Journal of Consumer Protection and Food Safety
https://doi.org/10.1007/s00003-024-01498-5

Journal of Consumer Protection and Food Safety
Journal für Verbraucherschutz und Lebensmittelsicherheit

METHODS

Optimizing exposure data collection for plant protection products: identifying ideal collectors with the fluorescent dye pyranine

Annika Ehmke[1] · Jens Karl Wegener[1] · Andreas Melfsen[2] · Eberhard Hartung[2]

Received: 13 September 2023 / Revised: 24 January 2024 / Accepted: 2 February 2024

Abstract

When approving plant protection products, exposure data are required for risk analysis. Exposure data can be collected for various exposure pathways, such as dermal, inhalation or ground sediment. For measuring exposures, pyranine, a fluorescent dye, and a collector can be used. However, the choice of collector material depends on the specific exposure pathway. This study aims to determine the most suitable collector, in combination with the tracer pyranine, for recording exposure through different pathways in practical trials.

Seven different collectors (Tyvek®, labels, plastic patches, paper patches, nylon filters, fibreglass filters, petri dishes) were subjected to laboratory and field tests to assess various quality parameters. Blank values, recovery rates, storability, and fluorescence degradation under UV-radiation were measured. Based on the results, a matrix was created summarizing which collector might be best suited to capture each exposure pathway. Almost all collectors demonstrated high recovery rates (Tyvek® 100%; labels 100%; plastic patches 100%; paper patches 100%; nylon filters 95%; fiberglass filters 60.9%) as well as good storability. Furthermore, all plastic-based collectors (labels, Tyvek®, plastic patches, petri dishes) showed a very good recovery rate above 95% when exposed to UV-radiation. However, nylon filters were not suitable for utilization under field conditions due to the rapid degradation of fluorescence under UV-radiation (recovery rate: 20–56%). Nevertheless, nylon filters showed stable recoveries under protected conditions and can be used to assess inhalation exposures under these conditions. Fibreglass filters, with recovery rates of 84–86%, were well-suited for testing inhalative exposures outdoors when a correction factor was applied. Tyvek® was the most suitable material for detecting total dermal exposure under field conditions. This is due to its quality characteristics and availability in a variety of sizes. Finally, petri dishes were ideal for collecting ground sediments.

Keywords Exposure measurements · Collectors · Fluorometry · Pyranine · Exposure pathways · Plant protection products

1 Introduction

To assess pesticide application risks, it is necessary to have an understanding of various drift pathways through which pesticides can impact human health or penetrate the environment, is required. In general, methods for gathering exposure data can be divided into 2D and 3D drift collecting (BfR 2023). Exposures via ground sediments (2D drift) and inhalative and dermal exposures (3D drift) were considered in this study. These different routes of absorption are known as exposure pathways (UBA 2018). Moreover, exposure measurements take place under practical conditions in the field or under protected environmental conditions (e.g., wind tunnel). Estimates of exposure are generated using models with extremely conservative assumptions. Data from measured exposures can be used to improve and/or validate these models (BfR 2023).

Fluorescent dyes as tracer in combination with collectors simulate pesticide behavior and movement (Pergher 2001; Salyani and Cromwell 1992). The dyes have no impact on

✉ Annika Ehmke
annika.ehmke@julius-kuehn.de

[1] Federal Research Centre for Cultivated Plants, Institute for Application Techniques in Plant Protection, Julius Kühn-Institute (JKI), Messeweg 11/12, 38104 Braunschweig, Germany

[2] Institute of Agricultural Engineering, Kiel University, Max-Eyth-Straße 6, 24118 Kiel, Germany

the spray liquid's physical characteristics, therefore, spray patterns and droplet sizes are unaffected (Fritz et al. 2011). High sensitivity, selectivity, and quick analytical methods for quantification are further advantages of fluorescent dyes (Cai and Stark 1997). Pyranine is a suitable tracer for spray drift determinations due to its minimal degradation over the necessary time period for sample collection, processing, and measurement (Nairn and Forster 2015). The Julius Kühn-Institute (JKI) guideline for measuring pesticide direct drift in the field also suggests using pyranine 120% when testing plant protection devices (Julius Kühn-Institut 2013). It has a low detection limit ($<1*10^{-4}$ µg/ml) (Nairn and Forster 2015), is water-solule, and can be removed from a variety of collectors with different surfaces, particularly plastic surfaces. Moreover, it is characterized by a high recovery rate (Herbst and Wygoda 2006) and a robust storability. When stored in the dark for >2 weeks, no degradation in fluorescence was observed, whether in a solution or a dried deposition on steel plates as collectors (Nairn and Forster 2015). The deposits of water-soluble pyranine demonstrated remarkable storability in the dark even after 8 weeks (Khot et al. 2011) with a maximum degradation of 3% on plastic cards. Herbst and Wygoda (2006) also discovered that after 8 days of storage in the dark, fluorescence did not decrease on artificial targets, petri dishes, and paper patches. On the paper patches it even increased slightly. Only on the rye leaves the fluorescence noticeably decreased.

