Comparison of standardized and novel methods for oil spill source identification in real spill scenarios reproduced in proficiency tests

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Scientific Workshop

"Ensuring reliable and accurate results of analytical processes"

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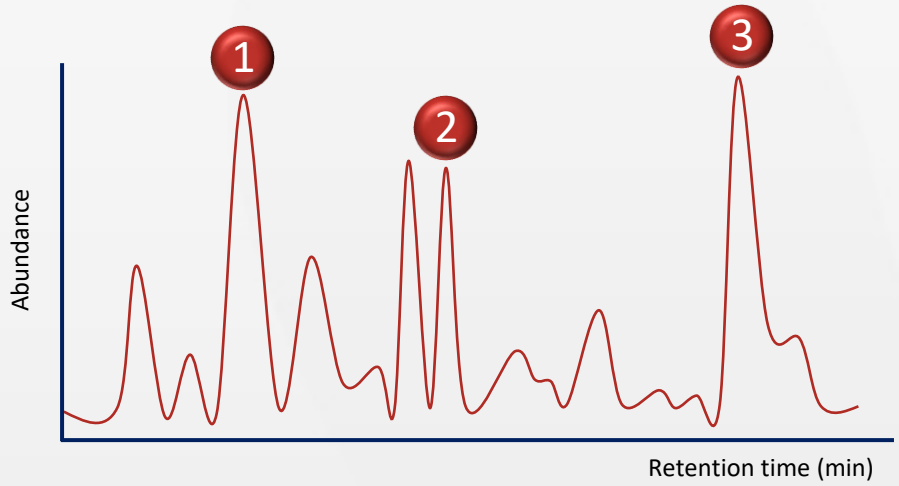
Introduction

Diagnostic ratios (DR)

Ratios between chromatographic signals of oil-discriminating compounds

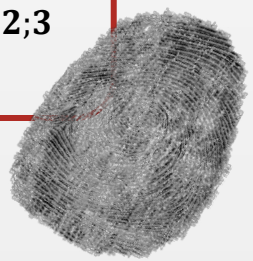
$DR_{1;2} = \frac{H_1}{H_2}$, with H_1 and H_2 as the heights of 1 and 2 chromatographic peaks



$DR_{1;2}$

$DR_{1;3}$

$DR_{2;3}$



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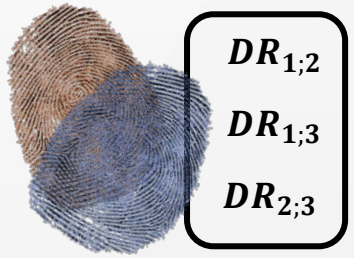
Introduction

