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ENVIRONMENTAL SCIENCE FOR THE EUROPEAN REFINING INDUSTRY

Dermal Exposure Studies for Fuels and Lubricants

Giulia Pizzella
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Determination of potential for dermal exposure from transfer of lubricants and fuel by consumers

▶ **CONSUMERS**

Preliminary evaluation of the dermal exposures associated with service station refuelling activities

▶ **WORKERS**

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- ▶ Consumer and worker uses are subject to the Registration, Evaluation, Authorisation & restriction of CHemicals (REACH) legislation.
- ▶ There is limited consumer and worker dermal exposure data for these products.
- ▶ **Consumer study:** aimed to characterize the magnitude of dermal exposure to the hands and forearms, and to assess the environmental and behavioural determinants of the exposures. Products: diesel , lubricants and cycle oil
- ▶ **Worker study:** aimed at characterising dermal exposure of service station attendants. Professional exposure: PROC 8b Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities.

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Determination of potential for dermal exposure from transfer of lubricants and fuel by consumers

► CONSUMERS



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Four Exposure situations were assessed in the study:

1. Filling a fuel tank with **diesel**
2. Filling an engine with **lubricating oil** (easy)
3. Filling an engine with **lubricating oil** (filling point more difficult to reach, hard)
4. Lubricating a bicycle chain with **cycle oil**

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Approach Taken

- ▶ Ten volunteers completed a series of exposure situations to simulate the activities for a total of 80 experimental runs (20 for each operation).
- ▶ Dermal exposure was assessed using
 - ▶ a validated **wipe sampling** method
 - ▶ the products' natural fluorescence under ultra-violet (UV) light.
 - ▶ the RiskofDerm methodology
 - ▶ Covering the hands, forearms and spills

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Approach Taken

- ▶ The filling practices of participants were observed and filmed to ensure that key 'exposure defining' events were captured

Table 16 Number of tests where spills and contamination were recorded to have occurred. Also the number of tests where low, medium and high care were taken and the volunteers complied fully with the instructions.

Situation	Spills	Contaminated	Compliance	Care - L	Care - M	Care - H
ES1 Diesel	13	10	20	1	2	17
ES2 Easy	8	9	20	2	9	9
ES3 Hard	12	5	20	5	8	7
ES4 Bike	18	8	15	1	3	16

L-low; M-medium; H-high

- ▶ An estimate was made during each test of the amount of product spilled
- ▶ The reasons for contamination varied between the exposure situations.

Table 17 Estimated quantity (ml) spilled during the tests, by exposure situation.

Quantity Spilled (ml)	ES1 Diesel	ES2 Easy	ES3 Hard	ES4 Bike
0	7	12	8	2
<20	5	8	9	17
20-50	1	0	3	1
50-200	3	0	0	0
200-500	2	0	0	0
>500	2	0	0	0

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- ▶ Wipes were taken pre- and post test on each hand and forearm
- ▶ The measured mass was provided in mg and converted in $\mu\text{g}/\text{cm}^2$ using average surface area for forearm and hands

Table 22 Summary of the levels ($\mu\text{g}/\text{cm}^2$) measured at post test for dominant and non-dominant hand shown separately for whether spills were recorded to have occurred or not.

Hand	Spill? (N)	AM	GM	GSD	MIN	MAX	90th %
Dominant	No (7)	17.66	2.12	10.93	0.25	96.21	81.05
	Yes (13)	19.16	3.01	11.27	0.25	76.06	73.47
Non-Dominant	No (7)	5.91	2.29	4.08	0.25	30.13	24.71
	Yes (13)	5.74	1.26	6.08	0.25	40.62	20.41

- Significantly higher dermal exposure was observed when a lower level of care was taken to complete the task.
- the within volunteer variation was relatively large (likely due to the few high measurements)