Some fluorescent dyes have been shown to be photosensitive. When exposed to UV-radiation, the fluorescence intensity decreases (Cai and Stark 1997; Cross et al. 1997; Goering and Butler 1974; Salyani 1993). For instance, when exposed to cumulative UV-radiation of 0.92 MJ/m^2, the 5 fluorescent dyes BASO Red 546, Brilliant Sulfaflavine, Fluorescein, Uvitex OB, and Rhodamine showed variable degrees of fluorescence degradation on paper targets of 73%, 8%, 71%, 18%, and 7%, respectively (Pergher 2001). The level of fluorescence degradaton under V-radation is influenced by a number of variables in addition to the choice of dye, including tracer concentrations, tracer droplet sizes, and collector types (Khot et al. 2011; Salyani 1993, 2003). For example, the fluorescence intensity of a pyranine solution decreased by 30% after 300 min of direct UV-radiation (Ehmke et al. 2023b). A fluorescence degradation for pyranine of 17% and 15% was observed on paper patches and plant leaves within 10 min under UV-radiation. When exposed to UV-radiation for 60 min, it further decreased by 40%. Otherwise, on petri dishes, white and black plastic, there was only a decrease in fluorescence of 0–5%. The degradation on these collectors did no change noticeably even after a long exposure to UV-radiation (Herbst and Wygoda 2006). Pyranine 10 G (Keystone Co., Chicago, IL USA) on steel plates and plastic cards showed a similar behavior (Khot et al. 2011; Nairn and Forster 2015). Depending on the experimental conditions and the exposure pathway under investigation, widely varying liquid volumes can occur. Therefore, the collector must be evaluated for its suitability with varying liquid quantities. It is important to investigate the stability of fluorescent dyes as well as the degradation of fluorescent deposits during storage and exposure to UV-radiation before applying them in field experiments for drift and exposure measurements (Khot et al. 2011), especially with the associated collector.

Butler Ellis et al. (2010) used Tyvek® coveralls to quantify potential dermal exposures to adult and child mannequins. This was done in combination with the food dye Brilliant Blue as a tracer. A common collector used for ground sediment measurements are petri dishes. Petri dishes are used at the JKI for drift measurements (Julius Kühn-Institut 2013). Data on drift and exposure are often collected using fluorometry. The comparison between different studies is difficult because various collectors and dyes were used.

This study aimed to determine the most suitable collector, in combination with the tracer pyranine in order to record different exposure pathways in future practical trials. The following questions were examined:

- What are the quality characteristics of individual collectors with regard to:
    - blank values
    - recovery rates (under laboratory and practical conditions)
    - storability?
- How to evaluate the quality parameters of a collector and derive the suitable field of application?

2 Materials and methods

2.1 Pyranine

This work used Pyranine 120% (TER Chemicals) as a fluorescent dye. It is a highly water-soluble yellow-green sodium salt powder and the JKI used it for years as a tracer for different technical tests, in particular for drift tests, due to its high fluorescent and hazard-free properties.

2.2 Collectors

Different collector materials (Table 1) were investigated for the following quality parameters in combination with pyranine: blank value, recovery rate (in the laboratory and in the field), and storability. All these parameters are important for later measurements of various exposure pathways

Table 1 Overview of the collectors including the manufacturer, area, material, typical amount of deionized water, and shaking time for sample analysis with the fluorometer

	Manufacturer	Type	Area [cm²]	Material	Deionised water* [ml]	Shaker time [min]
Paper patches	Macherey-Nagel (Düren, Germany)	MN 615, Ø 125 mm	122.72	Cellulose	40	10
Labels	Labelident (Schweinfurt, Germany)	ERT-F075, Ø 75 mm	44.18	Polypropylen	20	10
Tyvek®	Dupont (Wilmington, USA)	500 Xpert, cat. III type 5-B/6-B	36	Polyethylene	20	10
Plastic patches	Leitz (Stuttgart, Germany)	4770-00-02 Standard, A4	36	Polypropylen	20	10
Nylon filters	Noname[5]	hydrophilic, pore size 0.22 µm; Ø 50 mm	18.82	Nitrocellulose	20	40
Fibreglass filters	Machery-Nagel (Düren, Germany)	MN 85/220; pore size 0.22 µm; Ø 55 mm	18.82	Borosilicate glass microfiber	20	60
Petri dishes	Greiner Bio-One (Kremsmünster Austria)	Ø 145 mm, with vents; Ø 94 mm with vents	56.7 or 153.94	Polystyrene	20 or 40	10