Spill source identification

Compositional equivalence claim when all DR of Sp and SS are equivalent

Equivalent DR_{Sp} and DR_{SS}

Different DR_{Sp} and DR_{SS}



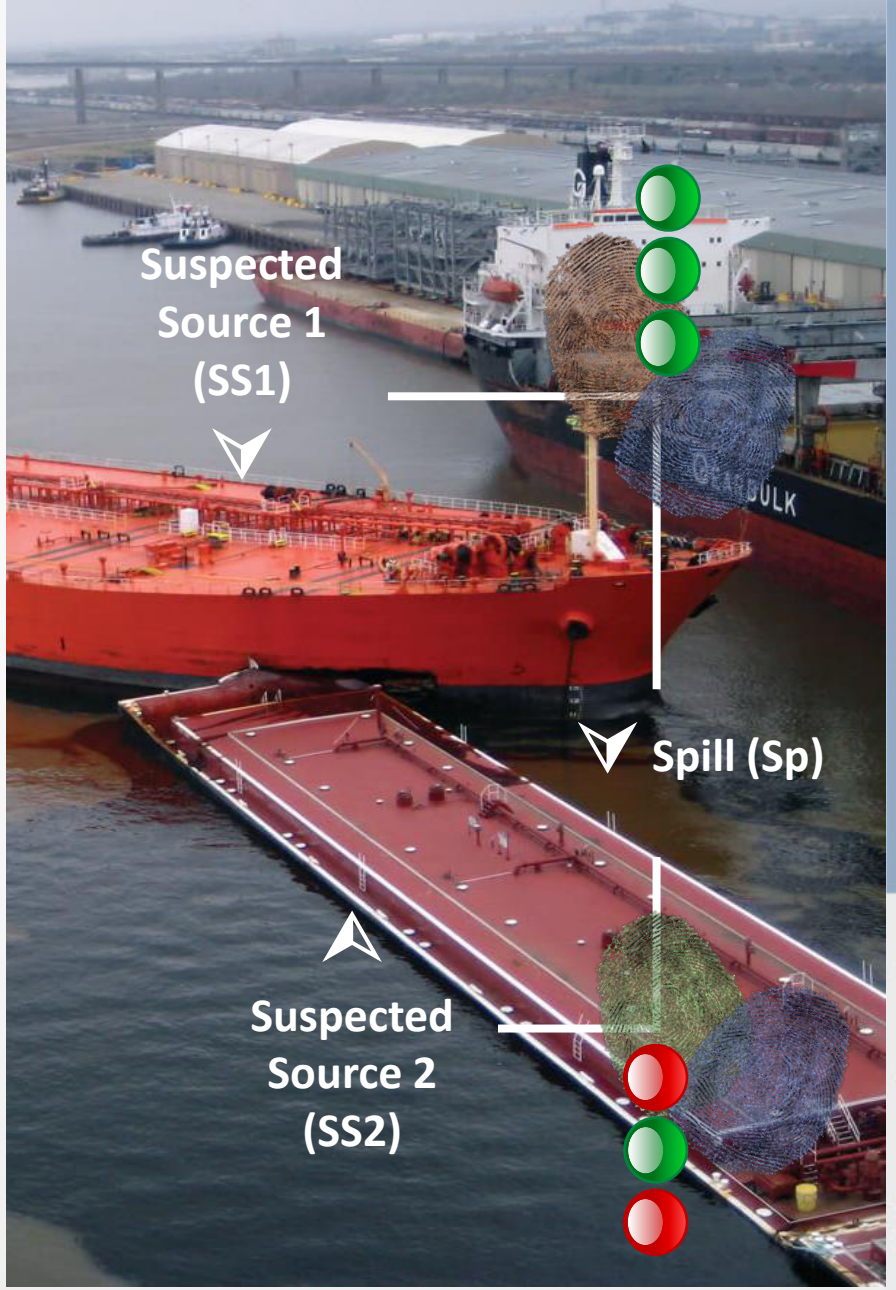
SS1 – Pollution source

All DR are equivalent

SS2 – Not the pollution source

Some DR are different

DR comparison approaches S-t SC MCM



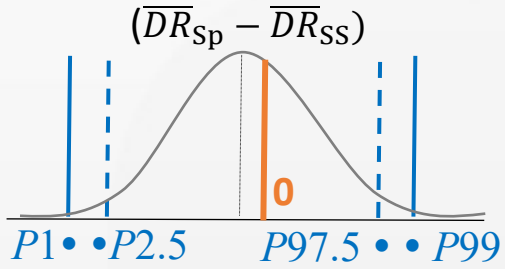
Introduction

DR comparison approaches

Define the criteria for comparing DR means observed in Sp and SS

Describes the real probability distribution of $(\overline{DR}_{Sp} - \overline{DR}_{SS})$

S-t Nordtest (1)

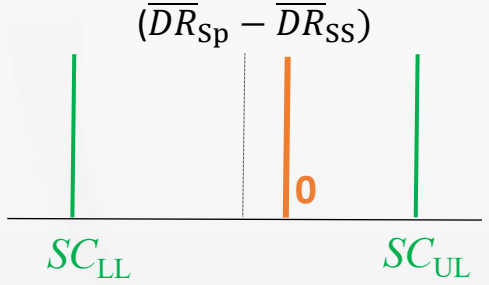


Assumes the normality of the $(\overline{DR}_{Sp} - \overline{DR}_{SS})$ probability distribution

$$\left|\overline{DR}_{Sp} - \overline{DR}_{SS}\right| \pm s_d \cdot t((1-P);\xi)$$

s_d – standard deviation of the $\overline{DR}$ difference;
P – confidence level;
ξ - degrees of freedom

SC CEN Standard (2)

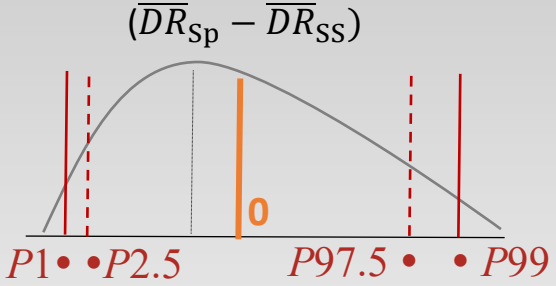


Assumes the most likely dispersion of the DR

$$\left|\overline{DR}_{Sp} - \overline{DR}_{SS}\right| \leq 0.14 \cdot \overline{DR}_{Sp\&SS}$$

With $\overline{DR}_{Sp\&SS} = \dfrac{(\overline{DR}_{Sp} + \overline{DR}_{SS})}{2}$

MCM Developed



Simulation by **Monte Carlo Method**, based on dispersion and correlation data of chromatographic signals

Percentiles for 95% and 98% confidence levels (Nordtest)

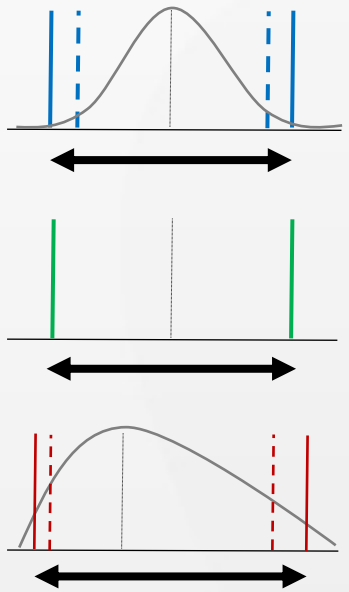
(1) P. S. Daling, et al., *Environ. Forensics*, **2002**, 3, 263-278.
(2) CEN, Oil spill identification - Petroleum and petroleum related products - Part 2: Analytical method and interpretation of results based on GC-FID and GC-low resolution-MS analyses, EN 15522 2:2023 E, CEN, 2023

