water of ca. 0.7% which is significantly lower than the concentrations derived from the conductivity measurements. Therefore it was concluded that the increase in concentration shown in Fig. 4-6b was a result of the NaCl diffusing out of the simulated pesticide and into the overlaying water layer whereas there was obviously no significant diffusion of PVP. Consequently there could theoretically be the risk of misinterpreting results from the conductivity measurements if, during rinsing, the tracer diffuses into the rinsing water while the sticky PVP solution keeps on sticking to inner pipe surfaces. However, as the above-mentioned results have shown, NaCl diffusion through the interface was only marginal within the very first seconds or minutes of rinsing. According to the Stokes-Einstein equation, the diffusion coefficient depends on the temperature, viscosity of the solvent and particle size (ATKINS & DE PAULA, 2006, TANTISHAIYAKUL et al., 1999). Data from WEAST (1977) showed that the diffusion coefficient of carbohydrates decreased with increasing relative molecule mass. The number-average molecular weight of the PVP K90 powder used in this study was, according to its manufacturer, 300 000 - 400 000 g mol$^{-1}$ (BASF, 2007).This is much more than the molecular weight of the tracer NaCl (58.44 g mol$^{-1}$) and could therefore be a reason why the PVP diffusion observed in this study was so much lower than the diffusion of the tracer NaCl.

Given that rinsing times in this study generally did not exceed ten minutes it was assumed that concentrations measured by the conductivity measuring cells or the hand held conductivity meter truly reflected the concentration of the simulated pesticide in the rinsing water and were not significantly biased by diffusion of the tracer into the rinsing water.

## 4.2 Reclaiming the simulated pesticide (pre-cleaning)

### 4.2.1 Effect of air pressure

Fig. 4-7 depicts the static pressure measured in a 3 m long test section at six sensor positions spaced 500 mm apart as a function of time. The test section was either empty (Fig. 4-7a, and c) or filled with simulated pesticide (Fig. 4-7b, and c) when the measurement started and the air valve for the push-back was released. Air then entered the test section through an air inlet at the end of the test section.

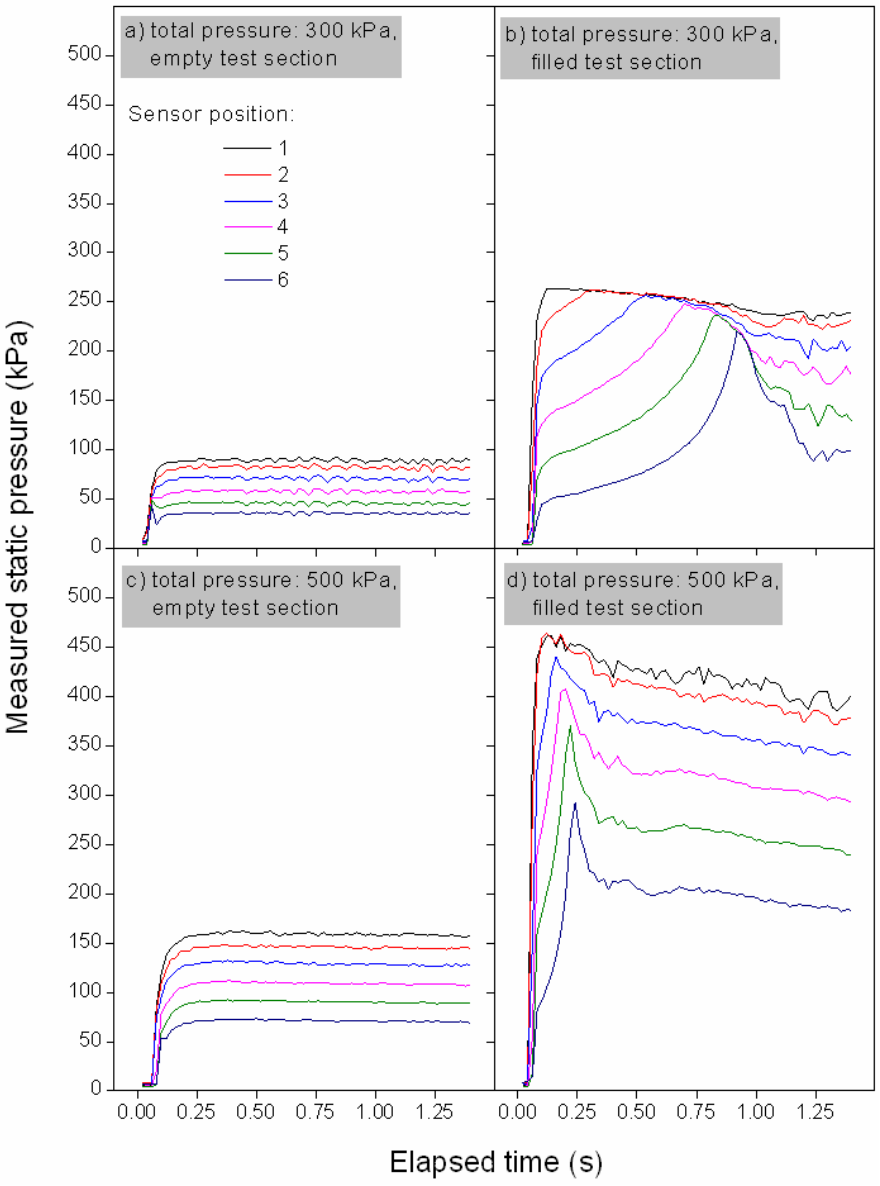


Fig. 4-7: Static pressure in a 3 m long test section at six sensor positions spaced 500 mm apart as a function of time during push-back at 300 kPa (a and b) or 500 kPa (c and d). The test section was either empty (a and c) or filled (b and d) when the push-back started.

The pressure curves in Fig. 4-7 clearly illustrate the pressure loss that occurred between the sensor positions while the air was streaming through the empty or filled test section. In all cases sensor position 1, the closest sensor position to the air inlet, had the highest pressure while the pressure at sensor position 6 (sensor position most distant from the air inlet) was significantly lower (less then 50%). As expected, the pressures measured in the empty test sections (Fig. 4-7a, and c) were rather low since the sensors where installed to measure the static pressure, not the total pressure. Here the air could simply take the path of least resistance and flow through the injection pipe towards the collecting tank. The flow velocity of the air was therefore comparatively high, leading to a high dynamic pressure (which could not be measured) and consequently a low static pressure. The pressure drop between sensor positions in Fig. 4-7a and c was almost constant but increased with increasing total pressure (ca. 10 kPa at 300 kPa total pressure, and ca. 20 kPa at 500 kPa total pressure), as a result of higher flow velocities.

Fig. 4-7b and d illustrate the initial dynamics of the push-back. The rise of each pressure curve can be seen as a result of the acceleration of the simulated pesticide by the expanding pressurized air. Upon initial release of the air valve there was an immediate increase in pressure at sensor position 1 whereas it took longer (but in all cases still less than a second) for the pressure to increase at the sensor positions more distant from the air inlet. This was probably due to frictional losses which the pressurized air had to overcome in order to accelerate the liquid and press it out of the test section. With each of the pressure curves in Fig. 4-7b and d the sharp rise is followed by a rapid decline. This decline stopped almost simultaneously at sensor positions 3 - 6 after 1.25 s for 300 kPa and after 0.30 s for 500 kPa. This was the instant where the core of the simulated pesticide had been pressed into the collecting tank so that the pipe’s cross section had become free of simulated pesticide. As a result of this, the flow velocity of the air increased which consequently led to lower static pressure at the sensors.

At 300 kPa it took ca. 1.25 s for the air to push the core out of the test section while air at 500 kPa reached the collecting tank after only 0.35 s. This corresponds to average flow velocities during the push-back of 2.4 m $s^{-1}$ (300 kPa) and 8.6 m $s^{-1}$ (500 kPa). After the core of the simulated pesticide had been pushed out there was obviously still a significant amount of residual sticking to the pipe’s inner surfaces reducing its cross section compared with an empty test section. The latter can be derived from the fact that in Fig. 4-7a and c (unused and empty pipe) the static pressure at the different sensor positions was significantly lower than in Fig. 4-7b and d, even after the pipe was “empty” with the air streaming into the collecting tank. WELCHNER (1993) reported that air that had pushed a viscous product out of horizontal pipes left a “channel” above the centre of the pipe’s cross section due to uplift of the air. At lower flow velocities (0 - 1 m $s^{-1}$) this channel was smaller, or rather, more residual product was in the pipe than at higher flow velocities (1 - 2.5 m $s^{-1}$). WELCHNER (1993) added that with vertical (instead of horizontal) pipes both high and low flow velocities led to equally low amounts of residual product in the pipe, probably because the air concentrically ousted the product. What is more, at low flow velocities (0 - 0.5 m $s^{-1}$) significantly less residual was found in vertical pipes compared with horizontal pipes. With the DIS, however, a vertical alignment of pipes would barely have led to less residual simulated pesticide in the test section since the flow rates of 2.4 - 8.6 m $s^{-1}$ applied during the push-back were considerably higher than the low flow rates applied by WELCHNER (1993) of only 0 - 0.5 m $s^{-1}$. In the literature there are so far only a few studies that the results in Fig. 4-7 could be compared with. WALENTA & KESSLER (1990a) and WALENTA & KESSLER (1990b) examined the behaviour of highly viscous liquids which were pushed out of a pipe by a rinsing fluid either more or less viscous than the product that was being reclaimed. The authors used a conductivity measuring cell to determine how the rinsing medium gradually replaced the product. This approach, although more accurate in describing the system in terms of cleanness, was not suitable in this study. The conductivity measuring cells available (see section 3.1.3) were not able to measure concentrations in this experiment since the cleaning medium for pre-cleaning was pressurized air. They were, however, suitable for measuring the presence or absence of a liquid which is why they were applied to ascertain the dynamics of pulsed water-air flow (see section 4.3.5).

### 4.2.2 Effect of air inlet position and pre-cleaning time

Fig. 4-8 and Fig. 4-9 illustrate the amount of residual simulated pesticide in pipe sections 1 through 6 after the air valve had been open for a defined period of time (i. e. pre-cleaning time) at a) 300 kPa, b) 400 kPa or c) 500 kPa respectively. The test bench was equipped with either one air inlet at the end of the 3 m long test section (Fig. 4-8) or with two air inlets, one at each end of the test section (Fig. 4-9).

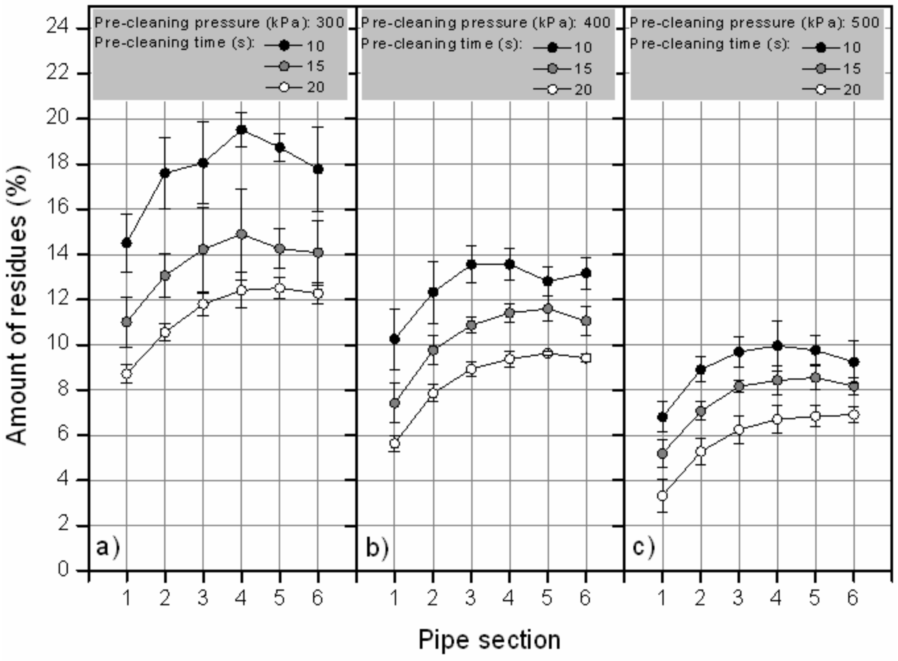


Fig. 4-8: Variation in residual simulated pesticide in the test section after the air valve had been open for 10, 15 or 20 s at a) 300 kPa, b) 400 kPa, and c) 500 kPa. The air inlet was placed at the end of the 3 m long test section. Error bars indicate standard deviations (n = 4).

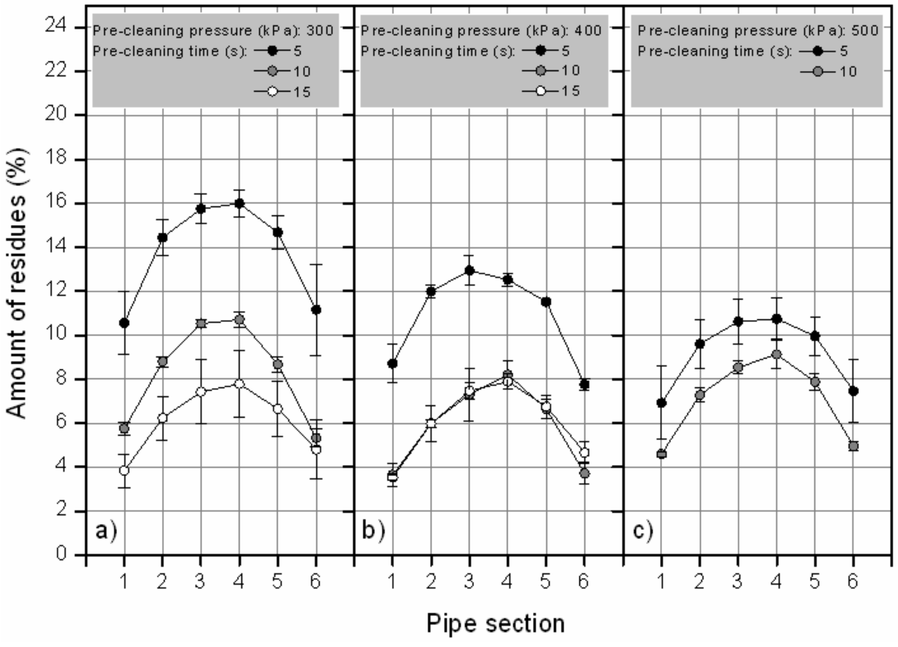


Fig. 4-9: Variation in residual simulated pesticide in the test section after the air valve had been open for 5, 10 or 15 s at a) 300 kPa, b) 400 kPa and c) 500 kPa. An air inlet was placed at each end of the 3 m long test section. Error bars indicate standard deviations (n = 4).

Fig. 4-8a shows that after pre-cleaning at 300 kPa the amount of residual in a pipe section could be up to 20% of the initial total mass. However, at pressures higher than that (400 and 500 kPa) it was possible to reclaim more than 90% of the initial mass of the simulated pesticide from the pipe. Fig. 4-8 also demonstrates that there was a strong non-linear gradient along the test section with section 1 (where the air entered the pipe) carrying the least amount of residual simulated pesticide. There was a sharp increase in residual from section 1 to section 3 whereas between sections 3 and 6 the graphs flatten, probably due to decreasing flow velocity and friction losses already discussed in section 4.2.1.

