Quantifying fullerene C_{60} and transformation products in water with LC LTQ Orbitrap MS

Norman workshop ENP in the environment, Koblenz 19&20 Oct 2010

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(E)NP in the aqueous environment

- Increasing production, application, consumption of ENP
- ENP in (aqueous) environment?
- ENP in drinking water?
- Need for analytical techniques in various (aqueous) environmental matrices
- Additionally: ENP can facilitate environmental transport of contaminants

ENP in the aqueous environment

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- ENP in (aqueous) environment?
- ENP in drinking water?
- Need for analytical techniques in various (aqueous) environmental matrices
- Additionally: ENP can facilitate environmental transport of contaminants

ENP facilitates transport of micropollutants

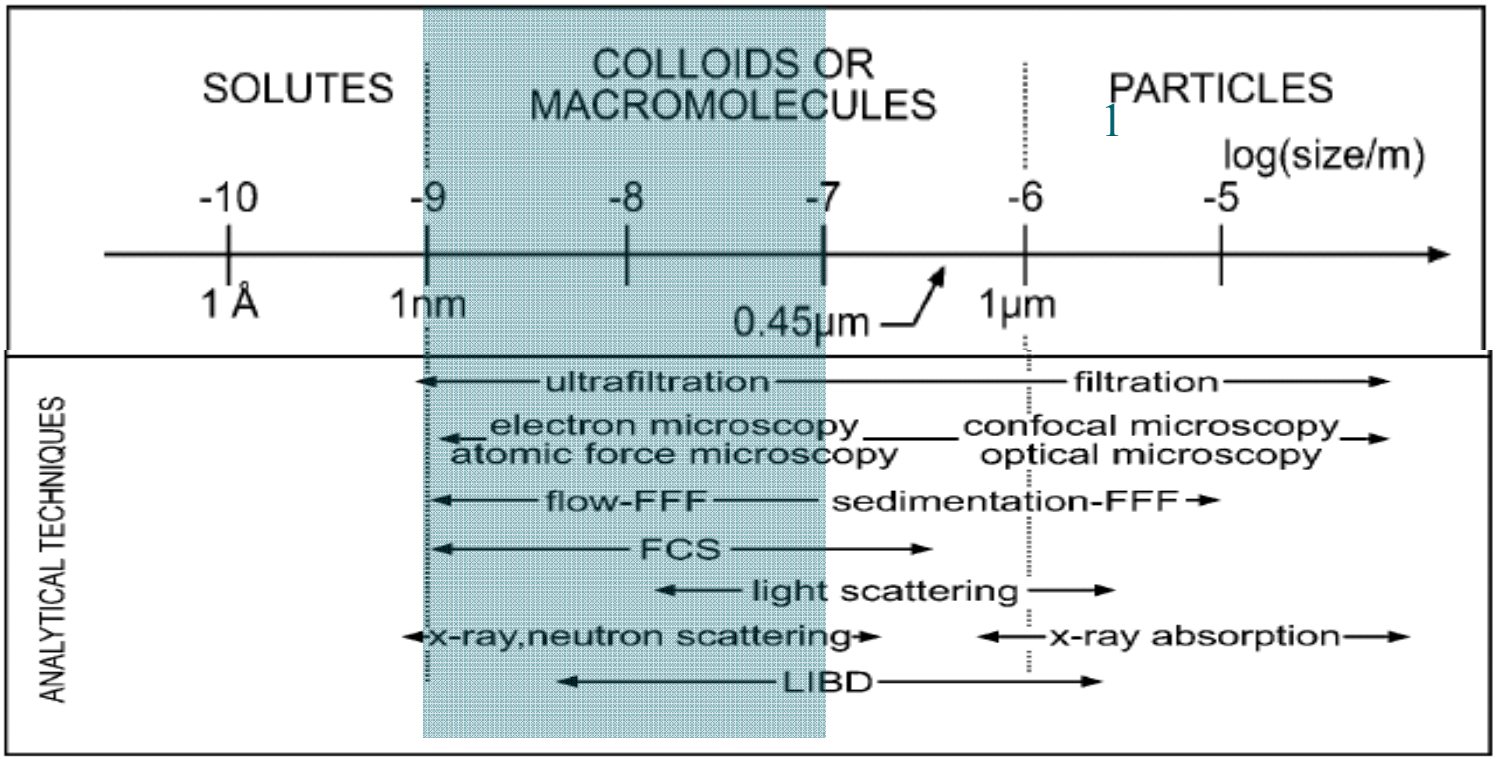
- High sorption & slow desorption of organic contaminants to ENP aggregates[1]