Research Goals

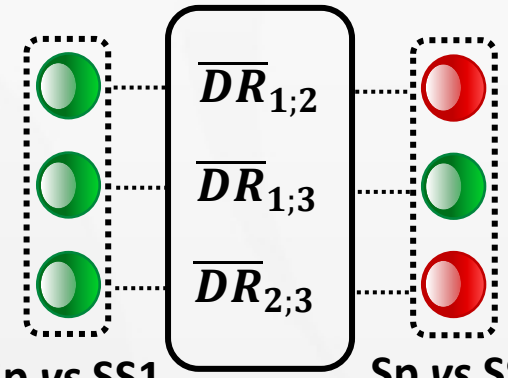
S-t SC MCM

Compararison of approaches

Criteria for $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ comparison



Compositional equivalence or difference claim



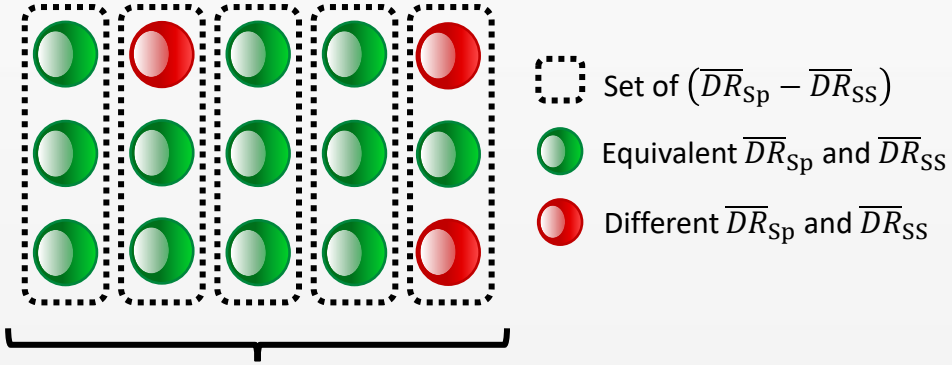
Sp *vs* SS1
Compositional equivalence

Sp *vs* SS2
Composicional difference

SS1 – Pollution source
SS2 – Not the pollution source

Identification quality

N sets of simulated $\left(\overline{DR}_{Sp} - \overline{DR}_{SS}\right)$



Total risk of true compositional equivalence claim

Percentage of simulated $\left(\overline{DR}_{Sp} - \overline{DR}_{SS}\right)$ sets with all $\overline{DR}_{Sp}$ and $\overline{DR}_{SS}$ equivalent

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Experimental

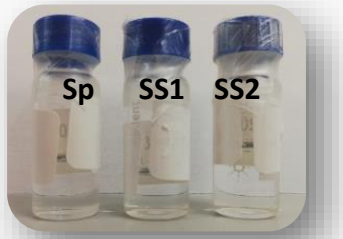
S-t SC MCM

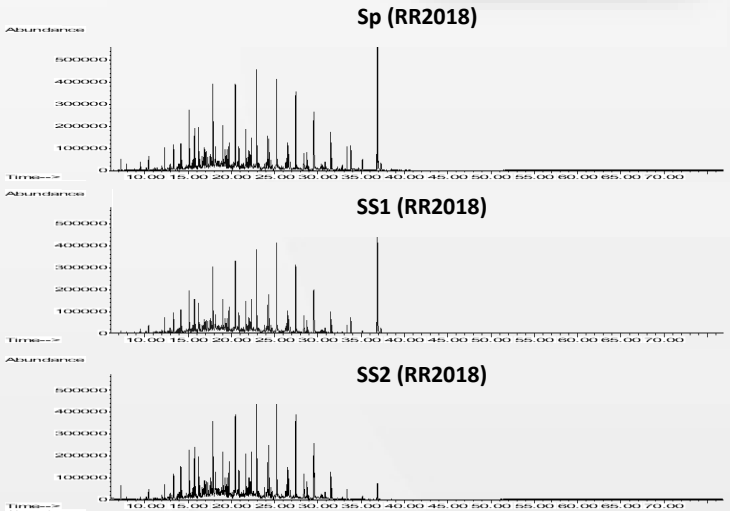
Round Robin Tests (RR)

Sp – Spill | SS1 e SS2 – Suspected source known to be and not to be the origin of the spill, respectively