Fig. 4-9 shows a more symmetric distribution of residues of simulated pesticide along the test section, reflecting the symmetric design of the test bench with its two air inlets. As expected the lowest amount of residual could be found in those pipe sections that where placed closest to the air inlet whereas the maximum was always in one of the two middle pipe sections. On the one hand, this experiment confirmed the observation that the simulated pesticide could be removed significantly more successfully at higher pressures than at low pressures. To give an example, after pre-cleaning at 300 kPa (Fig. 4-9a) some pipe section could still carry ca. 16% of the initial mass whereas at 400 kPa (Fig. 4-9b) and 500 kPa (Fig. 4-9c) it could be 10% or even lower. On the other hand, as can be seen from Fig. 4-9b and c, it occurred that the test section did not contain less residual after 15 s of pre-cleaning at 400 kPa compared with 10 s and even carried more residual at 500 kPa. This did not happen when only one air inlet was used for the push-back of the simulated pesticide (Fig. 4-8). The reason for this was probably ice formation in the tank outlet as a result of the rapid pressure drop in the air tank due to the quick release of large volumes of air. Beyond that the strong gradients depicted in Fig. 4-8 and Fig. 4-9 also suggest that the push-back with large amounts of air could potentially lead to residues drying if they are located very close to the air inlet. This, however, may be more of a concern if a test section (e. g. sprayer boom) much larger than in this part of the study was used and even larger amounts of air were consumed in the push-back.

In Fig. 4-10 the amount of air used in the above-mentioned experiments is plotted against the time the air tank was open.

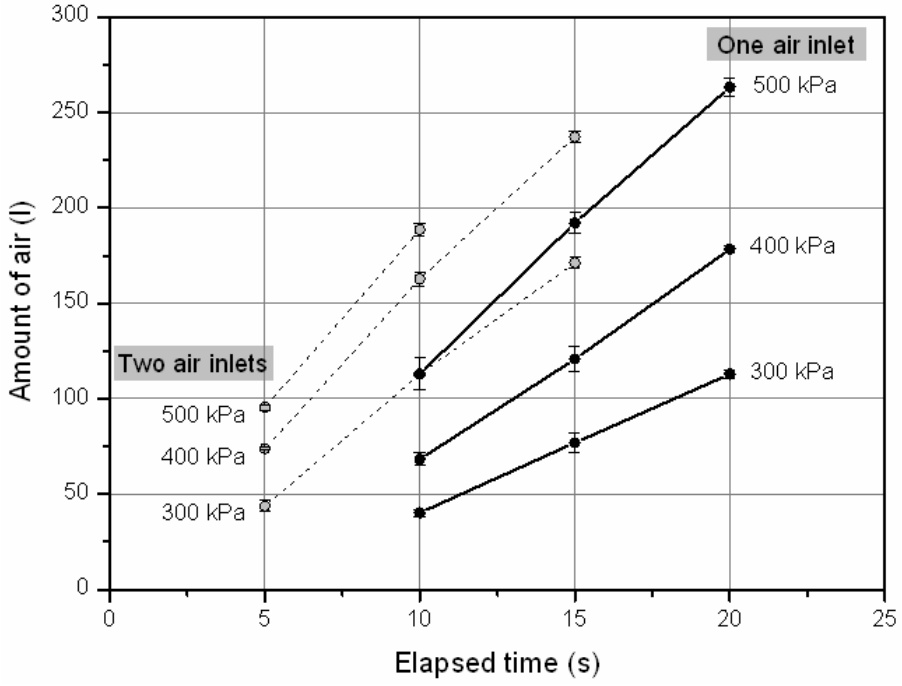


Fig. 4-10: Amount of air used for determining the distribution of residues along a 3 m long test section as a function of time when either one air inlet or two air inlets were used for the push-back. Error bars indicate standard deviations (n = 4).

Fig. 4-10 shows that, depending on the pressure and the time the air tank was open, between ca. 40 l and ca. 260 l of air where consumed in the push-back. This equates to air flow rates of between ca. 240 l min$^{-1}$ to 790 l min$^{-1}$ when one air inlet was used and between 525 l min$^{-1}$ and 1130 l min$^{-1}$ when the test bench was equipped with two air inlets. This explains why there where restrictions concerning pre-cleaning time and air pressure since the air tank used had a capacity of only ca. 55 l. Consequently the 500 kPa pre-cleaning treatment with two air inlets was only carried out for a maximum period of time of 10 s. What is more, the graphs depicted in Fig. 4-10 show that for the 10 s treatment (two air inlets) increasing the pressure from 400 kPa to 500 kPa caused less additional air consumption (26 l) than the increase from 300 kPa to 400 kPa (50 l) which was not the case when only one air inlet was used. Here, increasing the pressure from 300 kPa to 400 kPa increased the amount of air consumed by 28 l while additional 44 l were consumed at 500 kPa compared with 400 kPa. This confirms the assumption that the air outlet of the air tank narrowed due to ice formation.

In order to ascertain if the cleaning efficiency depended on air pressure and/or the arrangement of air inlets the average amount of residual in the test section was plotted against the amount of air consumed in the treatments as depicted in Fig. 4-11.

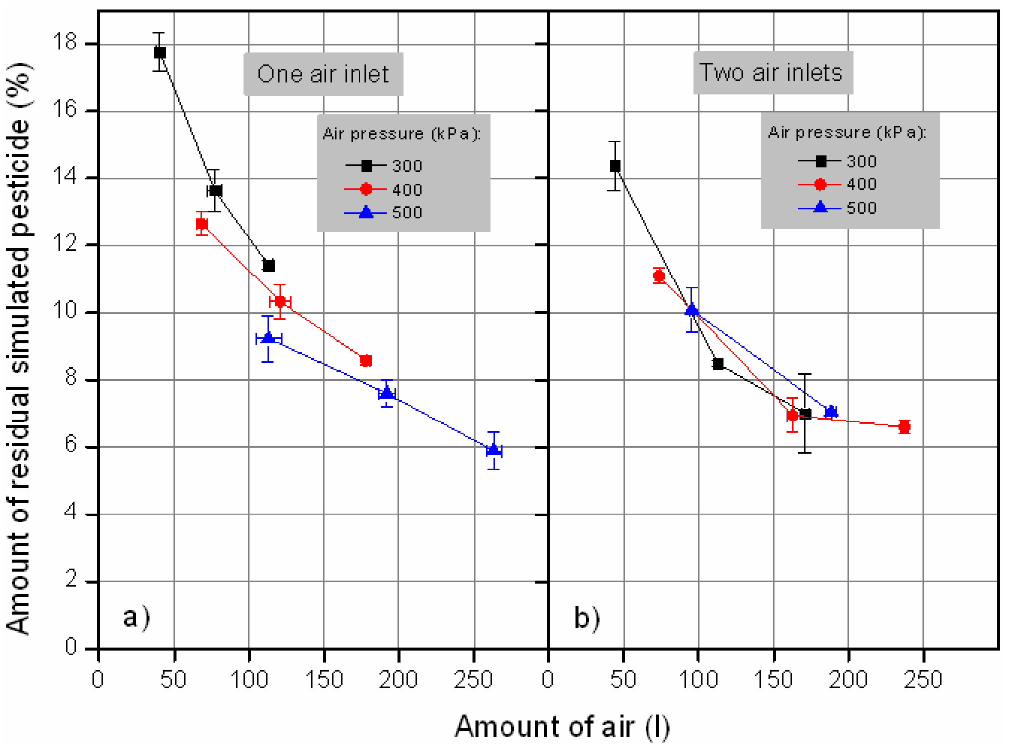


Fig. 4-11: Amount of residual simulated pesticide in the 3 m long test section as a function of the amount of air used for the push-back when either one (a) or two (b) air inlets where used. Error bars indicate standard deviations (n = 4).

The data depicted in Fig. 4-11 show an exponential decrease in residual as the amount of air released from the air tank increased. This means the air was most effective at the very beginning of the push back. To give an example, in Fig. 4-11a the first 50 l of air removed more than 80% of the simulated pesticide from the test section, whereas the following 200 l of air reclaimed only another 12%, leading to a minimum of 6% of the initial simulated pesticide mass in the pre-cleaned test section. Fig. 4-11a and b also show that the air at 300 kPa was slightly more effective at the beginning of the push-back when two air inlets were used, since ca. 40 l of air removed 3 - 4% more of the simulated pesticide from the pipe compared with one air inlet. However, with the amount of air increasing in both treatments this difference disappeared and was hardly measurable when more than 150 l of air had streamed out of the air tank. Fig. 4-11a also demonstrates that a given amount of air removed ca. 1% more of the simulated pesticide from the pipe when the pressure was increased by 100 kPa. In Fig. 4-11b, however, no such difference between pre-cleaning treatments at different pressures was measurable.

The aforementioned results indicate that on a mobile wide boom DIS sprayer a limited amount of air would be sufficient to remove at least 90% of the pesticide from the pipe. All that is needed is enough air at high pressure to effectively push the "core" out of the injection pipe. Air consumption beyond that would soon become too inefficient to be recommended for field use. Whether the amounts of residual simulated pesticide of between 6% and 18% depicted in Fig. 4-11 will be acceptable will depend on the application rate of the pesticide used. Residual amounts of 6% and 18% equated to ca. 15 g and 44 g residual pesticide in the 3 m wide test section. For a 21 m wide boom sprayer this would be equal to 105 g (6%) and 308 g (18%) total pesticide mass in the injection pipe after reclaiming. This would still be enough to treat an area of between 0.04 ha (6%) and 0.10 ha (18%) if a pesticide at an application rate of 3 l $ha^{-1}$ was used. If a low-dose sulfonyl-urea herbicide at an application rate of only 0.1 l $ha^{-1}$ was used, the residual amount would be enough to treat an area of ca. 1 ha (6%) and ca. 3 ha (18%). This indicates that the cleaning of high-dose pesticides will be less time and labour intensive than the cleaning of low-dose chemicals. The latter will pose a real challenge to wide boom DIS sprayers.

### 4.2.3 Effect of piping material

Fig. 4-12 shows the amount of simulated pesticide drained from 300 mm long pipes (ID: 10 mm) made of stainless steel, PVC, PTFE or glass as a function of time.

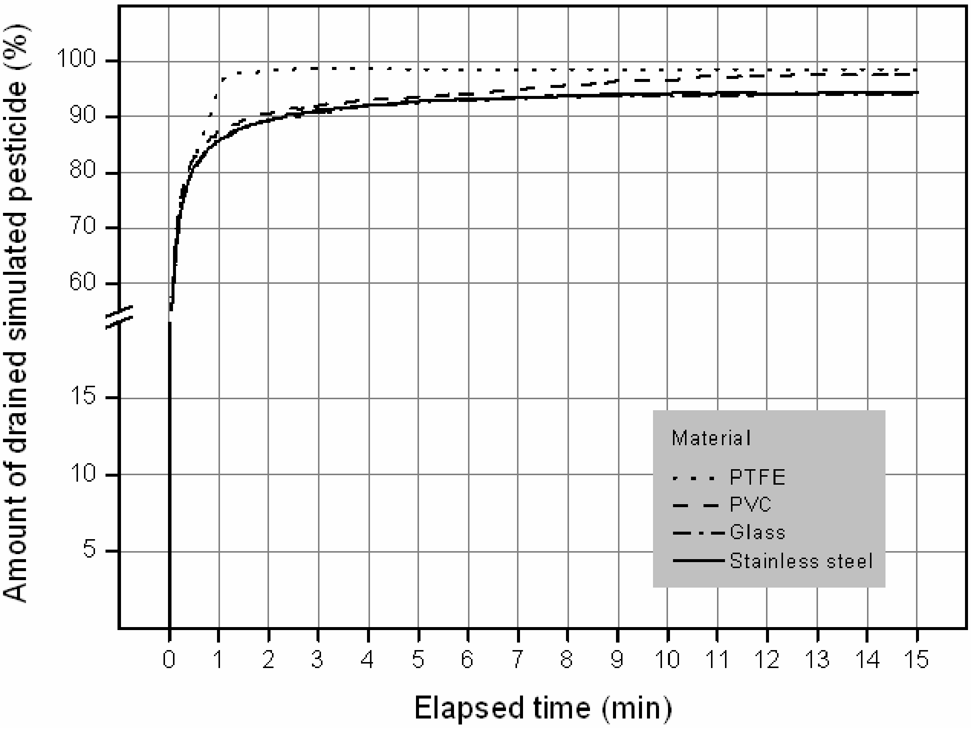


Fig. 4-12: Amount of simulated pesticide drained from 300 mm long pipes made of stainless steel, PVC, PTFE, and glass as a function of time. The amount of simulated pesticide filled in each pipe was 20 g (= 100%). The graphs show average values (n = 4).

Upon initial release of the valve there was almost no difference between the materials. However, after a fraction of a second, when the respective pipe was “empty” while simulated pesticide was still running down the inner pipe surface, differences between some of the materials became apparent. While there was no difference between stainless steel and glass (both curves lie on top of one another) the simulated pesticide ran out of the PTFE pipe most quickly followed by the PVC pipe. After 15 min the least amount of residual simulated pesticide was in the PTFE pipe (1.4%), again followed by the PVC (2.3%) pipe. With stainless steel and glass 5.7% and 5.9% remained in the pipe. With the PTFE pipes the increase in weight stopped abruptly after only 1 min while drainage did not stop within 15 min when pipes made of stainless steel, glass or PVC were used. This means the simulated pesticide ran down the pipe leaving only a few small droplets on the inner surface. This was also true for the PVC pipes where droplets ran down the surface more slowly. With stainless steel and glass after 15 min residual simulated pesticide was still covering the whole inner surface instead of forming droplets which also led to high quantities remaining in these pipes. LECLERCQ-PERLAT & LALANDE (1994) also found that glass and stainless steel could be equally cleanable whereas plastics where more cleanable. However, they noted that cleanability depended on the kind of stainless steel used and its surface finish.

The different tendency of stainless steel, PVC, PTFE and glass to retain the simulated pesticide can be explained by their hydrophobic properties. According to NASSAUER (1985) a material's hydrophobia can be described by its critical surface tension of wetting which is the surface tension of a liquid above which all liquids on this particular surface form contact angles greater than 0°. This means that a low critical surface tension of a material indicates its hydrophobic character. While critical surface tensions of PTFE and PVC (18.5 mN $m^{-1}$ and 39 mN $m^{-1}$ respectively, ZISMAN, 1964) are rather low, critical surface tensions of glass and stainless steel are much higher. NASSAUER (1985) mentions 130 mN $m^{-1}$ for glass and values of between 50 and 100 mN $m^{-1}$ for stainless steel. Thus PTFE and PVC can be expected to be less wettable by water than stainless steel or glass. Furthermore, NASSAUER (1985) states that both glass and stainless steel are strongly wettable by water due to electrical interactions between the material and water as a polar liquid. Obviously information from literature accords with the findings in Fig. 4-12 since the simulated pesticide, which was a water-based solution, drained from hydrophobic polyethylenes more quickly than from hydrophilic materials like stainless steel or glass.

In Fig. 4-13 the two materials that differed most in the drain-out experiment (stainless steel and PTFE) are compared with regards to their ability to be pre-cleaned by pressurized air.

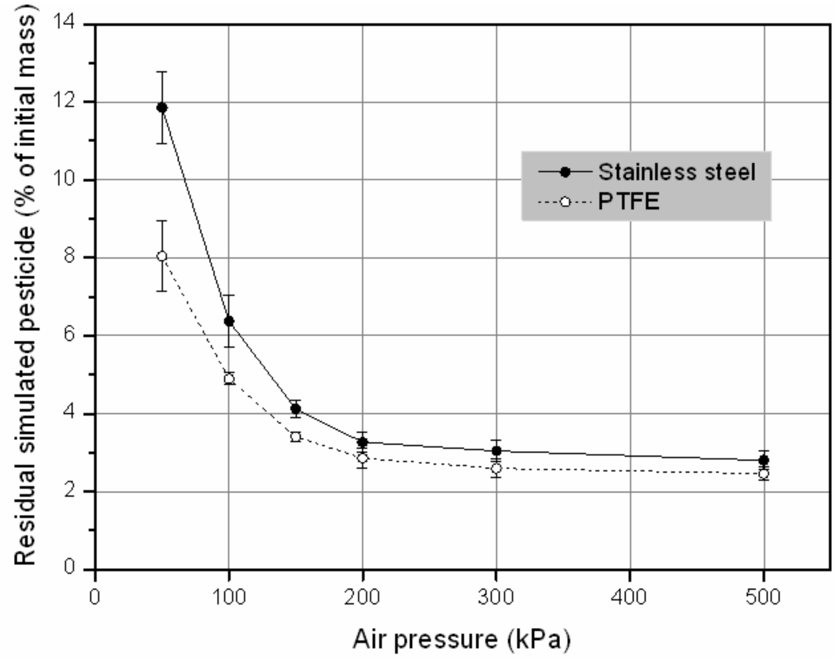


Fig. 4-13: Residual simulated pesticide in a 500 mm long test section (ID: 10 mm) made of either stainless steel or PTFE after pre-cleaning with air for 5 s at different pressures. Error bars indicate standard deviations (n = 6).