Compounds	log K_{ow}[a]	log K_{DOC}	log K_{C60}
Phe	4.56	4.48 ± 0.05 4.78 ± 0.05[b]	4.71 ± 0.04
Fla	5.16	5.26 ± 0.05 5.50 ± 0.04[b]	5.11 ± 0.02
Chr	5.81	5.91 ± 0.04 5.45 ± 0.01[c]	5.48 ± 0.09

- High mobility of ENP aggregates[2]

[1] Hu et al. 2008, ET&C 27:1868-1874
2 Espinasse et al 2007 EST 7396-7402

Analytical techniques



Often combination of techniques are used: fractionation + detection/microscopic techniques, LIBD/LIBS device, ICP-MS/UV

Klaine et al. 2008, ET&C 1825-1851

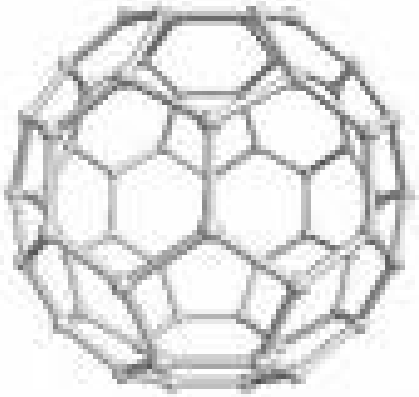
Drawbacks of techniques

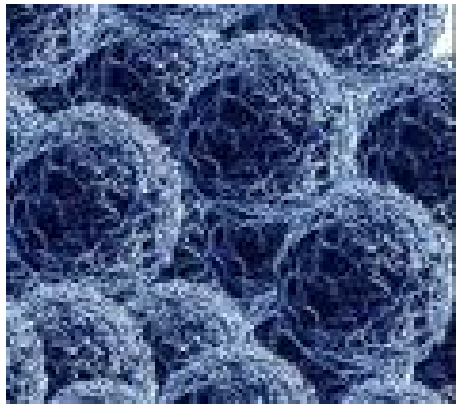
Current techniques often:

- semi-quantitative
- high detection limits
- unspecific
- aggregates / single molecules not distinguished

This study

- Fullerene in aqueous matrices
- Preparing suspensions
- Extraction
- Analysis
- Transformation products
- Field study





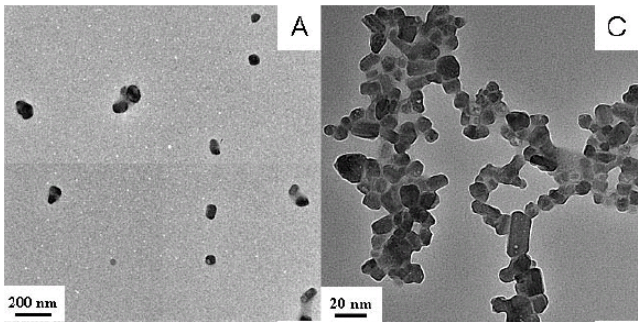
Environmental concentrations of fullerenes

- Concentrations in µg/L range have recently been observed in wastewater [3]
- PEC range from 0.0035 to 300 ng/L [1,2] in European SW (depending on sedimentation)
- Analytical techniques necessary for SW and DW at trace level

1 Boxall et al. 2007, Defra, UK
2 Gottschalk et al. 2009 EST 9216-9222
3 Farre et al 2010 J. Hydrol 44-51

Analytical challenges

- Suspensions vs. solutions
- Transformation products
- (Aqueous) matrix effects
- Extraction & separation
- Identification & sensitivity



LC analysis of fullerenes

- SPE, LC-UV, DL in the µg/L range [1, 2] (including concentration steps)
- SPE, LC-MS, detection limits approaching ng/L level [3,4] (including concentration steps)

1 Xia et al 2006 J Chrom A. 216-222
2 Bouchard et al 2008 J Chrom A. 153-159
3 Isaacson et al 2007 AC 9091-9097
4 Farre et al 2010 J Hydrol 44-51