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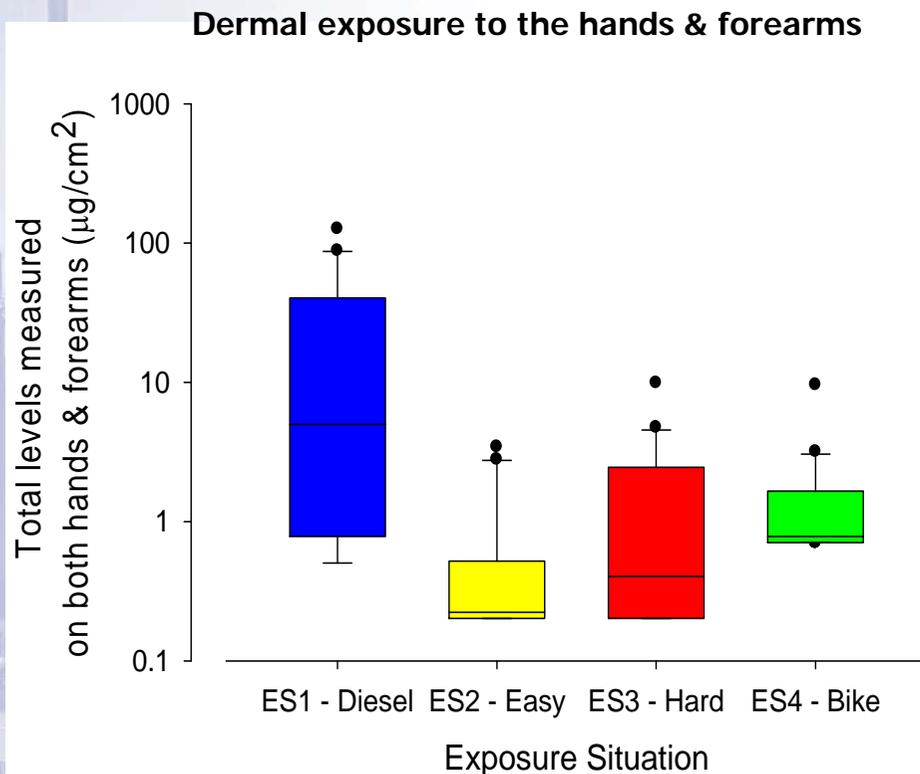


- ▶ A high proportion of samples was less than the limit of detection (ES1=38%, ES3=60%, ES2 and 4, both 78%).
- ▶ In ES2 Easy and ES3 Hard, the hand and forearm results ranged from $<0.1 \mu\text{g}/\text{cm}^2$ to $3.33 \mu\text{g}/\text{cm}^2$ and from $<0.1 \mu\text{g}/\text{cm}^2$ to $3.54 \mu\text{g}/\text{cm}^2$, respectively.
- ▶ In ES4 Bike, the hand and forearm exposures ranged from $<0.35 \mu\text{g}/\text{cm}^2$ to $5.25 \mu\text{g}/\text{cm}^2$.
- ▶ Not all volunteers fully complied with the ES4 instructions, thus highlighting that this situation may have more variability in consumer behaviour.

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Results : Dermal Transfer



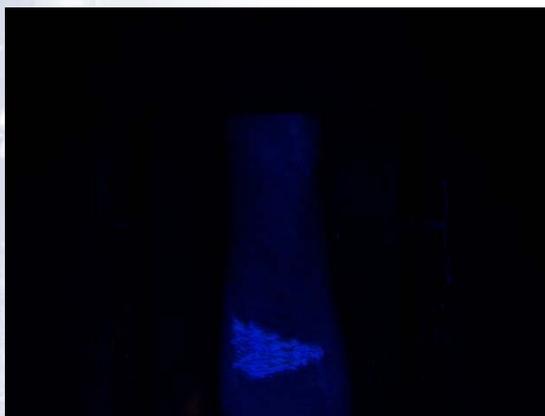
- ▶ The ratio of the total amount measured on the hands & forearms to the amount handled for ES1, 2 and 3 was less than 0.0001% whereas ES4 was 0.04%.
- ▶ There was no direct relationship between the amount handled and that measured in the wipe samples.
- ▶ For ES2, 3 and 4 both between and within volunteer variation was small.
- ▶ For ES1-diesel, the within volunteer variation was relatively large, likely due to the few very high values.

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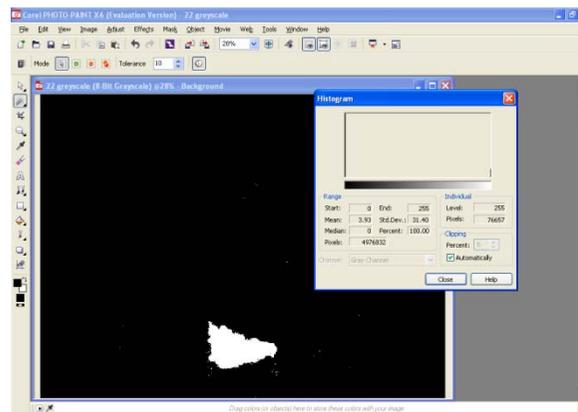
Results : Fluorescence