It is obvious from the graphs in Fig. 4-13 that the good cleanability of PTFE that was detected before (Fig. 4-12) also translated into PTFE being more cleanable during pre-cleaning with pressurized air. However, the difference between the two materials tested was more obvious at low pressures (50 to 150 kPa). Here the amount of residual in the PTFE pipe could be one third lower than in the stainless steel pipe (ca. 12% residual in the stainless steel pipe vs. ca. 8% residual in the PTFE pipe at 50 kPa). At higher pressures (200 - 500 kPa) differences in the amount of residual were marginal. At 500 kPa for instance the residual in the stainless steel pipe was 2.8% whereas it was 2.5% in the PTFE pipe. The fact that pressures as low as 50 kPa could still remove a significant amount of simulated pesticide was due to the test section being rather short (500 mm). The small length caused only marginal pressure losses. However, it is clear that pressures as low as this may not be suitable when larger test sections (e. g. a boom section or even a complete sprayer) are considered.

Although results gained from these tests suggest that the choice of piping materials used to set-up a DIS has an impact on the systems cleanability, findings are restricted to water based (simulated) pesticides only. Since there are also formulation types of agrochemicals which are not water soluble (KNOWLES 2008, RAMWELL et al., 2008) it is possible that these results would have been different if a hydrocarbon solvent based simulated pesticide had been used. However, the fact that PTFE is not only hydrophobic but features general non-adhesiveness (Dupont, 1996) indicates it can possibly help make DIS more cleanable independent of the formulation type used. AMSDEN & SOUTHCOMBE (1977) suggest that PTFE, along with titanium could be very suitable engineering materials for use in the construction of plant protection equipment as they are resistant to pesticide. However, the authors also note that these materials are difficult to manufacture and repair. LEWAN (2003) gives voice to the concern that PTFE can be porous and then difficult to clean. PTFE is also not resilient enough to provide a permanently tight seal (LEWAN, 2003). What is more, all differences shown in Fig. 4-12 and Fig. 4-13 became apparent only after the test section (injection pipe) was “empty”, that is, after the core of the simulated pesticide had already been push out. As pointed out in section 4.2.2 at this time the air was already becoming more and more ineffective. This is the reason why on a wide boom DIS sprayer the choice of material may not be the key parameter to improve cleanability if the efficient use of air is the top priority.

### 4.2.4 Effect of viscosity

Fig. 4-14 shows the effect of viscosity on drainage of the simulated pesticides over time.

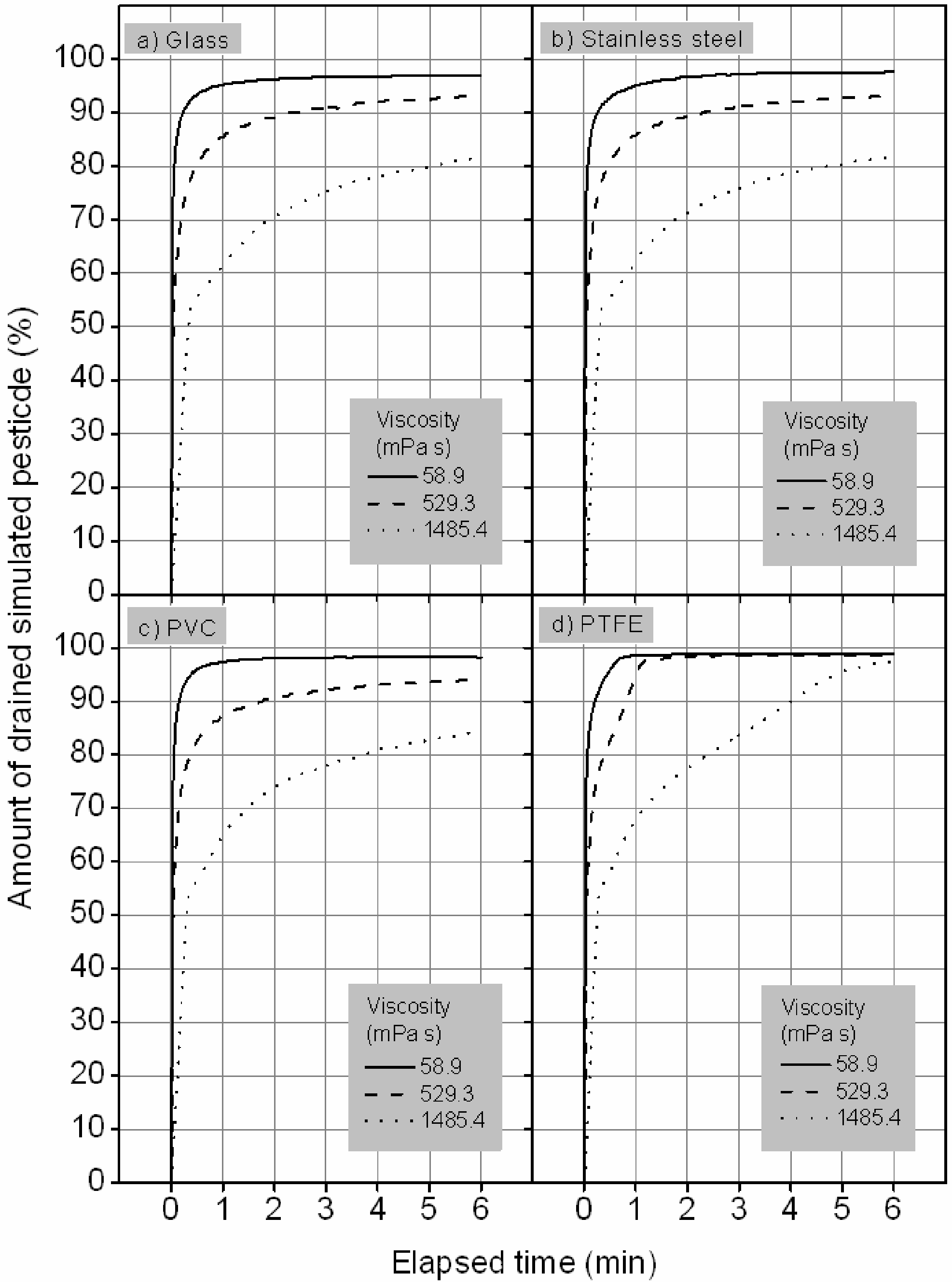


Fig. 4-14: Amount of simulated pesticide of different viscosities drained from 300 mm long pipes (ID: 10 mm) made of glass, stainless steel, PVC, or PTFE as a function of time. Prior to each trial, the respective pipe was filled with 20 g (= 100%) of simulated pesticide. Shown are average values (n = 4).

The higher the viscosity of the simulated pesticide, the longer it took for it to drain from the pipes. This was true for all materials tested and differences between them, which have already been discussed in section 4.2.3, became more apparent at higher viscosities. Viscosity also affected the drainage of the "core" of the simulated pesticide since (unlike in Fig. 4-12) differences between simulated pesticides of different viscosities became visible immediately after tap opening.

The PTFE's unwettability compared with the other materials tested proves true in Fig. 4-14d were the increase of drained simulated pesticide (at 1485.4 mPa s) was almost linear before it stopped abruptly after ca. 6 min. The amount of residual after 6 min increased almost proportionally with viscosity for stainless steel and glass where 2.8, 7.0 and 18.5% (glass, Fig. 4-14a) and 2.5, 6.6 and 18.1% (stainless steel, Fig. 4-14b) of the simulated pesticide of 58.9, 529.3 and 1485.4 mPa s respectively had not drained from the pipe. The amounts of residual in the other two pipes after 6 min were 1.8, 5.9, and 15.7% (PVC, Fig. 4-14c) and 1.2, 1.4, and 2.6% (PTFE, Fig. 4-14d) at the aforementioned viscosities.

According to ZHU et al. (1998), viscosities of most common pesticides lie between 0.92 mPa s and 800 mPa s. Other researchers investigating physical properties of pesticides for use in DIS considered viscosities of between 1.2 to 33 mPa s at a shear rate of 1000 $s^{-1}$ (GEBHARD et al., 1984) and ca. 6 to 80 mPa s at a shear rate of 1.79 $s^{-1}$ and various temperatures (COCHRAN et al., 1987). According to FRIESSLEBEN (2011) viscosities of the most important approved pesticide in Germany usually do not exceed 700 mPa s. The viscosities considered herein represented this range.

What can be derived from these drain-out experiments with regard to the cleaning procedure on the experimental wide boom sprayer is that the cleaning success will probably more strongly depend on the pesticide's viscosity than on the materials used, provided all materials comply with the principles mentioned by HASTING 2008 (see section 2.5.3). The reason for this is that the material had an effect only after the "core" of the simulated pesticide had been pushed out, while viscosity affected both the removal of the "core" and the removal of simulated pesticide adhering to the inner pipe wall. However, once the operator applies a highly viscous product the material used will significantly affect cleaning.

## 4.3 Rinsing of the hydraulic system

### 4.3.1 Effect of pre-cleaning time

Fig. 4-15 illustrates the concentration of simulated pesticide in the effluent of nozzles 1 through 6 as a function of time with time = 0 marking the instant when the rinsing water arrived at the first sensor.

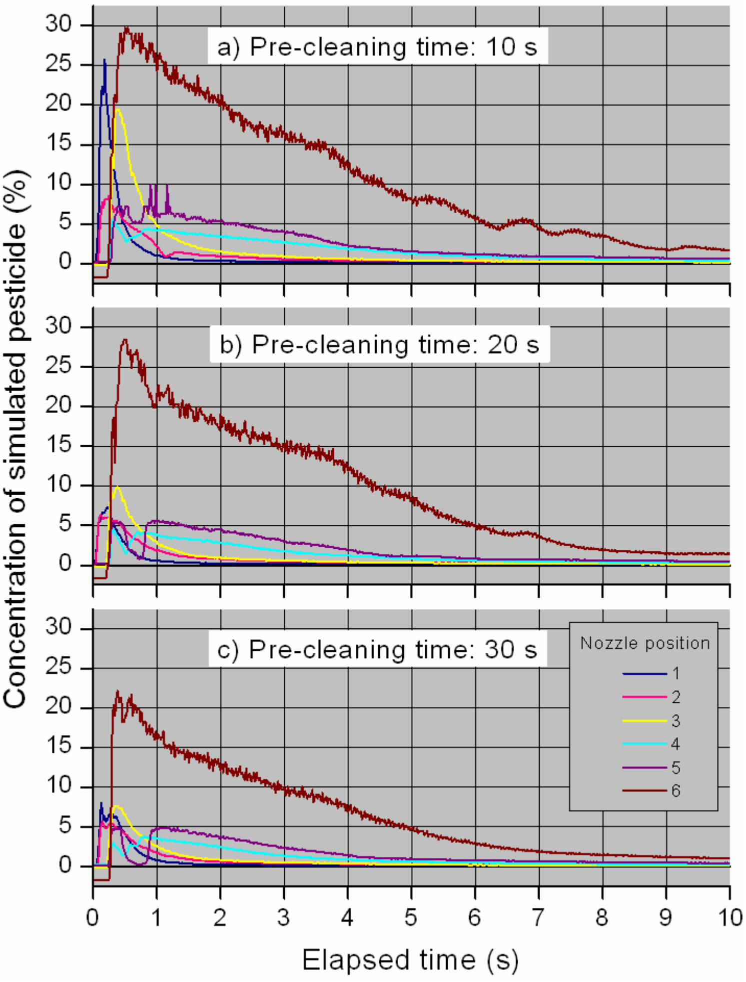


Fig. 4-15: Variation in simulated pesticide concentration in the effluent of nozzles 1 through 6 as a function of time. Pre-cleaning time was a) 10 s, b) 20 s or c) 30 s at 300 kPa.

In the effluent of nozzle 6 the initial concentration of simulated pesticide was 30% when pre-cleaning time had been only 10 s (Fig. 4-15a). Although Fig. 4-15b and c show that the initial concentration peaks could be reduced by a third through longer pre-cleaning times (20 s and 30 s), it is obvious that these concentrations were still much higher than in common spray mixes where, depending on the product, pesticide concentration can be 0.25% or far less (ANONYMOUS, 2011). The high initial concentrations at nozzle 6 were probably caused by rinsing water accumulating residues while entering the empty pre-cleaned test section. According to these results the rinsing water would have to be diluted by injection into the carrier (water) if a pesticide was used. The reason for this is that concentrations of common spray mixes can be much lower than the concentrations displayed in Fig. 4-15. To give an example, the application rates of common liquid herbicides for cereals in Germany range from 0.1 l $ha^{-1}$ to 3 l $ha^{-1}$ (ANONYMOUS, 2011). This leads to spray mix concentrations of between 0.03% and 1% if 300 l $ha^{-1}$ water were applied. After application these spray mix concentrations have to be further diluted through appropriate rinsing procedures to less than 1 - 2% of the original tank mix concentration (ROETTELE et al., 2010). Thus, cleaning could be a time consuming procedure as the flow rate of the rinsing water through each injection valve would be significantly lower than in this experiment (ca. 0.65 l $min^{-1}$, see Fig. 4-17a) if the dosing valves could not be opened completely due to high concentration.

The total flow rate in the experiment depicted in Fig. 4-15 was 3.9 l $min^{-1}$ which corresponds to flow velocities between the nozzle positions of between 0.83 m $s^{-1}$ (shortly upstream of nozzle 1) and 0.14 m $s^{-1}$ (shortly upstream of nozzle 6) with Reynolds Numbers of between ca. 8300 and ca. 1400. This indicates that in the test section there was both turbulent and laminar flow based on the Reynolds Numbers mentioned by LEWIS (2008). Given that several authors (e. g. GRASSHOFF & REINEMANN, 1993, PLETT & GRASSHOFF, 2007, WILDBRETT, 2006) state that most efficient cleaning can only be realized through turbulent flow it can be expected that the cleaning result would have been better if higher water flow rates had been realized. However modifications made to the valves in the course of another study in order to improve their dosing behaviour and power consumption led to maximum flow rates of only a third (ca. 0.2 l $min^{-1}$) of what was measured in this study, even at significantly higher water pressures (up to 800 kPa). As mentioned before, the concentration of the simulated pesticide in the rinsing water could require further dilution by injection into the carrier (water). If this procedure required injection rates lower than the aforementioned 0.2 l $min^{-1}$ (in order to avoid crop damage caused by toxic pesticide concentrations) cleaning efficiency would further decrease as a result of the low flow rates and the flow becoming laminar.

The fact that the concentration decay over time was different at different nozzle positions suggests that on a real DIS sprayer all dosing valves would have to be controlled individually in order to achieve a homogeneous, constant and not-phytotoxic concentration at all nozzles. In order to avoid this, the contaminated rinsing water would have to be homogenized before it is applied through the injection valves. This would also reduce the initial concentration if high quantities of water were used. What is more, the longer the test section, the more likely are concentrations even higher than the concentration depicted in Fig. 4-15. This could be particularly important with wide boom DIS field sprayers.

### 4.3.2 Effect of water inlet position

As mentioned in section 3.5.2 the test bench used to examine the effect of a middle water inlet and a middle water inlet plus two end water inlets was also equipped with two main air inlets, as opposed to the test bench with only one end water inlet which was equipped with only one main air inlet (see section 3.1). Despite these differences the aim was to keep the pre-cleaning treatments as comparable as possible, notably in terms of air pressure and the amount of air used for pre-cleaning. Therefore, Fig. 4-16 illustrates the amount of air consumed during the push-back depending on the number of main air inlets and the time the air tank was open.