LC analysis of fullerenes

1 – Prep. aqueous stock-suspension (24 mg/L)

2 – SPE and transfer to solvent

3 – LC/UV/MS for quantification

1 Preparation of aqueous suspension

C_{60} 'insoluble' in water (<10^{-9} mg/L[1] or lower[2])→ negatively charged aggregates

C_{60} in toluene

Toluene solution of C_{60} put into water

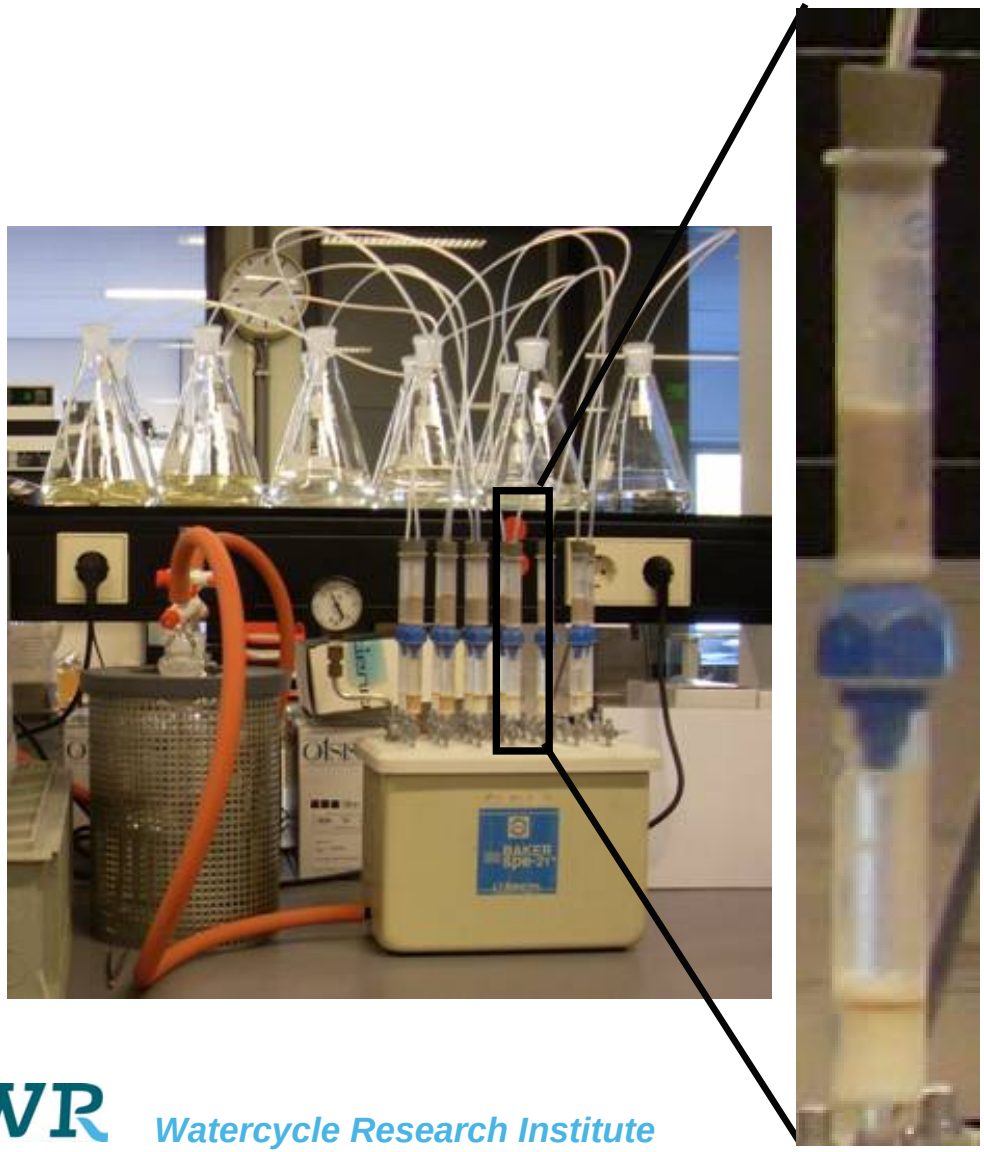
Evaporation of the toluene phase (sonication)