- ▶ As an alternative assessment of dermal exposure it was proposed that digital images of each hand (dorsal and palmar regions) and forearm would be collected under UV light in a light tight box prior to the individual completing the exposure scenario.
- ▶ Whole body images (front and back) were also be captured in a blackened out room.
- ▶ Sensitivity of fluorescent UV method only enables a qualitative assessment of dermal contact
 - ▶ Affected body locations and 'intensity' of the contamination
 - ▶ Method shown to have potential utility especially if baseline sensitivity improved via use of synthetic UV tracers (BUT issues relating to subsequent decontamination of affected equipment)



Post exposure image of left forearm under UV light

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Number of pixels fluorescing compared with pre-exposure image



Preliminary evaluation of the dermal exposures associated with service station refuelling activities

▶ WORKERS



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Phase 2

Evaluation of the **dermal transfer coefficient** from equipment surfaces to skin

Wipe samples -3 days, samples taken every hour 1 Station 1 attendant

Phase 1

1. Quantification of hydrocarbon levels on hands of attendants at the end of the work shift,
2. Quantification on nozzle grip, button panel, dispenser hoses,
3. protective capacity of the clothing worn

Washing of two hands and surfaces wipes for 3 days on 3 stations, 6 attendants

Questionnaires were given to the attendants in order to evaluate factors that may have altered results (use of hand cream, clothing..)
Other data were recorded: Type of service station, amount of fuel dispensed,...

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Dermal Exposure techniques: based on three sampling approaches:

- ▶ **Removal** : Wipe , hand washing removal of the contaminant from the skin by applying an external force equal to or greater than the force of adhesion of the contaminant to the skin by washing or wiping the surface
- ▶ **Interception**: patches – It intercepts the mass transport of the hydrocarbon by collecting the sample onto a medium (cutaneous surrogate) placed on the skin surface or on the clothing .
- ▶ **Surface sampling**: valid for hydrocarbon transfer from direct skin contact with a contaminated hard surface .Involves sampling the residual hydrocarbon on the surface in order to make an indirect inference regarding the dermal load (dermal transfer coefficient (DTC))

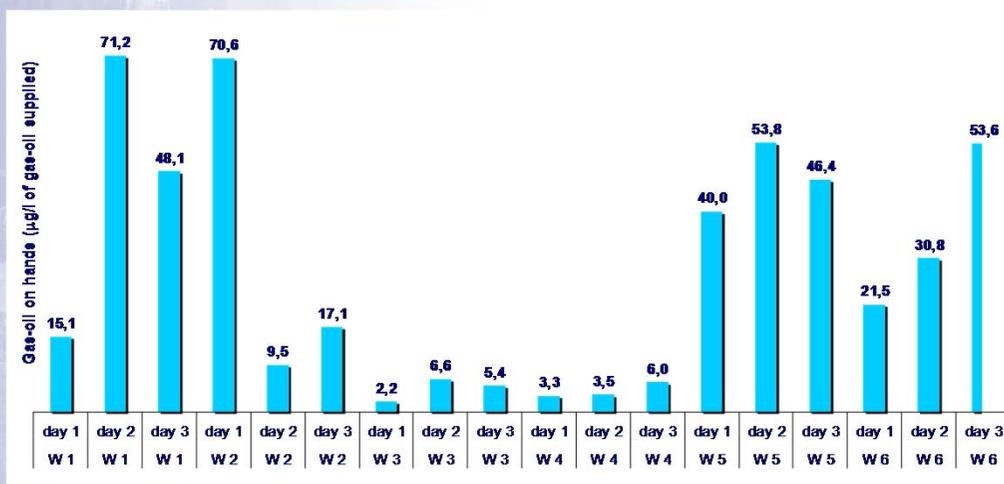
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▶ Hand Washing: 18 samples

High Variability:

- ▶ workers operate outdoors and are in contact with different surfaces which show different levels of residual products
- ▶ Different number of refuelling operations
- ▶ Removal of product due to Dermal transfer to other surfaces, evaporation or other factors



The measured exposures on hands were found to be much lower (worst case less than 1/5th) than the estimates predicted using exposure modelling tools such as ECETOC TRAv.2