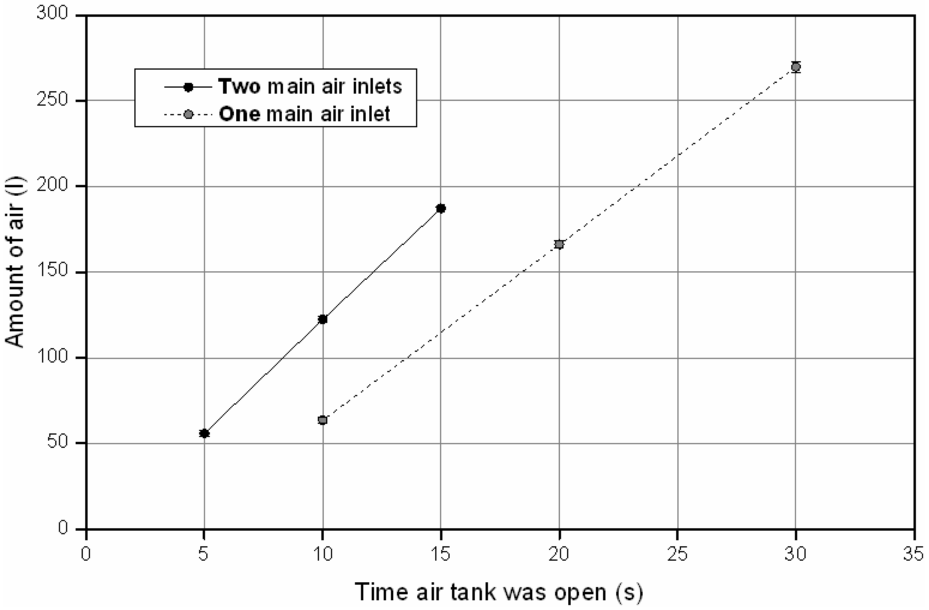


Fig. 4-16: Air consumption with one or two main air inlets used for reclaiming the simulated pesticide at 300 kPa. Error bars indicate standard deviations (n = 4).

From the results depicted in Fig. 4-16 it is obvious that it was possible to obtain almost equal amounts of air (ca. 56 l and ca. 64 l) in both pre-cleaning treatments when the air tank was kept open for 5 s (two main air inlets) and 10 s (one main air inlet). Therefore, in the experiments that were carried out to determine the effect of the water inlet position on the rinsing process (described below) these two pre-cleaning times where applied.

Equal flow rates through all nozzles independent of the water inlet position(s) were also required for comparable results. Fig. 4-17 shows the water flow rates at nozzle positions 1 through 6 while rinsing when different water inlet positions were used.

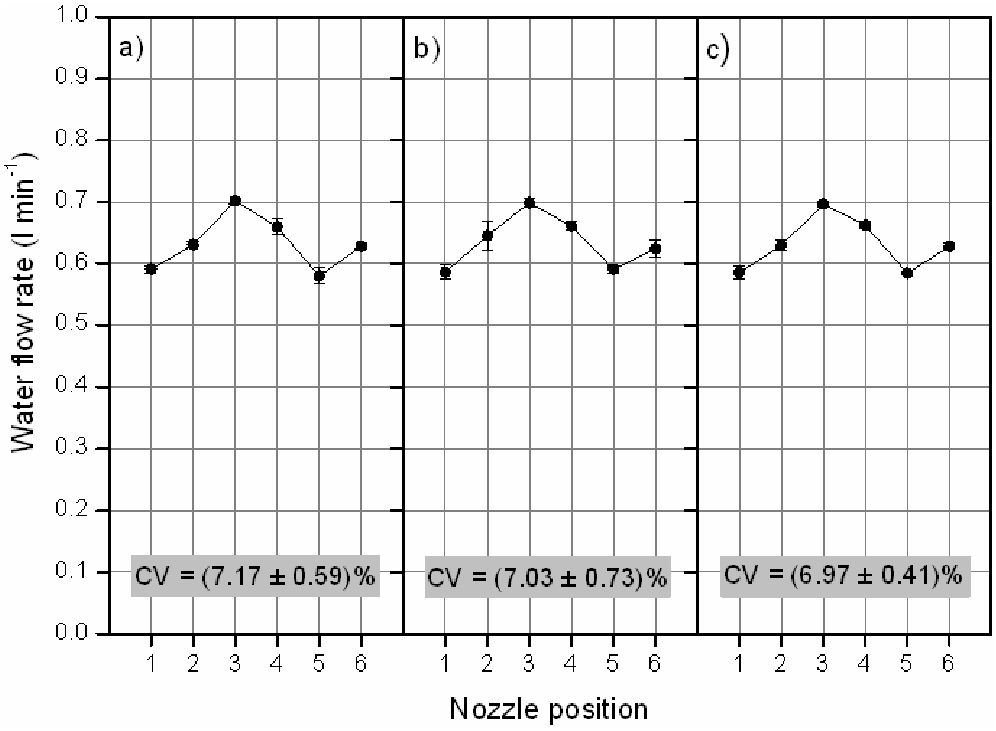


Fig. 4-17: Water flow rate while rinsing. The water inlet was placed a) at the end, b) in the middle or c) in the middle and at both ends of the test section. Error bars indicate standard deviations (n = 4). Also indicated are Coefficients of Variation (CV) ± standard deviation.

As the short error bars in Fig. 4-17 indicate flow rates were constant at individual nozzle positions, but not entirely consistent along the test section. However, different water inlet positions showed the same variation in flow rate between nozzle positions which resulted in a Coefficient of Variation (CV) in all treatments of ca. 7%. With a view to conventional crop sprayers a CV of ca. 7% indicates a still sufficient lateral spray distribution (BBA, 2002). It can therefore be assumed that results were not biased through a variation in flow rate. A possible explanation for the variation in flow rate between nozzle positions in Fig. 4-17 is that, despite a water pressure of ca. 400 kPa in all treatments, there certainly was a considerable pressure drop as the water streamed through the narrow injection valve and the mixing chamber before it entered the nozzle. This potentially led to the nozzles not being operated at the recommended pressure which then resulted in the comparatively high CV.

Fig. 4-18 shows the rinsing curves for nozzle positions 1 through 6 as measured by the conductivity measuring cells when different water inlet positions were used.

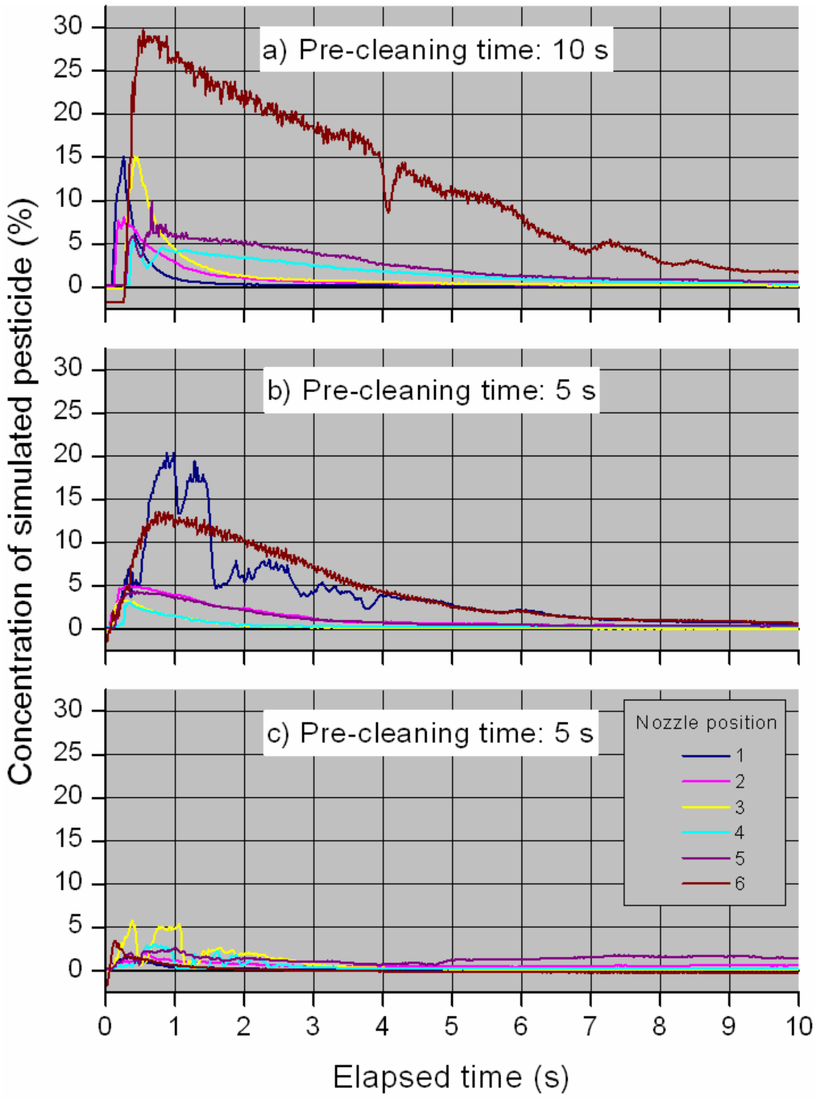


Fig. 4-18: Variation in concentration of simulated pesticide in the effluent of nozzles 1 through 6 as a function of time. The water inlet was placed a) at the end, b) in the middle or c) in the middle and at both ends of the test section. Pre-cleaning times were either 10 s (a) or 5 s (b and c).

By shifting the water inlet from the end of the test section (Fig. 4-18a) to the middle (Fig. 4-18b) the maximum concentration was reduced by around one third. This result was expected since the distance from each nozzle to the water inlet was reduced by a half. This also reduced the required rinsing time for the nozzles most distant from the water inlet by almost a half (Fig. 4-19a and b).

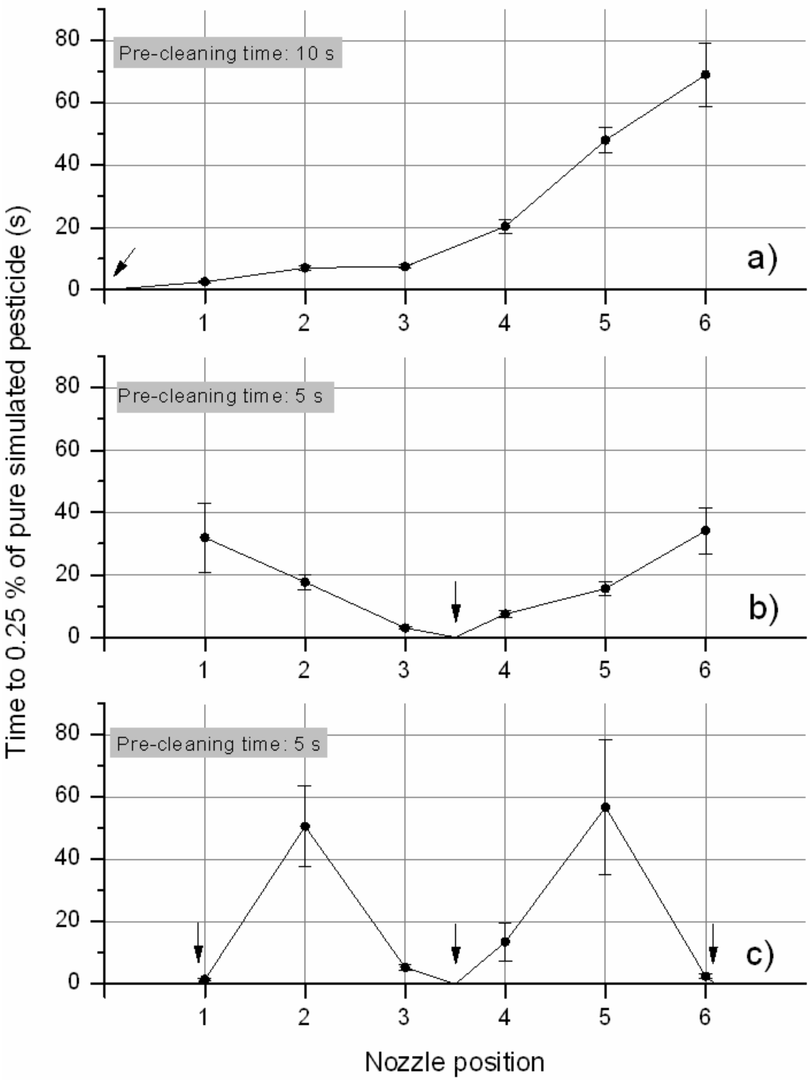


Fig. 4-19: Effect of water inlet position on the time taken for the concentration of simulated pesticide to reach 0.25% of the pure simulated pesticide concentration. The water inlet was a) at the end, b) in the middle or c) in the middle and at both ends of the test section. Error bars indicate standard deviations (n = 4). Arrows indicate water inlet positions.

By using two additional water inlets it was possible to further reduce the maximum concentration to 5% (Fig. 4-18c). Much less dilution would be necessary here if a real pesticide was used. That said Fig. 4-18c also shows that after ca. 5 s there was a slight increase in concentration at nozzle 5 and (less visible) at nozzle 2. It seems that the rinsing water in this part of the test section gradually changed its flow direction which slowed down the concentration decay (Fig. 4-19c). The large error bars, representing the standard deviations, emphasise the unstable flow near nozzles 2 and 5.

In order to describe the effect of different water inlets on the long term cleaning result supplementary discontinuous concentration measurements were necessary. Fig. 4-20 illustrates the variation in concentration of simulated pesticide in the effluent of nozzle 6 (middle or end water inlet) and nozzle 2 (three water inlets) as measured by the handheld conductivity meter.

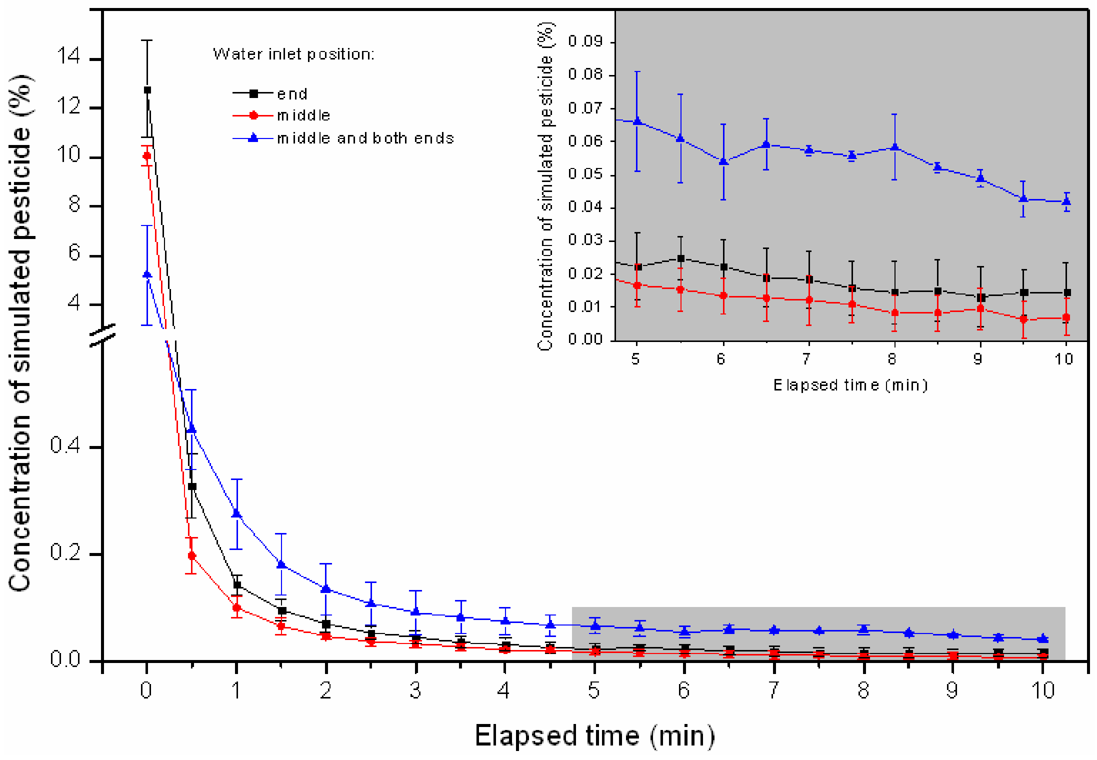


Fig. 4-20: Variation in concentration of simulated pesticide in the effluent of nozzle 6 (water inlet at the end or in the middle) and nozzle 2 (water inlet in the middle and at both ends). Pre-cleaning time was 30 s when the water inlet was at the end of the test section and 15 s otherwise. Air pressure: 300 kPa. Error bars indicate standard deviations (n = 4).