Diesel with biodiesel

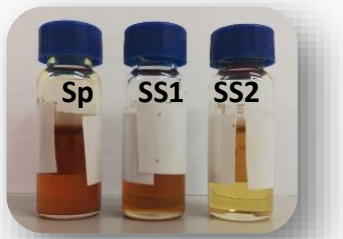
RR2018

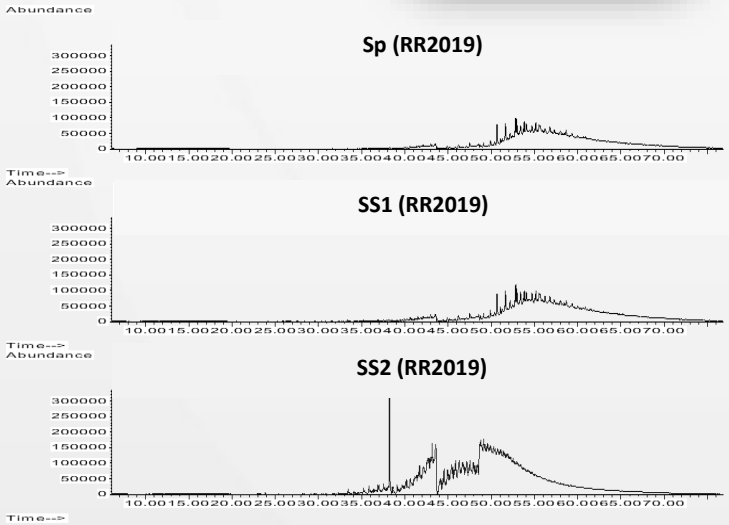




Lubricating oil

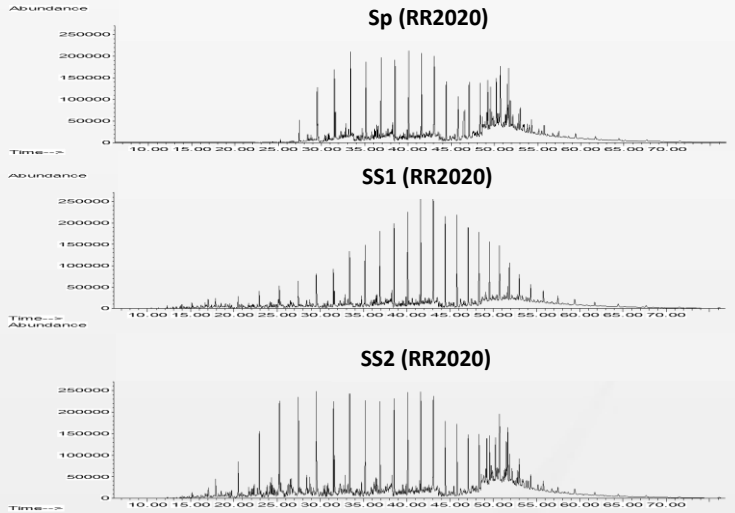
RR2019





Heavy fuel oil

RR2020



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Experimental

S-t SC MCM

Set of DR – fingerprint (DR list of the CEN Standard)

Diesel with biodiesel

RR2018

$DR01$	$DR09$	$DR16$	$DR47$	$DR56$
$DR02$	$DR10$	$DR17$	$DR48$	$DR57$
$DR03$	$DR11$	$DR19$	$DR49$	$DR60$
$DR04$	$DR12$	$DR20$	$DR51$	$DR61$
$DR06$	$DR13$	$DR21$	$DR52$	
$DR07$	$DR14$	$DR45$	$DR53$	
$DR08$	$DR15$	$DR46$	$DR54$	

32 DR

Lubricating oil

RR2019

$DR33$	$DR37$	$DR44$
$DR34$	$DR40$	$DR72$
$DR35$	$DR43$	$DR78$

9 DR

Heavy fuel oil

RR2020

$DR33$	$DR37$	$DR43$
$DR34$	$DR40$	$DR44$
$DR35$	$DR41$	$DR78$

Sp *vs* SS1 – 9 DR
Sp *vs* SS2 – 8 DR

9 or 8 DR

DR determined with chromatographic signals:
- with S/R > 5
- with precision < 7.5 %
- of unweathered compounds

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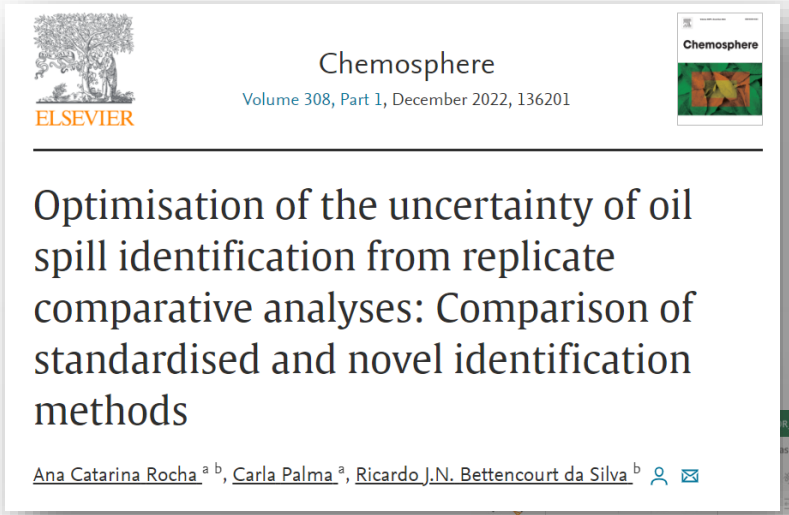
Experimental

Data acquisition and processing



Chemosphere

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Optimisation of the uncertainty of oil spill identification from replicate comparative analyses: Comparison of standardised and novel identification methods

Ana Catarina Rocha [a b], Carla Palma [a], Ricardo J.N. Bettencourt da Silva [b]