Filtration

C_{60} in water

1 Jafvert et al 2008 EST 5945-5950
2 Heymann 1996 FST 509-515

2 Solid Phase Extraction (SPE)



Filtration column

→ removal of big particles

Extracts : C_{60} in toluene

SPE column : C18

→ C_{60} sorbed in the matrix

3 LC-UV-MS

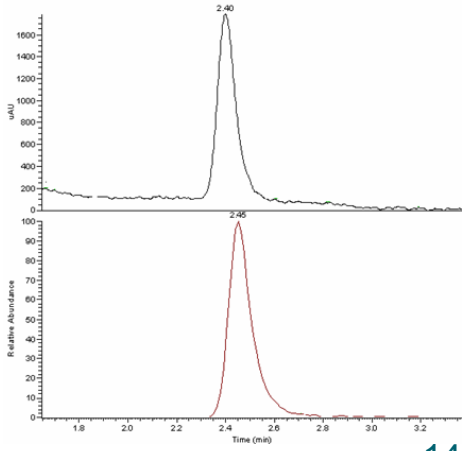
Separation : Liquid Chromatography (LC)

C18 column

RT C_{60} = 2.5 min

Detection :

- UV
- High resolution Mass Spectrometry



3 LC/UV/LTQ Orbitrap Hybrid Mass Spectrometer

Comparing techniques and mobile phases

- UV
- Orbitrap MS

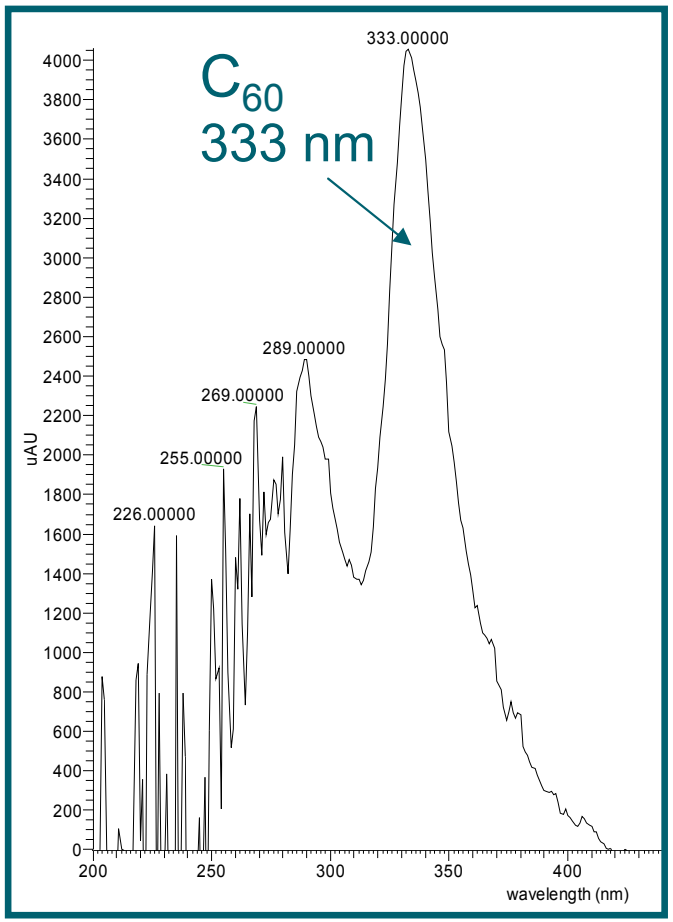
- APCI (atmospheric pressure chemical ionization)
- ESI (electrospray ionization)

- Toluene/methanol
- Toluene/acetonitrile[1]