The shapes of the rinsing curves confirm the logarithmic nature of the rinsing process reported elsewhere (PLETT & GRASSHOFF, 2007, WILDBRETT, 2006, NASSAUER & KESSLER, 1984). With the water inlet in the middle concentrations were 0.01% or lower after 8 min and could thus hardly be distinguished from pure tap water by the available metering device. With three water inlets the concentrations of the simulated pesticide did not go under 0.04% within 10 min and even increased occasionally, despite the low initial value. At these concentrations it would depend on the application rate of the respective product whether the sprayer can be considered clean. If a low-dose sulfonyl-urea herbicide had been used the pesticide concentration in the rinsing water would still have been equal to the concentration of the common spray mix, even after 10 min of rinsing. However, some pesticides require much higher application rates, e. g. 3 l ha$^{-1}$ (ANONYMOUS, 2011, see section 4.3.1). In this case the final concentration for the middle water inlet shown in Fig. 4-20 (ca. 0.01% of the pure simulated pesticide) would correspond to a 100-times dilution of spray mixture if 300 l ha$^{-1}$ of water were applied, a concentration that would comply with the thresholds mentioned by ROETTELE et al. (2010).

### 4.3.3 Effect of water pressure

Since with agricultural sprayers adjusting the water pressure is a common procedure to achieve a desired volumetric flow rate (compare section 3.5.3), different water pressures were tested in order to ascertain their impact on the cleaning result.

Fig. 4-21 illustrates the effect of rinsing water pressure (200, 300 and 400 kPa) on the time taken for the concentration of the simulated pesticide at the different nozzle positions to reach 0.25% of the pure simulated pesticide. In all cases the test section had been pre-cleaned with pressured air for 20 s at 300 kPa.

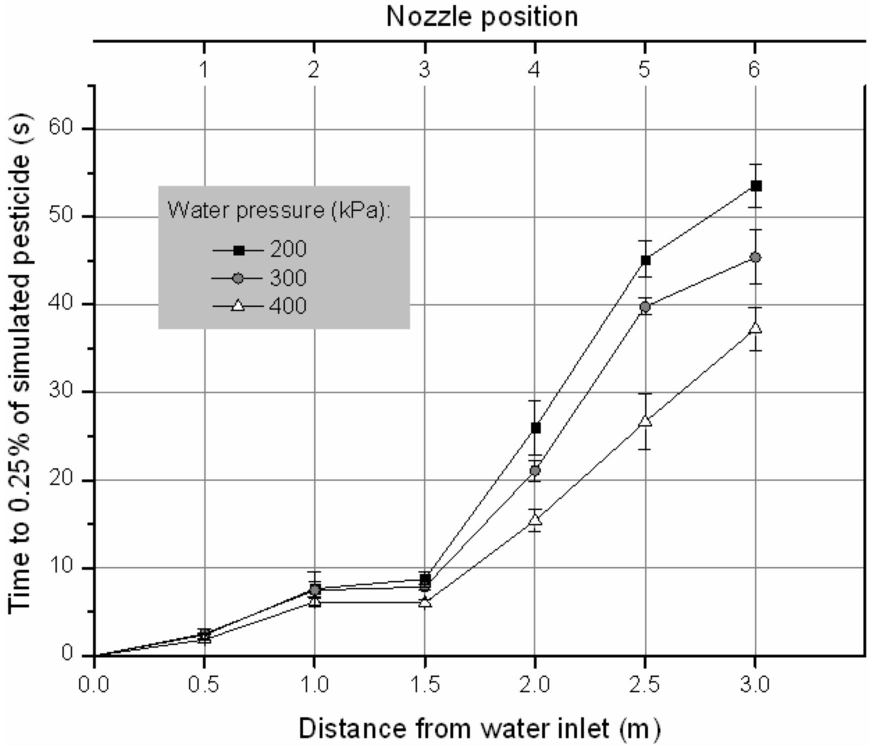


Fig. 4-21: Effect of water pressure and nozzle position on the time taken for the concentration of the simulated pesticide to reach 0.25% of the pure simulated pesticide. Error bars indicate standard deviations (n = 4).

The rinsing water pressures indicated in Fig. 4-21 resulted in total rinsing water flow rates based on the whole test section of 2.8 l min$^{-1}$ (200 kPa), 3.2 l min$^{-1}$ (300 kPa), and 3.7 l min$^{-1}$ which was one reason why the 400 kPa treatment was (on average at nozzle 6) 8 s faster than the 300 kPa treatment and 16 s faster than the 200 kPa treatment. At nozzle positions 1 to 3, however, the difference between the treatments was mostly less than a second and, therefore, rather small. Another possible reason for the water leading to a faster decline in concentration at higher pressures may have been that the water was not only faster at transporting the simulated pesticide out of the test section, but also more effective at higher flow rates due to increased mechanical action. Therefore, Fig. 4-22 shows the effect of water pressure on the relative amount of rinsing water consumed until the simulated pesticide in the rinsing water was diluted down to 0.25% of the pure simulated pesticide. In order to compare the different treatments depicted in Fig. 4-22 the amount of water used in the 300 and 400 kPa treatments was expressed as a percentage of the amount of water consumed in the 200 kPa treatment.

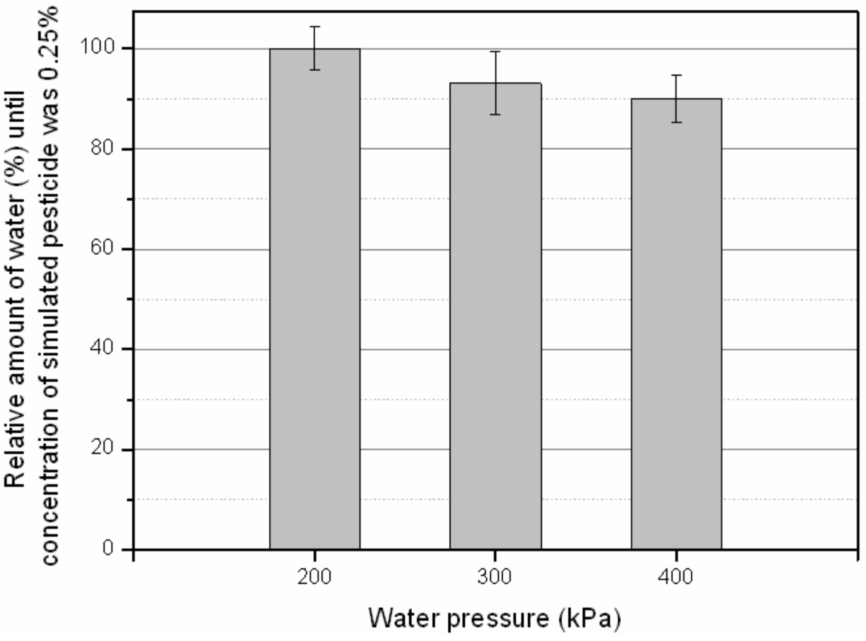


Fig. 4-22: Effect of water pressure on the amount of water used to reach a concentration of simulated pesticide of 0.25% in the rinsing water. Error bars indicate standard deviations (n = 4).

The result shows that 7% less water was necessary to reach the given threshold when water at 300 kPa instead of 200 kPa was used. By increasing the water pressure to 400 kPa further 3% could be saved compared with 300 kPa, bringing the amount of water used in the 400 kPa treatment down to only 90% of what was used in the 200 kPa treatment. Despite this, a one-way analysis of variance (ANOVA) that was performed using Tukey's means comparison test in Origin® 8.0 showed that the mean values in Fig. 4-22 did not differ significantly. The reason for this may have been the small number of replications (n = 4) combined with the fact that there was no wide difference in the rinsing water flow rates investigated. According to GRASSHOFF & REINEMANN (1993) and HOFFMANN & REUTER (1984) increased flow velocity leads to higher wall shear stress. Higher wall shear stress could be a reason why the water was slightly more efficient at higher pressures as flow velocities were higher as well when higher water pressures were applied. Reynolds Numbers for nozzle positions 1 through 6 ranged from ca. 6000 to ca. 1000 (200 kPa), ca. 6800 to ca. 1200 (300 kPa) and ca. 8300 to ca. 1400 (400 kPa) indicating the more and more turbulent flow with increasing water pressure. However, at all pressures the flow in the pipe section shortly upstream of nozzle 6 was laminar.

### 4.3.4 Effect of residence time

Fig. 4-23 illustrates the concentration of simulated pesticide in the rinsing water as a function of time. The two rinsing curves were measured at nozzle position 6 after the rising water had been sitting in the test section for either 0 min (= normal continuous rinsing) or 30 min. For clarity a third treatment (residence time 5 s) was not included in Fig. 4-23. Instead, it was added to the data in Fig. 4-24 and will be discussed later on.

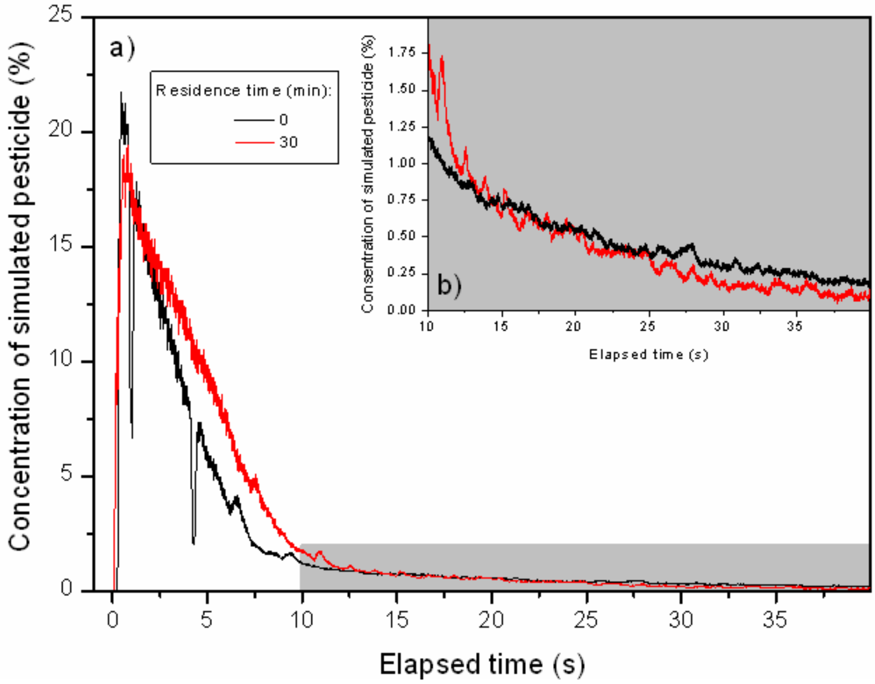


Fig. 4-23: Concentration of simulated pesticide in the effluent of nozzle 6 as a function of time after the rinsing water had been staying in the test section for either 0 min or 30 min.

As can be seen from Fig. 4-23 a residence time of 30 min measurably affected the progression of the rinsing curves. While the initial concentrations of both curves were almost similar (ca. 20% of the pure simulated pesticide) the subsequent progression of both curves differed significantly. The decline in concentration that followed was initially faster in the 0 min-treatment where concentrations could occasionally be one third lower than in the 30 min-treatment (Fig. 4-23a, e. g after ca. 5 s). However, as depicted in Fig. 4-23b, after ca. 17 s the 30 min-curve (red curve) cut the 0 min-curve (black curve). From then on concentrations in the 30 min-treatment remained lower than in the 0 min-treatment for the period of time remaining.

In discussing CIP systems MAJOOR (2003) stated that the cleaning solution has to be applied to soiled surfaces for at least 5 min and up to 1 h. WILDBRETT (2006) also noted that certain actions during the cleaning process require some time, for example the dissolution and diffusion of parts of the soil. Therefore the rinsing water probably had, after it had been sitting in the test section for 30 min, already accumulated some of the residual that had remained in the test section after pre-cleaning. It therefore initially carried more residual, at least until the volume that had been sitting in the pipe had left the test section. In the 0 min-treatment, however, residues of the simulated pesticide were still sticking to the inner pipe surfaces as the first volumes of rinsing water passed through, consequently carrying less residual.

Expected advantages of letting the rinsing water sit in the test section over a longer period of time were a reduction in time and amount of water required to achieve a given degree of cleanness. For this reason Fig. 4-24 presents the times taken for the concentration of the simulated pesticide in the effluent of nozzle positions 1 through 6 to reach 0.25% of the pure simulated pesticide. In addition to the aforementioned treatments Fig. 4-24 also includes a treatment in which the rinsing water had been sitting in the test section for only 5 min when the shut-off valves and RRV®s were opened and the actual rinsing process started.

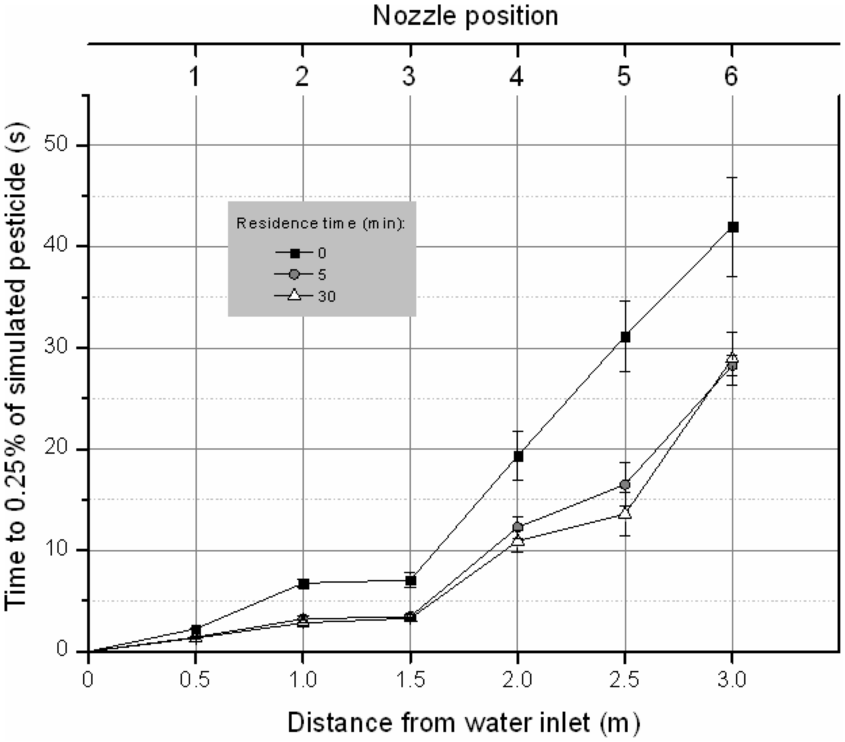


Fig. 4-24: Effect of residence time of the rinsing water and nozzle position on the time taken for the concentration of the simulated pesticide to reach 0.25% of the pure simulated pesticide. Error bars indicate standard deviations (n = 4).