*depending on the size of the used petri dish

[5] Available at: https://www.ebay.de/itm/154432890091

under field conditions. The different collector materials differ in properties and collector size (Table 1). With the exception of Tyvek® and plastic patches, all other materials are of circular shape. Tyvek® is available from the manufacturer in several sizes and shapes (protective coverall, tarp) and can be used in a wide range of settings. For this study, Tyvek® material and plastic patches were cut into squares (6*6 cm). Depending on the different exposure pathways, the requirements for the collectors differ. Dermal exposures require a collector attached to or wrapped around a body. Therefore, it should be flexible and preferably available in larger sizes (e.g., tarp material). For inhalation exposures, aerosol collecting pumps suck pyranine in practical tests. The collection pump has a filter head. This consists of 2 plastic rings between which the collector can be placed. A metal net placed behind the collector prevents the collectors from being sucked into the aerosol collection pumps. The collector material for inhalation exposure measurements must be permeable to air. This applies to the collectors' nylon and fibreglass filters, which have pore sizes of 0.22 µm (Table 1). Therefore, these filter heads are also considered in these investigations. For measuring ground sediments, collectors must be able to lay horizontally on the ground, in order to avoid contamination. Depending on the collector, there is a defined amount of deionised water and a certain shaker time necessary for the analysis.

2.3 Methods

The preparation and analysis steps for all materials and tests were identically except for the blank values. From the initial solution of 1 g pyranine/l deionised water, a diluted solution of 20.000 µg/l was prepared. The corresponding amount of this solution was used to contaminate the collectors with a pipette, so that after the addition of deionized water and the given shaking time (Table 1), the target concentrations (Table 2) were obtained. All samples were excited at the fluorometer (Shimadzu RF-6000, Shimadzu Deutschland GmbH, Duisburg, Germany) at a wavelength of 405 nm and emitted at a wavelength of 515 nm. The radiant power of fluorescence correlated with fluorescent substance concentration. Table 2 shows the measurement repetitions and the specific target concentrations for the different collectors in the corresponding tests.

2.3.1 Blank value

Blank values were used to determine the intrinsic fluorescence of the collectors. Therefore, only the pure collector was put into a petri dish. Deionized water was added and the solution was mixed at room temperature for a defined time (Table 1). A fluorometer was used to measure the samples. The limit of detection and the limit of quantitation derived from the corresponding calibration series.

2.3.2 Recovery rates (laboratory)

For assessing the recovery rates, the collectors were contaminated with a defined pyranine solution in a petri dish to reach the corresponding target concentrations (Table 2). After drying, a defined amount of deionized water is added and the resulting solutions were gently mixed at room temperature (20 °C) for a defined time (Table 1). Again, the samples were measured with the fluorometer. For each sample, the recovery rate was calculated as a percentage of the measured concentration to the ratio of the target concentration (Eq. 1).

Table 2 Experimental overview of the collectors including the number of replicates (n) and pyranine target concentration for contamination (targetconc. µg/l)

Collectors	Trials	Blank value	Recovery rate (Lab)	Storability (Lab)	Recovery rate without UV		Recovery rate with UV	
					15 min	30 min	15 min	30 min
Paper patches	n	3	10	5			7	7
	Targetconc. (µg/l)		50	7; 700			50	50
	Storage period (d)	0	0	49			3	
	Measuring rhythm			weekly			d 1; d 3	
Labels	n	3	10	5			7	7
	Targetconc. (µg/l)		50	7; 700			50	50
	Storage period (d)	0	0	23			3	
	Measuring rhythm			every 2nd day			d 1 and d 3	
Tyvek®	n	3	10	5			7	7
	Targetconc. (µg/l)		50	50			50	50
	Storage period (d)	0	0	38			3	
	Measuring rhythm			every 3rd day			d 1; d 3	
Plastic patches	n	3	10	5			7	7
	Targetconc. (µg/l)		50	50			50	50
	Storage period (d)	0	0	9			3	
	Measuring rhythm			daily			d 1; d 3	
Nylon filters*	n	3	10	5	5	5	7	7
	Targetconc. (µg/l)		50	50	50	50	50	50
	Storage period (d)	0	0	5	3		3	
	Measuring rhythm			daily	d 1; d 3		d 1; d 3	
Fibre glass filter*	n	3	10	5			7	7
	Targetconc. (µg/l)		50	50			50	50
	Storage period (d)	0	0	5			3	
	Measuring rhythm			daily			d 1; d 3	
Petri dishes	n	3	10	5			7	7
	Targetconc. (µg/l)		50	50			50	50
	Storage period (d)	0	0	5			3	
	Measuring rhythm			daily			d 1; d 3	

*The recovery rates with UV was examined for nylon filters and fiberglass filter with and without filter heads

Equation 1

$$\boldsymbol{recoveryrate}\,(\%) = \left(\frac{\boldsymbol{conc.sample}[\mu g/l]}{\boldsymbol{targetconc.}[\mu g/l]}\right) * 100$$