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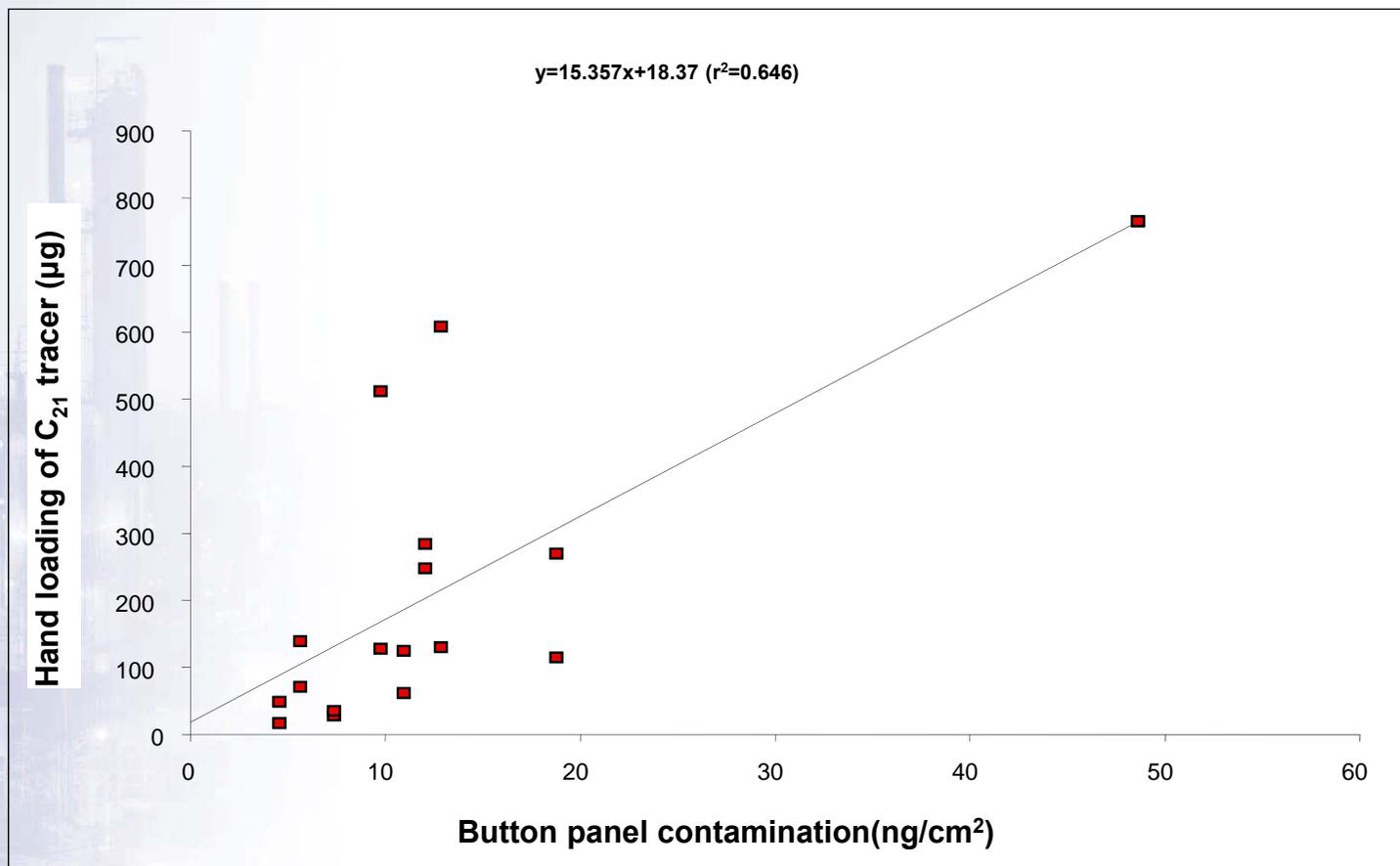
PADS: PROTECTIVE CAPACITY OF CLOTHING

- ▶ Measurement of hydrocarbon levels inside and outside the clothing in the same skin area to determine the protective capacity of the clothing worn: cotton work clothing may reduce hydrocarbon vapor concentrations 15%-60% but not from contact form liquid
- ▶ WIPES: DERMAL TRANSFER FACTOR (DTF)
- ▶ Ratio between the amount on hands (ng/h), and the average concentration on surfaces (ng/cm²) (pump nozzle grip and button panels), assessed every hour

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Results wipes and hand washing: levels of petroleum hydrocarbons on equipment



Linear regression analysis comparing C₂₁ contamination on the button panel with loading onto the hands

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1° study: CONSUMERS exposure – Products: Diesel, Lubricants
Test environment with volunteers – single operation

2° Study: WORKER exposure – Products: Diesel, Gasoline
Real life environment with workers – whole shift (phase 1)
hourly samples (phase 2)

A preliminary analysis of the two studies shows:

- When workers exposure for a whole shift is divided into one single refuelling operation the result is much lower than consumers' exposure
- The gap is reduced when considering lower results
- This difference may be due to: monitoring techniques, Workers' training, absorption , removal of product from hands for whole shift samples
- Measured workers' exposure are much lower than estimates form algorithms
- A detailed exposure assessment is complex for substances like gasoline and diesel and is affected by a lack of a universal validated measurement method

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