As the curves in Fig. 4-23 already suggested it took significantly longer in the 0 min treatment to reach the given threshold of 0.25% at all nozzles than in any other treatment (ca. 42 s, Fig. 4-24). With both the 5 min and the 30 min treatment this concentration was reached within only ca. 28 s which equals a reduction in rising time by approximately one-third. Interestingly there was almost no difference between the 5 min-treatment and the 30 min treatment as data points from both treatments lie almost on top of one another. This result points out that the process of dissolving residual simulated pesticide in the rinsing water took place within the first few minutes, after the test section had been filled with water but not within the first seconds. During the following 25 min no further mobilization of the residual took place, leading to similar rinsing time in the 5 min and the 30 min treatment. The fact that there was no difference between the 5 min and the 30 min treatment is on the one hand contradictory to the results discussed in section 4.1 (“Diffusion of the tracer”) only marginal changes in (tracer) concentration were measured within the first 60 min. On the other hand the diffusion test was static whereas here the filling of the pipe may have caused turbulences that thoroughly mixed the water and the residual, accelerating the diffusion. Since the pipe diameter was rather small (10 mm), it can be assumed that homogenization in the pipe section was completed after only a few seconds or minutes. What is more, the actual saving in time was negligible in consideration of the fact that a residence time of several minutes only resulted in time savings during rinsing of only ca. 14 s. As for the water savings, approximately 2.5 l of water were necessary to reach 0.25% with the 0 min-treatment whereas with the other treatments approximately 25% less water was consumed (ca. 1.9 l). With a wide boom DIS sprayer the effect of residence time on the cleaning result may be more pronounced since the total amount of water required would be higher, leading to a higher amount of water that can potentially be saved. As stated by several authors (e. g. WILDBRETT, 2006), residence time can be important when detergents or enzymes are used (which was not the case in this study) as they require a certain residence time to have an effect.

### 4.3.5 Effect of pulsed water-air flow

***Amount of water***

Fig. 4-25 illustrates the total amount of water flowing through the test section as a function of time when either pulsed water-air flow or continuous water flow was applied to rinse the pre-cleaned test section.

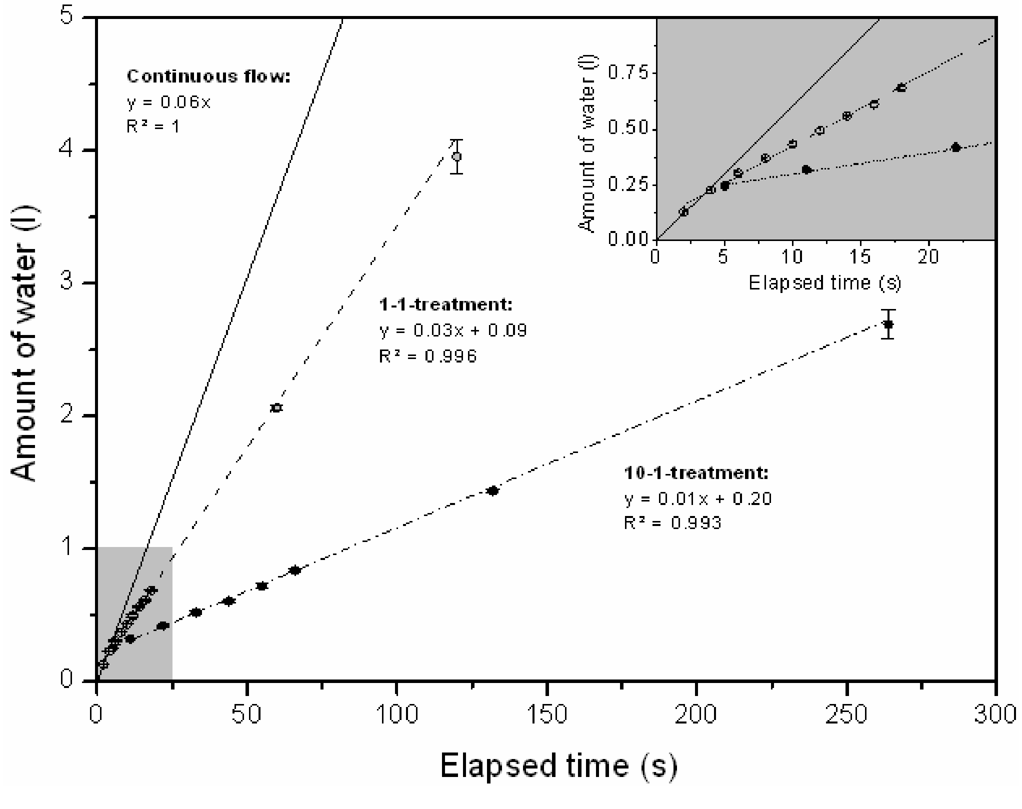


Fig. 4-25: Total amount of water flowing through the test section as a function of time when either pulsed water-air flow (1-1-treatment and 10-1-treatment) or continuous water flow was applied to rinse the pre-cleaned test section. Error bars indicate standard deviations (n = 3).

As can be seen from the slopes of the trend lines in Fig. 4-25 significantly less water ran through the test section over time with the pulsed flow treatments compared with continuous water flow. The detail in the upper right hand corner of Fig. 4-25 illustrates that at the very beginning of the rinsing procedure the amount of water that flowed through the test section within the first 5 - 7 s did not significantly differ between the continuous and the pulsed-flow treatments. This was because the test section had been filled with rising water before the RRV®s and shut-off valves were released and the actual rinsing process including measurements started. As a result of this, the air did not reach the nozzle most distant from the water inlet before all of the water had been pushed out of the test section. The trend lines used for calculating the amount of water consumed in the pulsed-flow treatments do therefore not pass through origin. This is important since the amount of water consumed in the pulsed flow treatments would have been underestimated, particularly at the very beginning of the rinsing procedure, if trend lines through origin had been used.

Fig. 4-26 depicts the flow rate at nozzle positions 1 through 6 when either pulsed water-air flow or continuous water flow was applied to the test section. The data used to create this figure was the same as in Fig. 4-25.

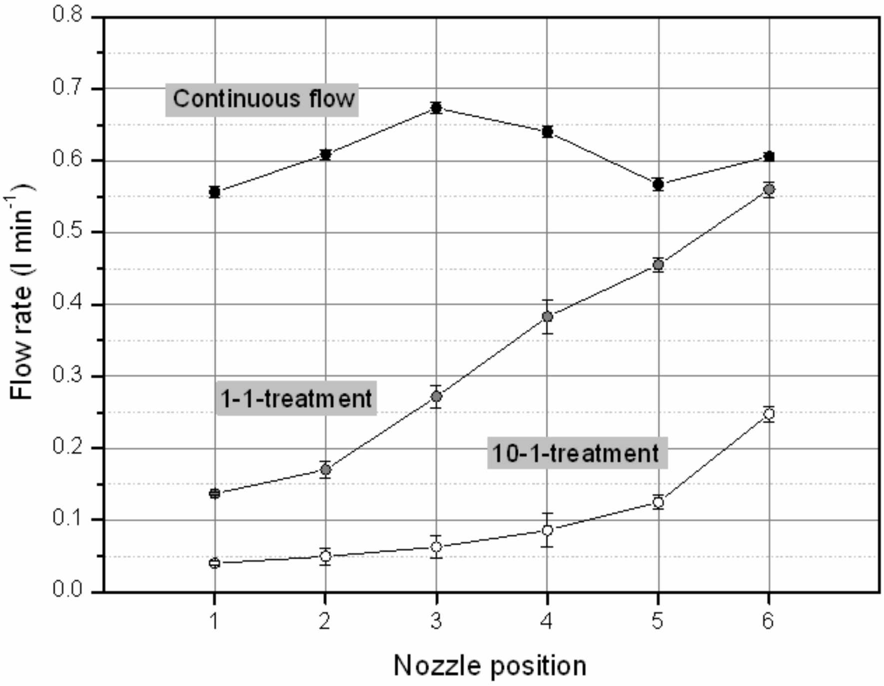


Fig. 4-26: Rinsing water flow rate at nozzle positions 1 through 6 when the test section was rinsed using either pulsed water-air flow (1-1-treatment and 10-1-treatment) or continuous water flow. Error bars indicate standard deviations (n = 3).

As the data plotted in Fig. 4-26 illustrates the flow rate was almost constant at all nozzle positions when the water flow was continuous (compare section 4.3.2) but strongly depended on nozzle position when the water flow was pulsed. With both pulsed-flow treatments the flow rate at the nozzle increased as the distance from the air/water inlet increased. With the 1-1-treatment flow rates ranged from 0.13 l $\text{min}^{-1}$ (nozzle 1) to 0.56 l $\text{min}^{-1}$ (nozzle 6) whereas with the 10-1-treatment flow rates ranging from 0.04 l $\text{min}^{-1}$ (nozzle 1) to 0.25 l $\text{min}^{-1}$ (nozzle 6) were measured. The reason behind this was the air which reached the nozzles near the water inlet first but kept pushing the water through other nozzles. One by one each nozzle position ran out of water which resulted in the last nozzle being supplied with significantly more water than those closer to the air inlet. With the 10-1 treatment this could lead to air streaming through the first nozzles for the most part of the rinsing procedure while at other more remote positions water was the predominant medium streaming through the nozzles. The average amount of effluent per pulse of nozzles 1 to 6 ranged from ca. 5 ml to ca. 19 ml (1-1-treatment) and from ca. 7 ml to ca. 46 ml (10-1-treatment).

***Dynamics of the pulsed water-air flow***

Fig. 4-27 and Fig. 4-28 show the alternating air-water flow through the test section as measured by the conductivity measuring cells when the air tank was either alternately open/closed for 1 s (Fig. 4-27) or alternately open for 10 s and closed for 1 s (Fig. 4-28). Time = 0 marks the instant where the air tank was opened for the first time.

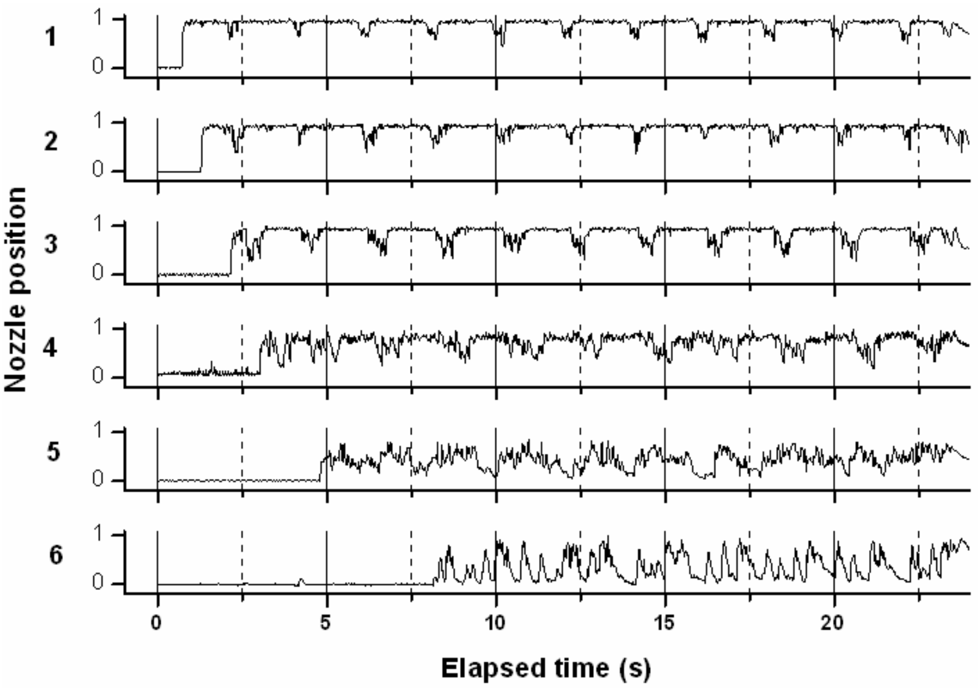


Fig. 4-27: Water-air flow through the test section as measured by the conductivity cells at different nozzle positions when the air tank was alternately open for 1 s and closed for 1 s. 0: only water in the sensor, 1: only air in the sensor.

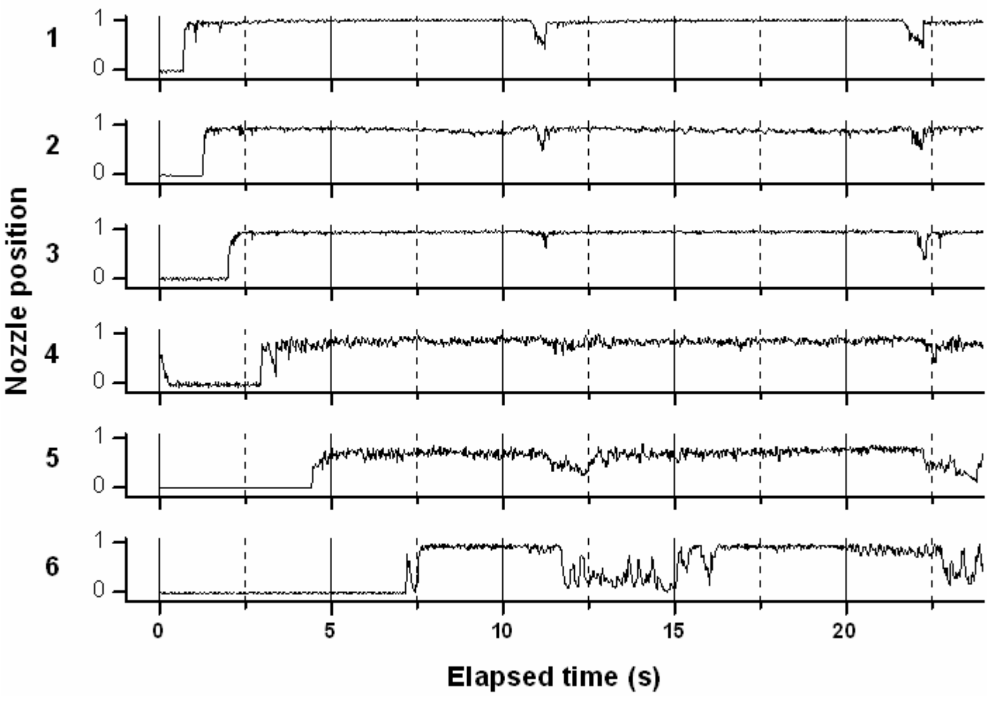


Fig. 4-28: Water-air flow through the test section as measured by the conductivity cells at different nozzle positions when the air tank was alternately open for 10 s and closed for 1 s. 0: only water in the sensor, 1: only air in the sensor.

In both cases the air arrived at the first nozzle ca. 1 s after air tank opening whereas it took ca. 7 s for the air to reach nozzle 6 since the air had to press out water that was initially in the pipe. At nozzles 1 to 3, distinct sensor signals indicate an alternation of air and water. The observation that these signals did not reach 0 suggests that the voltage drop caused by small water portions running through the sensors was not fully detected at the given sampling rate (50 Hz). To give an example, the average amount of water per pulse could be as low as 5 ml (1-1-treatment) and 7 ml (10-1-treatment). Signals from sensors at nozzles 4 to 6 appeared less defined as the effluent at these nozzle positions was composed of a water-air mixture rather than distinct water-air slugs. This could have been what GRASSHOFF & REINEMANN (1993) described as “dispersed bubble flow” and “plug flow” where the ratio of gas to liquid is rather low.

***Cleaning effect***

Fig. 4-29 shows the concentration of simulated pesticide in the rinsing water at nozzle 6 as a function of the amount of water when either continuous or pulsed water flow was applied to the test section.