Equation 2

$$\boldsymbol{storability}\% = \left(\frac{\boldsymbol{conc.sample}[\mu g/l]}{\boldsymbol{conc.referencesample}[\mu g/l]}\right) * 100$$

2.3.3 Storability

The change in recovery rates over time was utilized to assess the storage stability of the samples. Therefore, the material was prepared and contaminated in the same way as the recovery rate samples. After contamination, the samples were stored in the dark at room temperature (20 °C) for a defined period. At certain time intervals a specific number of samples were taken for analysis (Table 2). The further analyzing steps were as described for the recovery rate samples. The fluorescence from the reference value was measured on the same day as the samples were contaminated. Then the relative deviation of the recovery rate from the initial value was calculated (Eq. 2).

2.3.4 **Recovery rates under field conditions** with and without the exposure of UV-radiation

To determine whether there was a variation in fluorescence degradation depending on the different collector materials, the influence of UV-radiation on the recovery rate was investigated for all collectors. The sample preparation for the fluorometer measurement was identical to previous measurements. Half of the contaminated nylon- and fibreglass filters were exposed to UV-radiation in petri dishes and the other half in filter heads. All other collectors (paper patches, labels, Tyvek®, plastic patches, petri dishes) were contaminated and placed in petri dishes on laboratory trolleys outside the building. The samples were exposed to direct sunlight and wind. Samples of all collectors were collected after 15 and 30 min and stored in the dark until analysis. The weather data were recorded for both 15-minute measurement intervals with different devices. For the first 15 min of the experiment, the following mean values were obtained at a measurement interval of 1 min: air temperature at a height of 20 cm 21.1 °C[1], 32.9% relative humidity[2], 850 Wh/m² global radiation[3] and 6.8 m/s wind speed[4]. For the last 15 min of the experiment, the following mean values were obtained: air temperature at 20 cm height 21.3 °, 31% relative humidity, 850 Wh/m² global radiation and 7.8 m/s wind speed. Seven repetitions of each collector and each collection time were analyzed on the same day and referred as t0 values. The fluorescence from the reference value was measured directly on day 1 of contamination. Then, the relative deviation of the recovery rate from the initial value was calculated (Eq. 2). Further analyses for all collectors took place after 3 (t0 + 3) days of storage.

Nylon filters were also tested under protected conditions to determine their suitability for practical use in protected environments (without the influence of UV and wind), e.g. inside buildings. For this purpose, the contaminated samples were placed in petri dishes at the JKI test hall, away from light and wind. Analogous to the UV-radiation tests, the samples were collected after 15 and 30 min and stored protected from light until analysis. 5 repetitions were analyzed on the same day (t0). The analysis of the remaining samples took place 3 days later (t0 + 3).

2.4 Data analysis

Descriptive statistics were calculated for all data from measurements of the blank value, the storability and the recovery rates under laboratory and practical conditions using Microsoft Excel (2016). The graphics and tables were also created with Microsoft Excel (2016).

3 Results

3.1 Blank values

The blank values of all collectors were below both the detection limit (0.7 µg/l) and the quantification limit (2.1 µg/l).

3.2 Recovery rate under laboratory conditions

Figure 1 shows the recovery rates under laboratory conditions for paper patches, labels, Tyvek®, plastic patches, fiberglass filters, nylon filters and petri dishes. Ten repetitions were conducted for all materials. The petri dishes were used as a reference value (100%) for calculating the recovery rates of the other materials. In comparison, the recovery rates for paper patches, labels and Tyvek® are 100%, 99%, and 100%, respectively. Nylon filters have a 95% recovery rate. Significantly lower recovery rates were measured for fiberglass filters with a mean value of 60.9%.