Tested scenarios

Nordtest

S-t

$$n_{Sp} = n_{SS1} = n_{SS2} = 3$$

$$DR = \frac{A}{(A+B)}$$

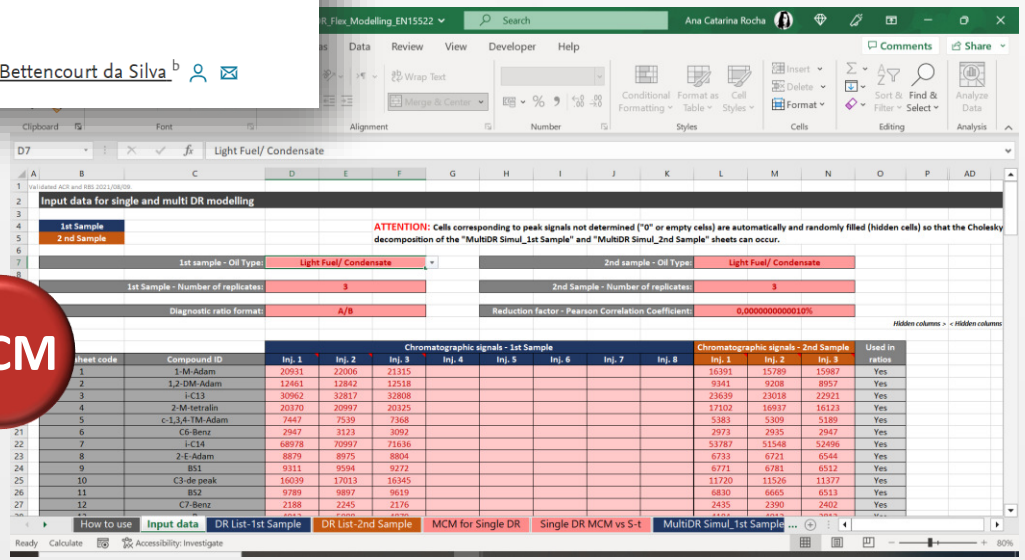
CEN Standard

SC

$$n_{Sp} = n_{SS1} = n_{SS2} = 2$$

$$DR = \frac{A}{B}$$

MCM



Input data for single and multi DR modelling

ATTENTION: Cells corresponding to peak signals not determined ("0" or empty celss) are automatically and randomly filled (hidden cells) so that the Cholesky decomposition of the "MultiDR Simul_1st Sample" and "MultiDR Simul_2nd Sample" sheets can occur.

1st sample - Oil Type: Light Fuel/ Condensate

2nd sample - Oil Type: Light Fuel/ Condensate

1st Sample - Number of replicates: 3

2nd Sample - Number of replicates: 3

Diagnostic ratio format: A/B

Reduction factor - Pearson Correlation Coefficient: 0,0000000000010%

Sheet code	Compound ID	Chromatographic signals - 1st Sample Inj. 1	Inj. 2	Inj. 3	Chromatographic signals - 2nd Sample Inj. 1	Inj. 2	Inj. 3	Used in ratios
1	1-M-Adam	20931	22006	21315	16391	15789	15987	Yes
2	1,2-DM-Adam	12461	12842	12518	9341	9208	8957	Yes
3	i-C13	30962	32817	32808	23639	23018	22921	Yes
4	2-M-tetralin	20370	20997	20325	17102	16937	16123	Yes
5	c-1,3,4-TM-Adam	7447	7539	7368	5383	5309	5189	Yes
6	C6-Benz	2947	3123	3092	2973	2935	2947	Yes
7	i-C14	68978	70997	71636	53787	51548	52496	Yes
8	2-E-Adam	8879	8975	8804	6733	6721	6544	Yes
9	B51	9311	9504	9272	6771	6781	6512	Yes
10	C3-de peak	16039	17013	16345	11720	11526	11377	Yes
11	B52	9789	9897	9619	6830	6665	6513	Yes
12	C7-Benz	2188	2245	2176	2435	2390	2402	Yes

How to use | Input data | DR List-1st Sample | DR List-2nd Sample | MCM for Single DR | Single DR MCM vs S-t | MultiDR Simul_1st Sample

2 DR comparison trials

(with independent analysis of Sp):

- Compositional equivalence proof
- Increase the total risk of true compositional equivalence claim

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Results

S-t SC MCM

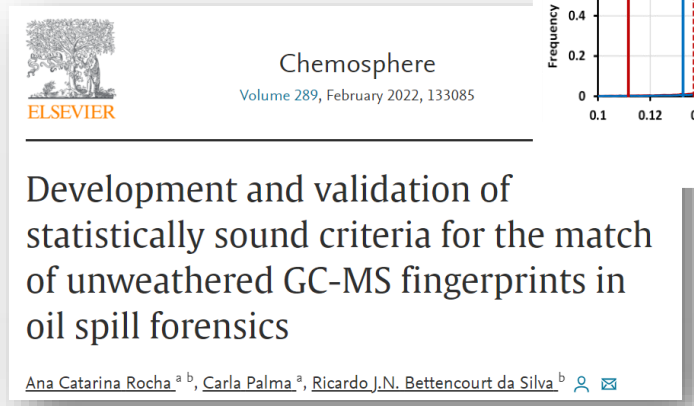
Comparison of the DR criteria (confidence intervals)

Previous studies - evaluated the criteria obtained by the three approaches (unweathered samples and different DR comparison conditions):

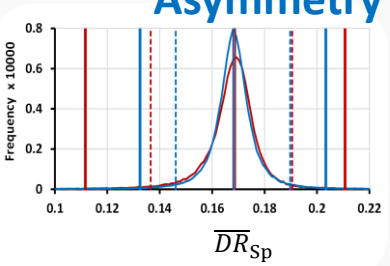
- non-normal probability distributions of $\overline{DR}_{Sp}$ and $(\overline{DR}_{Sp} - \overline{DR}_{SS})$:
  - Asymmetrical;
  - Flattened.

- dimension of confidence intervals affected by:
  - degrees of freedom (S-t);
  - mean DR (SC);
  - mean values, dispersion and correlation of chromatographic signals used in the calculation of DR (MCM).