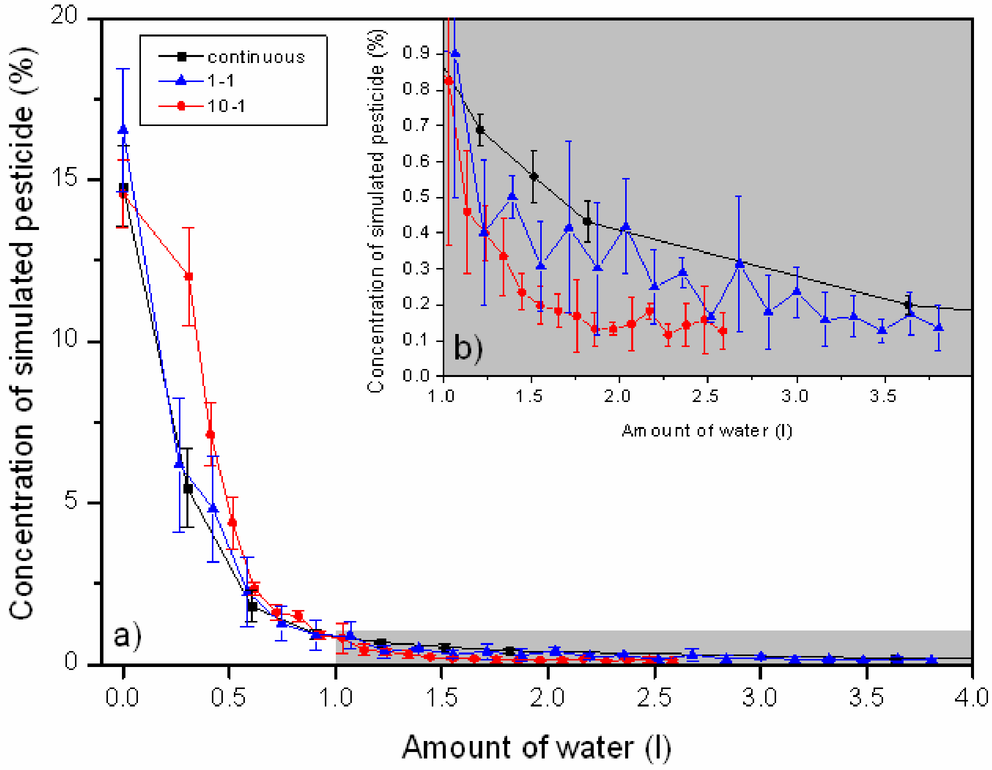


Fig. 4-29: Concentration of the rinsing water at nozzle 6 as a function of the amount of water. Water flow was either continuous or pulsed (1-1: air tank alternately 1 s open and 1 s closed, 10-1: air tank alternately 10 s open and 1 s closed). Pre-cleaning with pressurized air: 30 s at 300 kPa. Error bars represent standard deviations (n = 3).

The rinsing curves in Fig. 4-29 indicate that pulsed water-air flow improved the cleaning efficiency of the rinsing water. At the very beginning of the pulsed flow treatments a given amount of rinsing water carried more of the simulated pesticide out of the test section than in the continuous flow treatment (see Fig. 4-29a), leading to a faster decline of concentrations of the simulated pesticide in the rinsing water later on (see detail Fig. 4-29b). The initial concentrations in the effluent could be higher than 15% following a 30 s pre-cleaning procedure which was in accordance with findings discussed earlier (see section 4.3.1). The 10-1-treatment was more efficient than the 1-1-treatment probably because of the high proportion or air. This led to higher absolute flow velocities of the rinsing water and stronger mechanical effects in the 10-1-treatment where the test section had been emptied almost completely through pressurized air when water entered the test section again (Fig. 4-28). At that point, the water only had to oust the fast escaping air and therefore quickly entered the test section. Processing the data depicted in Fig. 4-28 showed that it took ca. 0.76 s for the rinsing water to travel from nozzle 1 to nozzle 6 as it entered the “empty” test section. This corresponds to a flow velocity of ca. 3.3 m $s^{-1}$ which was almost seven times faster than the average flow velocity with continuous rinsing (0.48 m $s^{-1}$).

GRASSHOFF & REINEMANN (1993) reported that velocities of migration of slugs in their experimental milking system were between 5 and 17 m $s^{-1}$ and therefore considerably higher than what is usually achieved with conventional circulation cleaning (1.5 - 2 m $s^{-1}$). The authors noted that wall shear stress at the pipe wall can be described as the product of the fluid’s density, a friction factor and the squared fluid velocity (GRASSHOFF & REINEMANN, 1993). Therefore, slug-flow led to average wall shear rates of 50 and 150 N $m^{-2}$ which was 10 - 30 times higher than with conventional circulation. This formula applied to the average flow velocities observed with continuous rinsing and the 10-1 treatment resulted in average wall shear rates of 2 N $m^{-2}$ and 53 N $m^{-2}$ respectively so the factor by which wall shear rates increased was ca. 25. Despite this improvement the results also show that, due to the comparatively low flow velocities, mechanical action in this study was rather low compared with what is commonly achieved in dairy cleaning operations. However, in the literature there are also examples where pulsed water flow only had a minor effect on the removal of the soil used (e. g. JENSEN et al., 2007).

A disadvantage of using pulsed water-air flow to clean the DIS test section becomes apparent from Fig. 4-30, particularly with a view to in-field operations. It shows the concentration of the effluent at nozzle 6 as a function of time when the water flow was either continuous or pulsed. The concentration data used to create the graphs was the same as in Fig. 4-29.

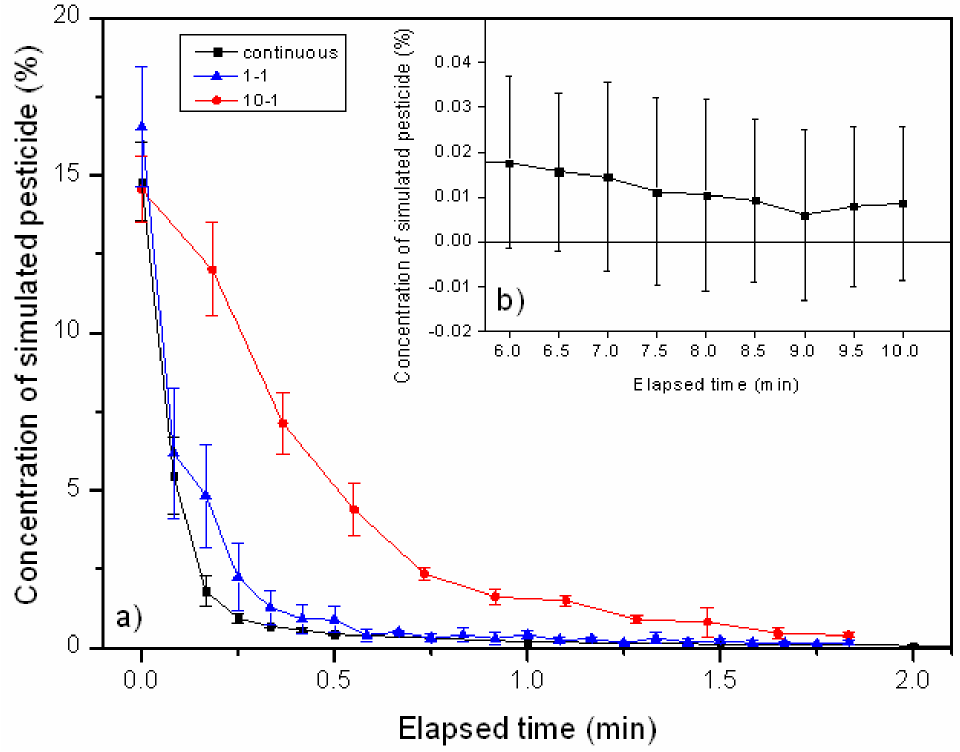


Fig. 4-30: Concentration of the rinsing water at nozzle 6 as a function of time. Water flow was either continuous or pulsed (1-1: air tank alternately 1 s open and 1 s closed, 10-1: air tank alternately 10 s open and 1 s closed). Pre-cleaning with pressurized air: 30 s at 300 kPa. Error bars represent standard deviations (n = 3).

It becomes apparent that the increased effectiveness of the water could only be realized through an increased expenditure of time, particularly with the 10-1-treatment. Even with continuous rinsing (which was the fastest cleaning procedure) it took almost 10 min for the concentration of the simulated pesticide in the rinsing water to reach 0.01% (Fig. 4-30b). Depending on the actual pesticide used this concentration could still cause biological damage, particularly when low dose herbicides, such as sulfonyl-ureas, are used (READ & TAYLOR, 1998). With a wide boom DIS sprayer this cleaning procedure would be likely to be even more time consuming due to longer injection pipes. What is more, the 10-1-treatment consumed ca. 30 l of air for each 10 s long air pulse, which means there were restrictions due to the limited amount of pressurized air available. Another reason why the pulsed-flow treatments may not be suitable for application in the field is possible spray drift caused by air leaving the nozzles.

### 4.3.6 Effect of temperature

Fig. 4-31 illustrates the effect of rinsing water temperature on the amount of simulated pesticide residues in 500 mm long horizontal pipes made of stainless steel or PTFE after rinsing.

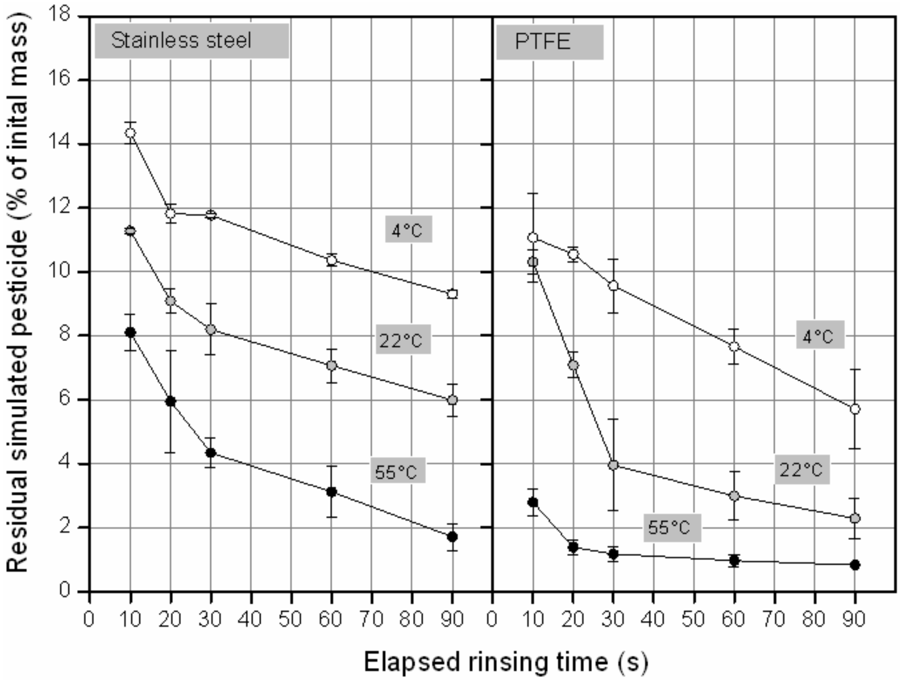


Fig. 4-31: Amount of simulated pesticide in pipes made of stainless steel or PTFE after cleaning with water at different temperatures as a function of time. Water flow rate: ca. 1 l $min^{-1}$. Error bars indicate standard deviations (n = 3).

With both materials tested hot water (55°C) led to significantly (with PTFE up to eight times) less residual simulated pesticide than cold water (4°C). This was expected since the simulated pesticide was water soluble and the dissolving power of water is known to increase with temperature (JAMES & LORD, 1992, BASF, 2007). What is more, results in Fig. 4-31 confirm the aforementioned superior cleanability of PTFE as it retained less simulated pesticide than stainless steel when rinsed with water for the same period of time and at the same temperature. Although high temperatures obviously help clean the DIS more thoroughly this approach requires hot water to be available which might not be the case on a mobile DIS. Another pre-condition would be that there are no interactions between the (real) pesticide and hot rinsing water that could cause environmental or technical damage. FISHEL (2001) stated that temperatures recommended for storing liquid pesticides are usually between 4 to 38°C, which is in accordance with recommendations of most safety data sheets of commonly used pesticides. For some pesticides temperatures of up to 54°C do not affect product safety or stability if they are not exposed to these temperatures for longer than 2 weeks (e. g. Bayer CropScience AG, 2007). This implies that with some pesticides the use of warm water (e. g. 55°C) could indeed contribute to thorough DIS sprayer cleaning. However there are temperature limitations mentioned in the German Best Plant Protection Practices according to which pesticide shall not be applied at (air) temperatures above 25°C since this could lead to substantial losses through volatilization (BMELV, 2010).

## 4.4 Cleaning of an experimental wide boom DIS sprayer

### *1) Continuous rinsing*

Fig. 4-32 illustrates the concentration of the simulated pesticide when the DIS field sprayer was rinsed continuously. The total rinsing water flow rate was 4.2 l min$^{-1}$ which equals 0.2 l min$^{-1}$ per nozzle. The nozzle flow rate was therefore three times lower than the flow rate on the test bench (compare section 4.3.2) due to modifications made to the valve in order to improve dosing behaviour and power consumption. The amount of residue that was still in the injection pipe after reclamation equalled 24% of the initial mass in the injection pipe.

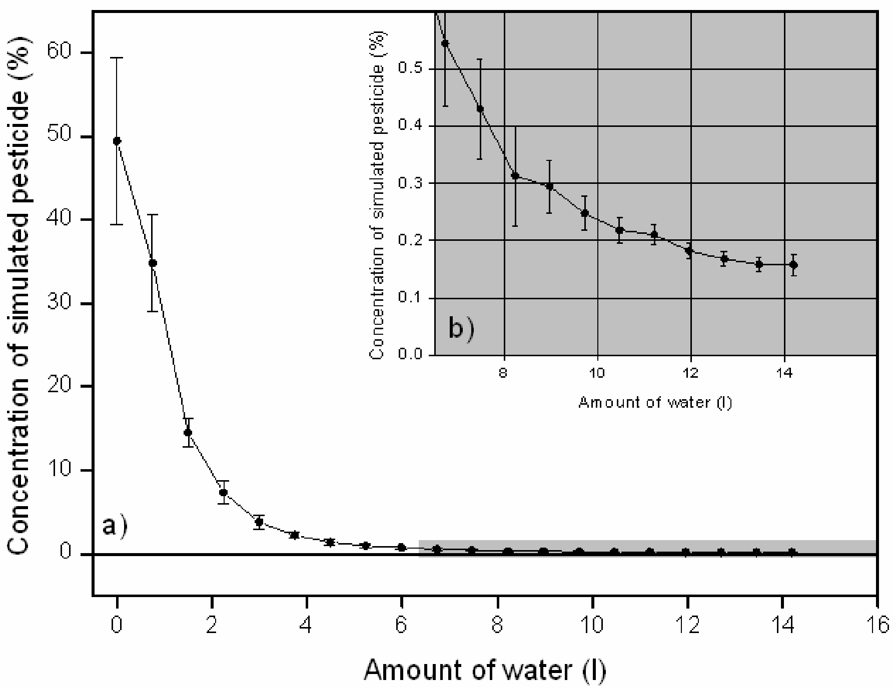


Fig. 4-32: Concentration of simulated pesticide in the effluent of the nozzle most distant from the water inlet as a function of the total amount of water used for rinsing. Error bars indicate standard deviations (n = 4).

As expected, the initial concentration of the simulated pesticide in the rinsing water (ca. 50%) was significantly higher than what was measured on the test bench where the initial concentration did not exceed 30% (see section 4.3.1). This was clearly a result of the sprayer's injection pipe being more than three times as long as the injection pipe on the test bench. The rinsing water therefore accumulated more residual simulated pesticide as it travelled from the pressure tank towards the nozzles. What may have contributed to the high initial concentration is that pre-cleaning could reclaim only ca. 76% of the simulated pesticide from the injection pipe. This was ca. 14% less than what could be achieved on the test bench where more than 90% could be removed (see section 4.2.2). The reason for this was the smaller air inlet which led to pressure loss as well as to less air streaming through the injection pipe during the push-back. The length of the injection pipe further added to the pressure loss already caused by the narrow air inlet.

While rinsing, Reynolds numbers decreased along the injection pipe as a result of decreasing flow velocities. They ranged from ca. 8900 near the tank outlet to less than 450 in the section shortly upstream of the last injection unit. The rinsing water flow in the last 3 m of the boom was therefore almost entirely laminar, based on the Reynolds Numbers mentioned by LEWIS (2008). This could have been avoided if alternative valve settings had been used. However, the dosing behaviour of the injection valves was a top priority and did not allow higher throughput rates. However, even flow rates similar to the ones on the test bench (0.65 l min$^{-1}$) would still have led to laminar flow in the most remote parts of the injection pipe.