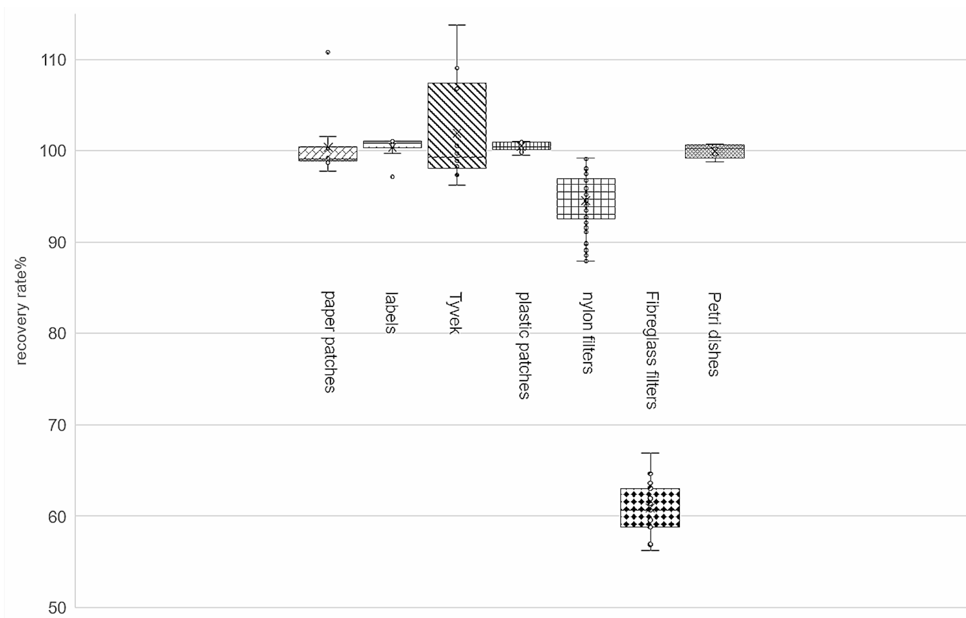

Fig. 1 Recovery rates under laboratory conditions of different collectors. All materials were contaminated by pipette with a defined target concentration of a pyranine solution. The petri dish is used as a reference and for the calculation of the recovery rates

[1] Erdoberflächen Temperaturgeber 2.1241.00.900 Thies Clima

[2] Wetter und Strahlungsschutz –compact 1.1025.55.xxx Thies Clima

[3] Pyranometer CM6B/7B Kipp & Zonen

[4] Kombinierter Windgeber 020853/08/05 Thies Clima

Table 3 Storability of different collectors ($n=5$). The mean recovery and the coefficient of variation (CoV %) are shown

Collector	Target conc. [µg/l]	Storage days [d]	Mean recoveries and coefficient of variation (CoV %)	
			Low conc.	High conc.
Paper patches	7 (low conc.); 700 (high conc.)	1	100 (2)	100 (2)
		13	100 (0)	100 (1)
		36	104 (1)	99 (1)
		49	107 (1)	100 (1)
Labels	7 (low conc.); 700 (high conc.)	1	100 (3)	100 (2)
		7	107 (6)	108 (4)
		14	99 (2)	100 (2)
		23	103 (1)	101 (2)
Tyvek	50	1	100 (1)	
		10	97 (2)	
		24	99 (4)	
		38	97 (1)	
Plastic patches	50	1	100 (3)	
		5	99 (1)	
		9	103 (1)	
Nylon filters	50	1	100 (2.1)	
		3	96 (3.1)	
		5	95 (2.4)	
Fibreglass filters	50	1	100 (0.6)	
		3	98 (0.9)	
		5	98 (0.8)	
Petri dishes	50	1	100 (0.8)	
		3	100 (0.6)	
		5	101 (0.9)	

conc. = concentration

Table 4 The recovery rate under field conditions for all collectors with UV exposure and additionally for nylon filters without UV exposure

Collector	Storage time [d]	UV exposure [min]			
		15		30	
		Recovery [%]	CoV [%]	Recovery [%]	CoV [%]
Paper patches	0	80	1	69	2
	3	80	4	71	4
Labels	0	97	1	96	1
	3	95	1	93	1
Tyvek®	0	96	4	95	5
	3	90	9	91	8
Plastic patches	0	100	3	98	1
	3	98	2	97	3
Petri dishes	0	99	1	100	5
	3	99	1	98	2
Nylon filters in filter heads	0	56	20	38	29
	3	53	19	40	22
Nylon filters	0	20	30	20	29
	3	21	39	21	6
Nylon filters in protected environment	0	102	3	99	3
	3	97	2	93	3
Fibreglass filters in filter heads	0	86	2	80	2
	3	85	6	81	2
Fibreglass filters	0	84	1	81	6
	3	84	4	84	4

CoV = coefficient of variation

Note that additional laboratory experiments have shown that the recovery rate of paper patches was highly depended on the charge batch and ranged between 24 and 100%. The batch used here had a recovery rate of 100% and therefore, represents the best case. There was no difference in quality between different batches for all other used materials.

3.3 Storability

The various collector types have various target concentrations, storage times, and measurement rhythms (Table 2). The tests were carried out in different projects at different times, which explains the various storage durations, which were not related to the collector. To determine if there was any influence of higher and lower concentrations on storability, 2 different target concentrations (7 and 700 µg/l) were included for paper patches and labels. For all other collectors, the same target concentration of 50 µg/l was used. Paper patches were stored for 7 weeks. The measurement frequency was once a week. The length of storage for labels was 23 days with the analysis every second day. Tyvek® was stored for 38 days and measured every third day. Plastic patches were stored for 9 days with daily analysis. For nylon filters, fiberglass filters and petri dishes, the storage period was 1 week and the measurement rhythm was daily.