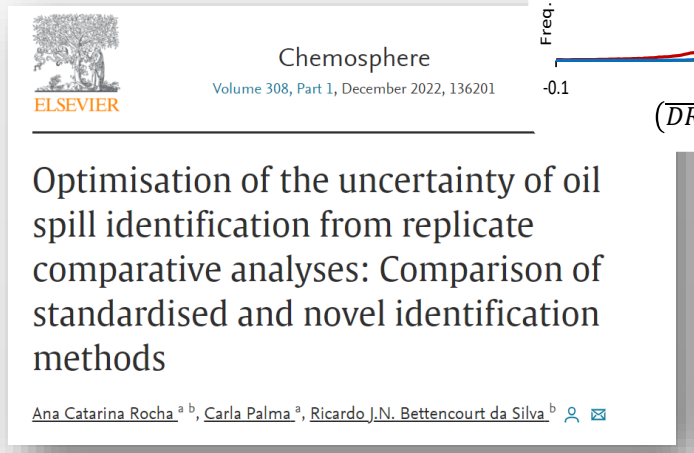
Present study - similar conclusions to those of previous studies (weathered samples of RR).

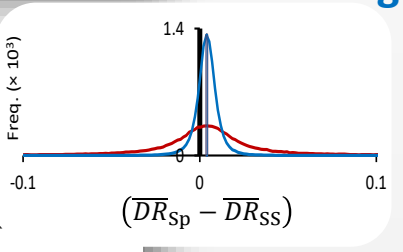


Asymmetry



Flattening





^ MCM ; ^ S-t
_ *P*1 and *P*99
... *P*2.5 and *P*97.5

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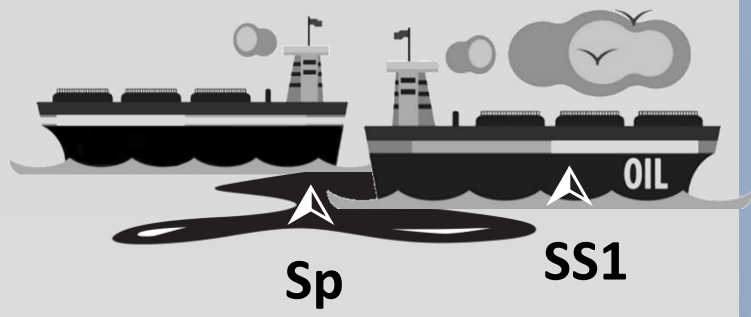
Results

Compositional equivalence claim

Comparison between Sp and SS1



Nordtest scenario (98%)

- Diesel

S-t

Compositional difference

MCM e **SC**

Compositional equivalence

- Lub oil and HFO

MCM, S-t e SC

Compositional equivalence

	MCM		S-t		SC	
	1st trial	2nd trial	1st trial	2nd trial	1st trial	2nd trial
Diesel	$DR04$ $DR21$	$DR12$	$DR03$ $DR04$ $DR07$ $DR12$ $DR13$ $DR21$ $DR51$ $DR53$	$DR03$ $DR12$ $DR13$ $DR21$ $DR52$	All DR	All DR
Lub oil	All DR		All DR		All DR	
HFO	All DR	All DR	$DR37$	All DR	All DR	All DR

Equivalent $\overline{DR}_{Sp}$ e $\overline{DR}_{SS}$

Different $\overline{DR}_{Sp}$ e $\overline{DR}_{SS}$

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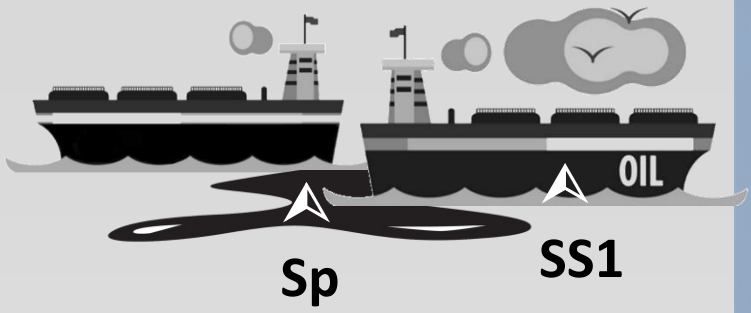
Results