The results depicted in Fig. 4-32 called for an alternative rinsing method because the high and inconsistent concentrations (compare section 4.3.1) would require individual valve control according to the actual concentrations. This would not be feasible due to the high complexity of the electronic control and the actual concentrations of pesticide in the rinsing water at individual nozzle positions being unknown. This is why apart from the continuous rinsing method a homogenization method was also applied to the DIS field sprayer.

### *2) Rinsing after homogenising the contaminated rinsing water*

Fig. 4-33 illustrates the rinsing curve that was measured when the contaminated rinsing water was homogenized before being pressed through the nozzles. The amount of water used for homogenization was ca. 4 l. The flow rate of the rinsing water was 4.2 l min$^{-1}$. After reclamation the amount of simulated pesticide in the injection pipe was ca. 17.4% of what was initially in the pipe. This percentage was equal to 128.7 g of residual pesticide in the injection pipe.

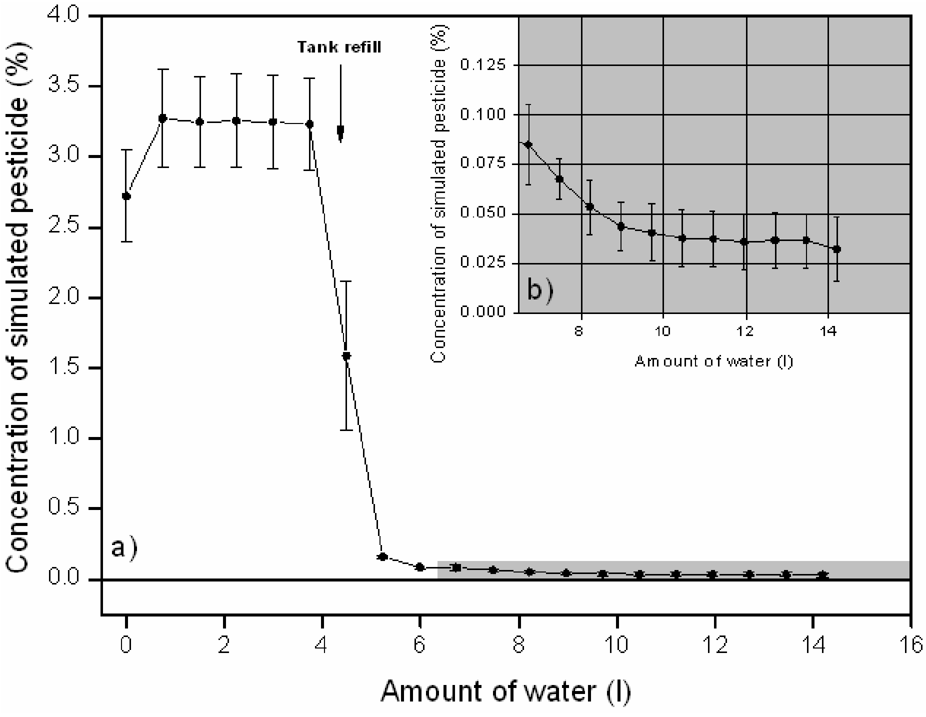


Fig. 4-33: Concentration of simulated pesticide in the effluent of the nozzle most distant from the water inlet as a function of the total amount of water used for rinsing. Error bars indicate standard deviations (n = 4).

The curve progression in Fig. 4-33 was significantly different from all other rinsing curves measured in this study. An initial concentration of ca. 2.7% was followed by a slight increase in concentration to ca. 3.2%. This concentration was then maintained until the pressure tank was empty. The arrow in Fig. 4-33 marks the instant where the cleaning process was interrupted and the pressure tank was refilled with 10 l of fresh rinsing water. What then followed was a concentration decay as already observed with continuous rinsing.

The initial concentration was almost 20 times lower with homogenization (Fig. 4-33) than with continuous rinsing (Fig. 4-32). Apart from a small initial increase in concentration (which was due to residual water in the injection unit diluting the very first sample) the first six data points in Fig. 4-33 show that the contaminated rinsing water had been thoroughly homogenized when it was leaving the nozzles. This implies that no changes in concentration over time would have to be expected during cleaning in the field and dosing valves could be controlled uniformly. Provided the concentration of the pesticide in the rinsing water was known it would be possible to inject the rinsing water into the carrier (water) at a constant injection rate.

***Suitability for field use***

The rate at which the homogenized contaminated rinsing water will have to be applied to the crop will depend on the amount of residual pesticide in the injection pipe after reclamation, the application rate of the pesticide as specified by the manufacturer, the ground speed, and the working width of the sprayer. The higher the application rate of the pesticide used, the smaller the area that can be treated with a given amount of residual pesticide will be. The higher the ground speed, the higher the required injection rate to apply a given volume of contaminated homogenized rinsing water to this given area.

In the following section the parameters and results from the abovementioned experiment (Fig. 4-33) were used to calculate the injection rates per dosing valve that would be required to inject the homogenized rinsing water into the carrier at different ground speeds, if pesticides of different application rates were used. This theoretical consideration is crucial since the dosing valves have a limited range of flow rates. This means there could be restrictions with respect to the amount of water that can be used for homogenization and the time it might take for it to be applied to the crop. Although the above experiment included only one half of the sprayer boom, the following considerations refer to the full working width (= 21 m) including 42 nozzles.

As mentioned earlier, ca. 17.4% (= 128.7 g) of the simulated pesticide were still in the test section (= half working width) after reclamation, bringing the theoretical total pesticide load in the entire boom to 257.4 g. In order to achieve the same homogeneous concentration as in Fig. 4-33 (ca. 3.2%) 8 l of water (instead of 4 l) would have been necessary. Application rates of common liquid herbicides for cereals in Germany range from 0.1 l ha$^{-1}$ to 3.0 l ha$^{-1}$ (ANONYMOUS, 2011). This means the 257.4 g of residual pesticide in the injection pipe would have been enough to treat an area of between ca. 2.6 ha (0.1 l ha$^{-1}$) and 0.1 ha (3 l ha$^{-1}$), if one of these herbicides had been used. According to SÖKEFELD et al. (2004) the relevant range of ground speeds for DIS is from 6 to 12 km h$^{-1}$. Fig. 4-34 depicts the calculated required injection rates of the homogenous rinsing solution as a function of ground speed for pesticides of different application rates. For this calculation the amount of water for homogenization of the aforementioned 257.4 g of residual pesticide was assumed to be 8 l. The working width of the sprayer was assumed to be 21 m. The assumed number of nozzles (each with one RRV®) was 42.

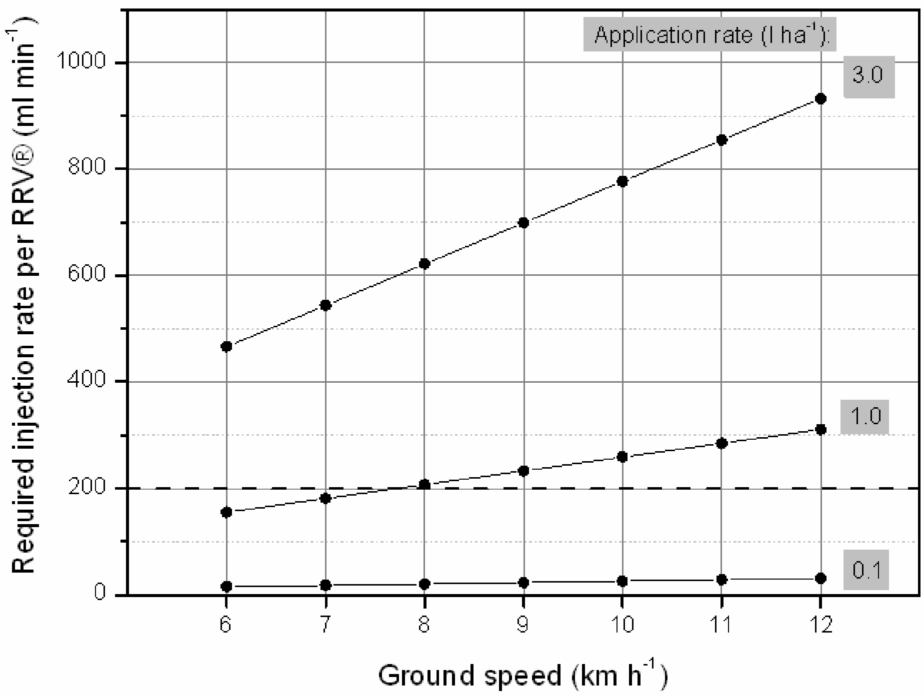


Fig. 4-34: Required injection rate as a function of ground speed and at application rates of either 0.1 l ha$^{-1}$, 1.0 l ha$^{-1}$, or 3.0 l ha$^{-1}$.

The dashed line in Fig. 4-34 (at 0.2 l min$^{-1}$) represents the maximum injection rate of each of the RRV®s on the experimental sprayer. The fact that the curve for a high application rate of 3 l ha$^{-1}$ lies considerably above the red line indicates that the homogenized rinsing water would have been too diluted to be applied through the narrow RRV®s, if 257.4 g of a pesticide of this application rate had been homogenized with 8 l of water. The same is true for the middle application rate of 1.0 l ha$^{-1}$ at ground speeds of 8 - 12 km h$^{-1}$. This problem can be avoided through lower ground speeds and through higher pesticide concentrations in the rinsing water (e. g. less water for homogenisation). To give an example, required injection rates for an application rate of 3.0 l ha$^{-1}$ would have ranged from 58 - 116 ml min$^{-1}$ at 6 - 12 km h$^{-1}$ if only 1 l of water had been used for homogenisation. For an application rate of 1.0 l ha$^{-1}$ required injection rates would have decreased to 97 - 194 l min$^{-1}$ if 5 l of water had been used for dilution of the 257.4 g residual pesticide. For the low application rate of 0.1 l ha$^{-1}$ the required injection rates in

Fig. 4-34 do not exceed the maximum injection rate of the RRV®s as they range from only 16 to 31 ml min$^{-1}$.

Hypothetical times taken for the push-out of the homogeneous rinsing water can be derived from ground speed, working width, amount of residual and the required application rate. For the required injection rates below 0.2 l min$^{-1}$ in Fig. 4-34 the times that would be required for the DIS to apply all of the homogenized rinsing water to the field would range from 1.1 min (1.0 l ha$^{-1}$, 7 km h$^{-1}$) to 12.3 min (0.1 l ha$^{-1}$, 6 km h$^{-1}$). However, this does not include the time taken for homogenization. What is more, after the homogenized rinsing water has been pushed out of the pressure tank, the sprayer would still have to be cleaned like a conventional sprayer (which may take another 10 to 15 min or even longer), if a very tenacious low-dose sulfonly-urea herbicide was used.

# 5 Conclusions

A test bench representing a 3 m wide boom section of a DNIS was developed, allowing for detailed investigations of the parameters influencing the cleaning process.

Instead of real pesticides, safe-to-use PVP solutions were used to contaminate defined test sections in a controlled manner. The simulated pesticides were tested for dynamic viscosity, density, and surface tension. Viscosities in cleaning experiments ranged from ca. 50 mPa s to ca. 1400 mPa s, a scope that can be seen as representative of viscosities of real pesticides. In most experiments the viscosity of the simulated pesticide used was ca. 250 mPa s, which was more viscous than most approved pesticides in Germany. Densities and surfaces tensions were very close to the ones of water. The simulated pesticide was a water-based formulation and therefore only represented pesticides that are water soluble concentrates. Methods for quantification of residual simulated pesticide were identified and used. They included gravimetrical measurements as well as conductivity measurements. Both allowed continuous and discontinuous data acquisition.

Drain-out experiments showed that some of the materials tested differed considerably with regard to their ability to be cleaned. PTFE retained the least residues but the literature assumed that it may not be the best engineering material as it can be porous and difficult to machine. The drain-out experiments also showed that the viscosity of the pesticide will likely affect the cleanability of DIS more than the material, provided the materials are resistant to the product and are non-porous.

The amount of residual simulated pesticide in the injection pipe after reclamation could be as high as 20% of the initial pesticide mass at low air pressure (300 kPa) and less than 8% at high air pressure (500 kPa). The pressurized air used for reclamation proved to be most effective at the beginning of the push-back, while only marginal further removal of residual pesticide could be realized once the “core” had been pushed out of the injection pipe. Applying very large amounts of air during the push-back can therefore not be recommended for DIS. Instead, a limited amount of air should be used as effectively as possible, e. g. through application of high air pressures.

The maximum concentration of simulated pesticide in the rinsing water could be as high as 30% for a 3 m test bench. This is more concentrated than conventional spray mixes and would require further dilution if a real pesticide was used. Extended pre-cleaning times could reduce the maximum initial concentration to ca. 20%. Through additional water inlets the initial concentration could be further reduced to ca. 5%. However, this did not solve the problem of concentrations being different at different nozzle positions during the rinsing process. This could only be achieved through homogenization of the contaminated rinsing water.

The degree of cleanliness of the DIS could not be determined by a general threshold describing the pesticide's concentration in the rinsing water. The reason for this is that application rates vary significantly among different pesticides. On the test bench, concentrations of simulated pesticide in the rising water could be as low as 0.01% after 10 min of rinsing. This concentration would still be equal to conventional spray mixture, if a low-dose sufonyl-urea herbicide was used. However, if the product was a high-dose pesticide this concentration would be 100 times more dilute than conventional spray mixture, which would then comply with concentration thresholds established in the literature.

Water at high pressure proved to remove residual simulated pesticide more efficiently than water at low pressure. Although the results from the test bench did not differ significantly, it can be assumed that with a wide boom DIS sprayer water savings are possible through rinsing at high water pressures.

A 5 min residence time of the rinsing water in the test section led to higher concentrations at the beginning of the rinsing process and lower concentrations later on, compared with continuous rinsing. Water and time savings were ca. 25%. Extending the residence time to 30 min did not lead to more water or time savings.

The effectiveness of the rinsing water could be improved by applying pulsed water-air flow. However, this was only possible through application of large volumes of pressurized air, which may not be available on a mobile DIS field sprayer. What is more, the release of air through the nozzles may result in unacceptable spray drift and can therefore not be recommended for field use.

Hot rinsing water removed considerably more of the simulated pesticide from test sections made of either stainless steel or PTFE than cold water. According to safety data sheets of common pesticides in Germany, certain pesticides are resistant to temperatures higher than 50°C, while most of them are not. However, this implies that the use of hot or warm rinsing water can be an option for at least some pesticides used in DIS.

Comparative experiments on a wide boom DIS sprayer confirmed the expectations derived from the test bench experiments. The amount of residual simulated pesticide after reclaiming ranged from 17 - 24%. With continuous rinsing, the maximum initial concentration of simulated pesticide in the rinsing water was ca. 50%. An alternative method which included the homogenization of the contaminated rinsing water was developed. By applying this method, the concentration of the simulated pesticide in the rinsing water was reduced to 3% and remained constant throughout the rinsing process. This makes this method suitable for field use, as it allows for the injection valves of the DIS field sprayer to be controlled uniformly when applying the contaminated rinsing water to the field. However, the amount of residual pesticide in the injection pipe must be known.

Theoretical calculations showed that the required injection rates could exceed the maximum flow rate of the dosing valves, if high quantities of water were used for homogenization. Therefore, a preferably small amount of water seems to be the best option for homogenization when the wide boom DIS sprayer is to be cleaned after operation in the field.

Although the aforementioned homogenization method seems to be a promising procedure for cleaning in the field, there clearly is the need for more research on factors influencing the cleaning process and more development of cleaning processes, as the DNIS has not yet been tested using real pesticides. Apart from its cleanability, the future success of this DNIS will also depend on the system’s dosing behaviour and the availability of automatic weed sampling techniques as well as the saving of time, pesticide, and costs that can be realized through the DNIS technology. However, this can only be completely reviewed when the DNIS has been operated in the field under real-life conditions.

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