No fluorescence degradation could be found for paper patches after 7 weeks storage compared to the starting value (reference sample), or at high/ low concentration levels. At lower target concentrations, there is even a slight increase in fluorescence at the end of the storage period (+ 7%). A similar result was found for the storability of labels over 3 weeks and the storability of plastic patches after 9 days. The final mean recovery for both materials was 103%. Also, for petri dishes, with a mean recovery of 101% no decrease in pyranine fluorescence could be detected during storage within 1 week. Tyvek® showed a small decrease in mean recovery after 38 days of 3%. The recovery rate decreased slightly for nylon filters by 5% and fibreglass filters by 2% after 5 days (Table 3).

3.4 Recovery rate under field conditions

On the first day of the analysis, a noticeable difference in the recovery rates under UV-radiation was observed for paper patches, nylon filters, and fiberglass filters in filter heads, with an increase in exposure time (Table 4). On day

1, the fluorescence of paper patches decreased after 15 and 30 min of UV-radiation (recovery rate 80% and 69%). After 3 days of storage, there was no further degradation visible. Labels and Tyvek® show only a minimal difference in fluorescence degradation (1%) with increasing UV-radiation duration. On the other hand, a reduction in fluorescence of between 6 and 4% could be observed after 3 days of storage for Tyvek®. The highest recovery rates were observed for plastic patches and petri dishes with 100 and 99% after 15 min of UV-radiation on day 1. Both prolonged UV-radiation and storage led to further fluorescence degradation. Nylon filters in filter heads showed a recovery rate of only 56% after 15 min of UV-radiation. After another 15 min, the recovery rate dropped by another 18%. Nylon filters without filter heads demonstrate the lowest recovery rates compared to all other collectors with a recovery rate of 20% after 15 and 30 min UV-radiation. A storage of 3 days did not lead to a further significant decrease in fluorescence. In contrast, nylon filters show a recovery rate of over 100% after 15 min and 99% after 30 min in a protected environment. After 3 days storage, the recovery rate decreased by 5 – 6%. Fiberglass filters with and without filter heads show similar recovery rates. The recovery rate is between 86% and 84% after 15 min of UV-radiation on day 1. A further 15 min of UV-radiation lead to a fluorescence decrease of 6% with filter heads and 3% without. Storage for more than 3 days does not lead to further significant fluorescence degradation.

3.5 Assessment matrix for different collector types

The results from the laboratory and practical tests were the basis for the matrix assessment of different exposure pathways (Table 5). The classification of recovery rates was included in the evaluation of quality parameters (recovery rate and storability) and the field of applications (protected environments or field conditions). The classification was based on a personal assessment by the authors. The table also shows what information can be collected when measuring exposures through the respective collector (total exposures, point information or exposure path). This evaluation results primarily from collector properties and available collector size/area. Whether a collector can record total exposures or point information depends primarily on the size of the material. If a collector can cover a body, total exposures can be recorded. In addition, a recommendation is made for which liquid quantities the collector seems suitable. This classification is based on empirical values from preliminary tests at the JKI.

Both the recovery rate under laboratory conditions and the storability can be considered as very good for all collectors, except for fiberglass filters (Table 5). Fiberglass filters have an average recovery rate of 61% under laboratory conditions and are therefore, were classified as satisfactory. Tyvek® was the only material considered as suitable for total exposure applications. For measuring point information, paper patches, labels, plastic patches and petri dishes were also considered as suitable. All of the mentioned collectors, except petri dishes, were assigned to the dermal exposure pathway. Nylon filters and fiberglass filters could be used for inhalation exposures and petri dishes for ground sediment exposures. Petri dishes and paper patches can be used for collecting liquid over a wide range, from low to high liquid quantities. Tyvek® for low to medium and all other collectors for lower liquid quantities. For the assessment of the field of application, the results of recovery rates under field conditions were included. All plastic materials (labels, Tyvek®, plastic patches and petri dishes) were regarded as very good for use in field trials with UV-radiation. Paper patches and fiberglass filters were considered as good/satisfactory. Nylon filters were the only collectors that were rated poorly for the use in field trials. However, nylon filters were very good for use in protected environments. All other collectors were not tested under these conditions.

Table 5 Assessment matrix for various collector types

		Paper patches	Labels	Tyvek®	Plastic patches	Nylon filters	Fibreglass filters	Petri dishes
Quality parameters	Recovery rate	++	++	++	++	++	o	++
	Storability	++	++	++	++	++	++	++
Capture from:	Total exposures	-	-	++	-	NR	NR	NR
	Point information	++	++	++	++	NR	NR	++
	Exposure path	dermal	dermal	dermal	dermal	inhalative	inhalative	ground sediment
	Liquid quantity	H	L	M	L	L	L	H
Field of application	Protected environment	NT	NT	NT	NT	++	NT	NT
	Field trials	o/+	++	++	++	-	o/+	++

The qualitative scale is as follows: ++ very good, + good, o satisfactory, - poor. A recovery rate up to 95% is classified as very good, up to 80% as good, < 80% as satisfactory and <60% as poor. NR = not relevant and NT = not tested. H stands for a high liquid quantity, M for a medium quantity and L for a low quantity

4 Discussion

In this study, various collectors in combination with pyranine were tested. The study evaluated quality factors, including recovery rates under laboratory and environmental conditions, blank values, and storability. The findings served as the basis for the assessment matrix, which provides recommendations on the most suitable material for detecting individual exposure pathways.