Compositional equivalence claim

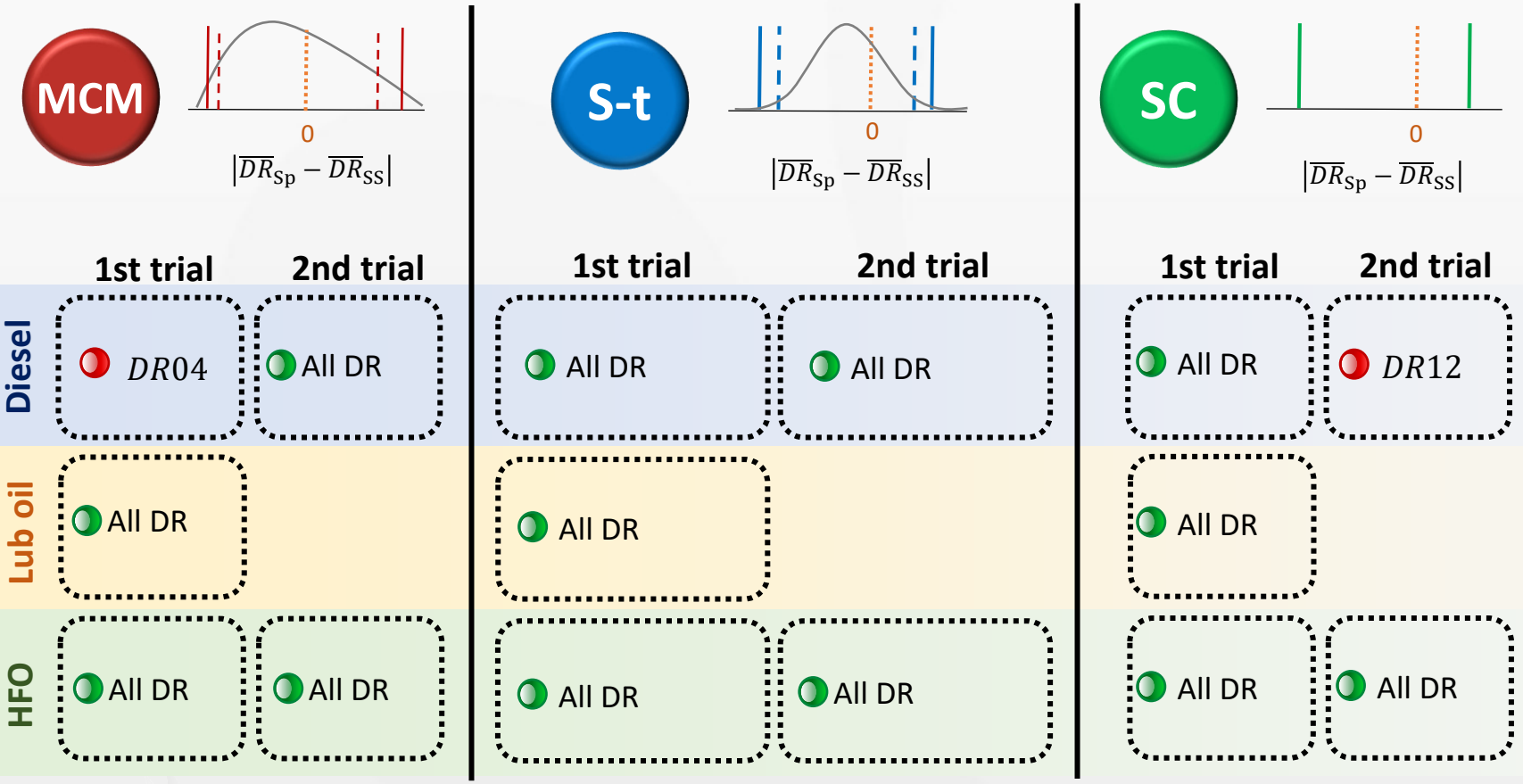
Comparison between Sp and SS1



CEN scenario (98%)

MCM, S-t e SC Compositional equivalence

Diesel, Lub oil and HFO



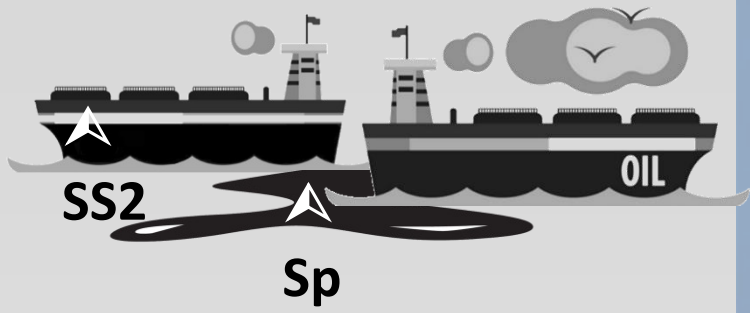
Equivalent $\overline{DR}_{Sp}$ e $\overline{DR}_{SS}$

Different $\overline{DR}_{Sp}$ e $\overline{DR}_{SS}$

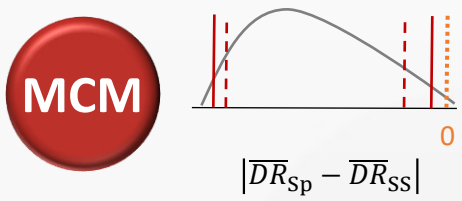
Results

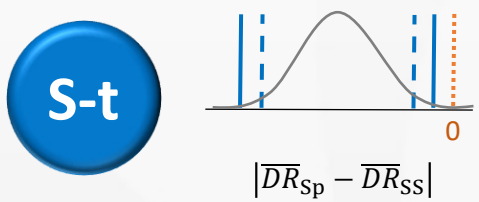
Compositional difference claim

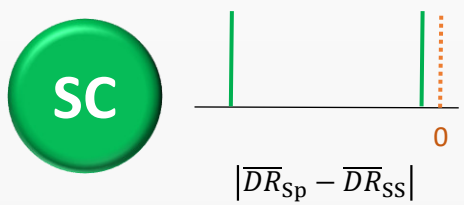
Comparison between Sp and SS2



MCM, S-t e SC
Composicional difference







	MCM		S-t		SC	
	Nordtest	EN 15522-2	Nordtest	EN 15522-2	Nordtest	EN 15522-2
Diesel	16 DR (50.0 %)	14 DR (43.8 %)	22 DR (68.8 %)	10 DR (31.3 %)	5 DR (15.6 %)	13 DR (40.6 %)
Lub oil	Trial not performed – no DR determined in SS2		Trial not performed – no DR determined in SS2		Trial not performed – no DR determined in SS2	
HFO	5 DR (62.5 %)	4 DR (50.0 %)	6 DR (75.0 %)	4 DR (50.0 %)	4 DR (50.0 %)	5 DR (62.5 %)

Nordtest scenario (98%)

- MCM e S-t identify more different DR than SC
- S-t identifies more different DR than MCM (questionable performance)

CEN scenario (98%)

- SC identifies more different DR than S-t
- SC and MCM identify practically the same different DR

Equivalent $\overline{DR}_{Sp}$ e $\overline{DR}_{SS}$

Different $\overline{DR}_{Sp}$ e $\overline{DR}_{SS}$

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Results

Comparison by Student's *t* test (95% confidence level)
Dfferent risks: MCM < S-t or SC ; MCM > S-t or SC
Equivalent risks: ≈

Total risk of true compositional equivalence claim (δ)

Comparison between Sp and SS1 considering a single DR comparison trial

- **All approaches estimate δ less than 98%**
- **MCM estimates δ greater than S-t e SC**

Mean values of δ
3 simulations

Scenario	RR	MCM 95%	MCM 98%	S-t 95%	S-t 98%	SC
Nordtest	Diesel	83.3	93.4	62.3	78.7	91.5
	Lub oil	86.1	94.4	67.8	81.5	85.5
	HFO	87.2	95.0	66.8	81.1	89.7
EN 15522-2	Diesel	82.9	93.2	81.8	93.3	18.3
	Lub oil	85.7	94.4	86.3	94.8	54.6
	HFO	87.2	94.9	83.9	93.7	72.2

Scenario	RR		$\bar{\delta}_{S-t}^{95\%}$	$\bar{\delta}_{S-t}^{98\%}$	$\bar{\delta}_{SC}$
Nordtest	Diesel	$\bar{\delta}_{MCM}^{95\%}$	>		<
		$\bar{\delta}_{MCM}^{98\%}$		>	>
	Lub oil	$\bar{\delta}_{MCM}^{95\%}$	>		>
		$\bar{\delta}_{MCM}^{98\%}$		>	>
	HFO	$\bar{\delta}_{MCM}^{95\%}$	>		<
		$\bar{\delta}_{MCM}^{98\%}$		>	>
EN 15522-2	Diesel	$\bar{\delta}_{MCM}^{95\%}$	>		>
		$\bar{\delta}_{MCM}^{98\%}$		≈	>
	Lub oil	$\bar{\delta}_{MCM}^{95\%}$	≈		>
		$\bar{\delta}_{MCM}^{98\%}$		≈	>
	HFO	$\bar{\delta}_{MCM}^{95\%}$	>		>
		$\bar{\delta}_{MCM}^{98\%}$		>	>

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Results

Comparison by Student's *t* test (95% confidence level)
Dfferent risks: MCM < S-t or SC ; MCM > S-t or SC
Equivalent risks: ≈

Total risk of true compositional equivalence claim(ω)

Comparison between Sp and SS1 considering two DR comparison trials

- **All approaches estimate ω greather than 98%, with the exception of S-t and SC (in their reference DR comparison conditions)**
- **MCM estimates ω greater than S-t e SC**

Mean values of ω
3 simulations

Scenario	RR	MCM 98%	S-t 98%	SC
Nordtest	Diesel	100.0	97.02	99.96
	HFO	100.0	97.9	99.86
EN 15522-2	Diesel	100.0	99.8	91.5
	HFO	100.0	99.76	98.5

Comparison among approaches

Scenario	RR		$\bar{\omega}_{S-t}$	$\bar{\omega}_{SC}$
Nordtest	Diesel	$\bar{\omega}_{MCM}$	>	>
	HFO	$\bar{\omega}_{MCM}$	>	>
EN 15522-2	Diesel	$\bar{\omega}_{MCM}$	≈	>
	HFO	$\bar{\omega}_{MCM}$	>	>

Comparison with 98%

Scenario	RR	$\bar{\omega}_{MCM}^{98\%}$	$\bar{\omega}_{S-t}^{98\%}$	$\bar{\omega}_{SC}^{98\%}$
Nordtest	Diesel	>	<	>
	HFO	>	≈	>
EN 15522-2	Diesel	>	>	<
	HFO	>	>	>

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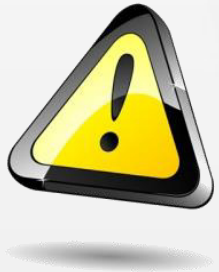
Take home messages

① Compositional equivalence and difference claims were correctly identified by the three approaches;

② 2nd DR comparison trial required to prove the compositional equivalence (MCM and S-t applied to Nordtest scenario) and to increase the total risks above 98%.

Risk



③ δ and ω estimated by MCM were significantly different from those estimated by S-t and SC;

④ ω showed to be greater than 98%, except ω estimated by S-t and SC in their reference DR comparison conditions.

S-t SC

☑ **Weaknesses of the approaches in the DR comparison conditions for which they were designed**

MCM

☑ **Statistically sounder approach**

☑ **Better quality identifications**

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Thank you for your kind attention!

Study presented

ELSEVIER

Science of The Total Environment

Available online 6 May 2023, 163930

In Press, Journal Pre-proof What's this?

Review

Statistically sound comparison of standardized and simulation methods for oil spill source identification in real spill scenarios

Ana Catarina Rocha [a b], Ricardo J.N. Bettencourt da Silva [b], Carla Palma [a]

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To the Bonn-OSINet for the volounter organisation of Round Robins Tests on oil spill identification

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NEXT STEP

Investigate the relationship between the probabilities of true and false compositional equivalence claims (likelihood ratios) for a better assessment of the identification quality