In terms of recovery rates, storability, and resistance to UV-radiation degradation, all collectors considered for dermal exposure measurement (paper patches, labels, Tyvek®, plastic patches), as well as petri dishes for collecting ground sediments, consistently yielded very good results in all experiments. Regarding storability, these findings are in agreement with those of Herbst and Wygoda (2006). The behavior of the collector types, nylon and fiberglass filters, utilized for inhalative exposure measurements, not only differs from that of the other collectors but also varies between them in terms of recovery rates in the laboratory and under practical conditions. Although pyranine is water-soluble, it did not guarantee effective washability for all collectors. Surface forces, incorporation into the material, or chemical reactions can all result in dye binding (Herbst and Wygoda 2006). This could be one of the reasons why fiberglass filters had a substantially lower laboratory recovery rate than nylon filters. Despite that, fiberglass filters showed no further fluorescence degradation under UV influence. Molnar et al. (2023) used fiberglass filters with an air sampling pump based on this study. These experiments measured inhalation exposures in a tractor cabin during the application of plant protection products. Because of its small pore size, the observed data show that fiberglass filters, when combined with the applied methodology, can collect even the smallest aerosol particles.

Besides, the type of the dye, the tracer concentrations, the tracer droplet sizes, and the collector types may have affected the intensity of fluorescence degradation under UV-radiation for nylon filters (Khot et al. 2011; Salyani 1993, 2003). Here, the fluorescence decreased up to a recovery rate of 20% on nylon filters under UV-radiation. Filter heads had some UV protective effects on fluorescence degradation, since nylon filters in filter heads had a recovery rate up to 38%. But overall, they seemed to be unsitable for field trials. On the other hand, they were very usable in protected environments. Under field conditions, fiberglass filters demonstrate a decrease in fluorescence with a recovery rate of up to 80%. But still, fiberglass filters were suitable for field experiments when a correction factor is used. Field recovery samples were used to determine this correction factor. Field recovery samples are contaminated with a known concentration and are exposed to the same environmental conditions and for the same duration (in a contamination-free environment) as the samples during the exposure measurement (Dawick et al. 2020). A correction factor can be calculated using the percentage reduction in the recovery rate of the field recovery samples. The correction factor is used if the recovery rate of the field recovery samples is less than 95% (Dawick et al. 2020).Visual observations from practical trials are used to asess the suitability of given collectors for various liquid quantities. For a strong data base, additional experimental work would be needed. But despite this, the result of this study provide a clear data basis for a first assessment of different collector types and a determination which material is best suited for which application scenario and amount of liquid quantities. Higher exposure quantities can only be collected in horizontally arranged petri dishes. Due to their absorbent properties, paper patches are also suitable for higher amounts of liquids, when they are attached vertically to objects, for example. Because the liquid cannot permeate the plastic material, it can only be held on the surface for a limited amount of exposure quantities. Plastic patches and labels are therefore best suited for lower exposure quantities. Although Tyvek® also consists of plastic, it has a woven structure that allows it to deal with medium exposure levels on the surface when positioned vertically. Due to our findings, Tyvek® full-body coveralls were already used in field trials with the tracer pyranine by Ahrens et al. (2023) to assess dermal exposures of bystanders (adults and kids) and by Molnar et al. (2023) to evaluate total dermal exposures of operators in the tractor cabin. Generally for inhalation exposures, small liquid amounts can be expected. Due to the pore size of nylon filters and fiberglass filters, these collectors were evaluated as particularly suitable for collecting small amounts of liquid.

5 Conclusion

- High recovery rates, good storability for various time durations and concentration levels under laboratory conditions were demonstrated for all collectors with the dye pyranine except fiberglass filters. The recovery rates for fiberglass filters were satisfactory (60%).
- If exposed to UV-radiation, the use of paper patches, labels, Tyvek®, plastic patches, and petri dishes is recommended because of the very good recovery rates.
- Tyvek® combined with pyranine is a promising material for detecting total dermal exposures in field testing.

- Nylon filters are recommended for the use in a protected environment like laboratory conditions, and fiberglass filters for use under field conditions.
- It is recommended that the charge batch of each collector should be checked before usage in practical trials for the compatibility with the individual dye, as well as for recovery rates, storability, fluorescence degradation under UV-radiation, and the expected liquid quantity to guarantee plausible, reliable and repeatable results.

Acknowledgements The author would like to thank Mrs. Marina Dercks and Mrs. Celina Ehlers for their contributions to this work.

Funding Open Access funding enabled and organized by Projekt DEAL. Some of the trials were carried out as part of the Prax REDUCE project. The project Prax REDUCE is supported by funds of the Federal Ministry of Food and Agriculture (BMEL) based on a decision of the Parliament of the Federal Republic of Germany via the Federal Office for Agriculture and Food (BLE) under the innovation support program.
Open Access funding enabled and organized by Projekt DEAL.

Data availability Raw data were generated at JKI, Federal Research Centre for Cultivated Plants, Institute for Application Techniques in Plant Protection, Messeweg 11/12, 38104 Braunschweig, Germany. The data is openly available in a public repository that issues datasets with DOIs: The data that support the findings of this study are openly available in OpenAgrar at https://doi.org/10.5073/20230614-144819-0 (Ehmke et al. 2023a).

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

Ahrens K, Röver M, Peter E, Molnar G, Martin S, Wegener JK (2023) Development of a method for measuring exposure of residents and bystanders following high crop application of plant protection products. J Kulturpflanzen 75(05–06):138–150

BfR (2023) Risikobewertung von Pflanzenschutzmitteln. Available from https://www.bfr.bund.de/de/risikobewertung_von_pflanzenschutzmitteln-70187.html

Butler Ellis MC, Lane AG, O'Sullivan CM, Miller P, Glass CR (2010) Bystander exposure to pesticide spray drift: New data for model development and validation. Biosyst Eng 107(3):162–168

Cai S-S, Stark J (1997) Evaluation of five fluorescent dyes and triethyl phosphate as atmospheric tracers of agricultural sprays. J Environ Sci Health B (6):969–983

Cross JV, Murray RA, Ridout MS, Walklate RJ (1997) Quantification of spray deposits and their variability on apple trees. Asp Appl Biol 48:217–224

Dawick H, MacDonald A, Chan J, Stevens M, Childs K, Saint-Mart J, Hamey P (2020) Proposals for new transfer coefficient (TC) values for worker re-entry activities in vineyards. https://croplifeeurope.eu/wp-content/uploads/2020/08/Final-BROV-re-entry-project-report-rev-1.pdf

Ehmke A, Melfsen A, Wegener JK, Hartung E (2023a) Dataset: Quality parameters of different collectors in combination with the fluorescent dye pyranine. Available from https://www.openagrar.de/receive/openagrar_mods_00087573

Ehmke A, Melfsen A, Wegener JK, Hartung E (2023b) Influence of the urease inhibitor suspension (Atmowell®) on the fluorescent dye pyranine and its spray and drift behavior in wind tunnel measurements. J Environ Sci Health B 58(3):210–216

Fritz BK, Hoffmann WC, Jank P (2011) A Fluorescent Tracer Method for Evaluating Spray Transport and Fate of Field and Laboratory Spray Applications. J ASTM Int 8(3):125–125

Goering CE, Butler BJ (1974) Analysis of paired microresidues using filter fluorometry. Weed Sci 22(5):512–515

Herbst A, Wygoda H-J (2006) Pyranin –ein fluoreszierender Farbstoff für Applikationstechnische Versuche. Nachrichtenbl Deut Pflanzenschutzd 54(9):233–238

Julius Kühn-Institut (2013) 7-1.5 Messung der direkten Abdrift von flüssigen Pflanzenschutzmitteln im Freiland. https://www.openagrar.de/servlets/MCRFileNodeServlet/openagrar_derivate_00000400/7-1.5%20Messung%20der%20

Khot LR, Salyani M, Sweeb RD (2011) Solar and storage degradations of oil- and water-soluble fluorescent dyes. ASABE Appl Eng Agric 27(2):211–216

Molnar G, Ahrens K, Wegener JK, Röver M, Peter E, Martin S, Dittmar S (2023) Development of a selective testing method to pesticide aerosols for characterization and comparison of agricultural tractor cabs classified according to EN 15695-1. J Kulturpflanzen 75(05–06):130–137

Nairn JJ, Forster WA (2015) Photostability of pyranine and suitability as a spray drift tracer. NZPP 68:32–37

Pergher G (2001) Recovery rate of tracer dyes used for spray deposit assessment. Trans ASABE 44(4):787

Salyani M (1993) Degradation of fluorescent tracer dyes used in spray applications. Pesticide Formulations Application Syst :215–226

Salyani M (2003) Droplet size affect durability of spray deposits. Pesticide Formulations Application Syst :221–233

Salyani M, Cromwell RP (1992) Spray and drift from ground and aerial applications. Am J Agric Biol Sci 35(4):1113–1120

UBA (2018) Expositionsschätzung. Available from https://www.umweltbundesamt.de/themen/gesundheit/belastung-des-menschen-ermitteln/expositionsschaetzung