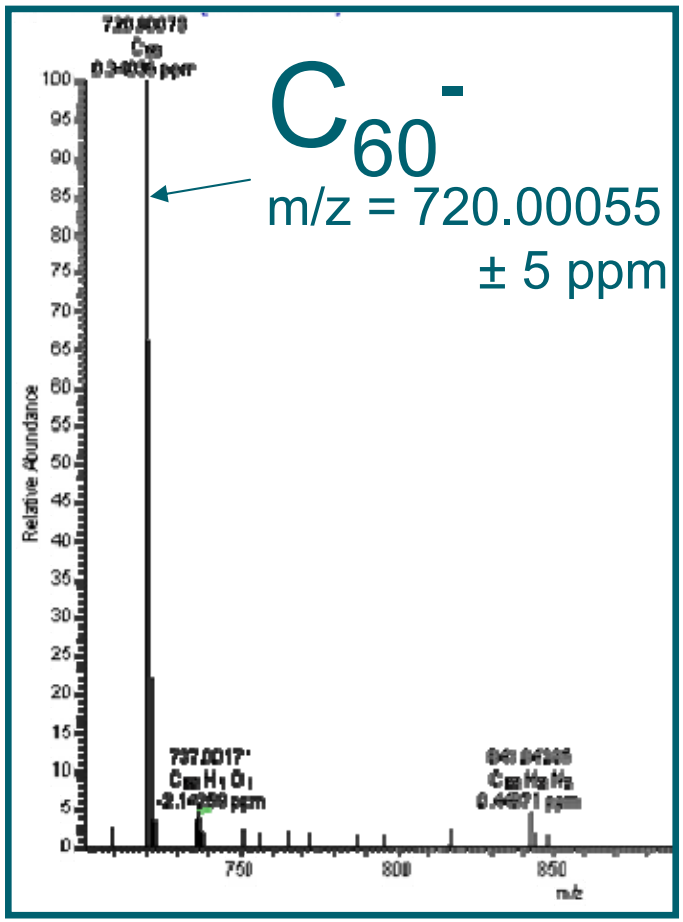
[1]Kawano et al, 2006, Rap Comm MS 2783-2785

3 LC/UV/LTQ Orbitrap

UV



MS



Negative ion mode

3 LC/UV/LTQ Orbitrap

- ESI vs APCI
- toluene/methanol vs toluene/acetonitrile

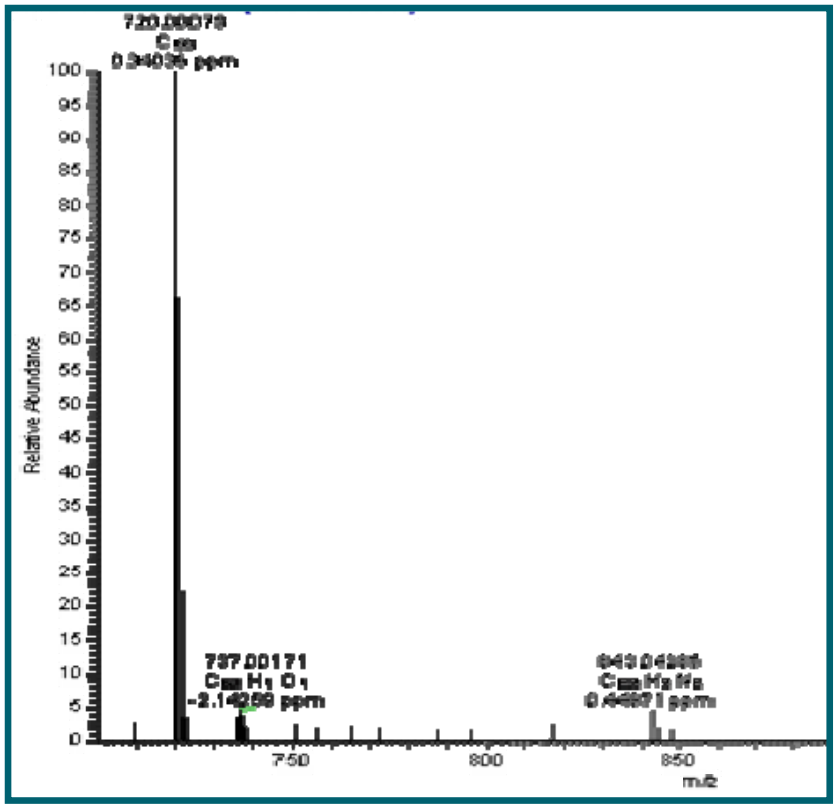
	toluene/ methanol	toluene/ acetonitrile	Calibration curves
ESI	390*	1*	Not linear at concentrations > 100 µg/L
APCI	65*	120*	Linear up to 5 mg/L

*Normalized area of the MS peak

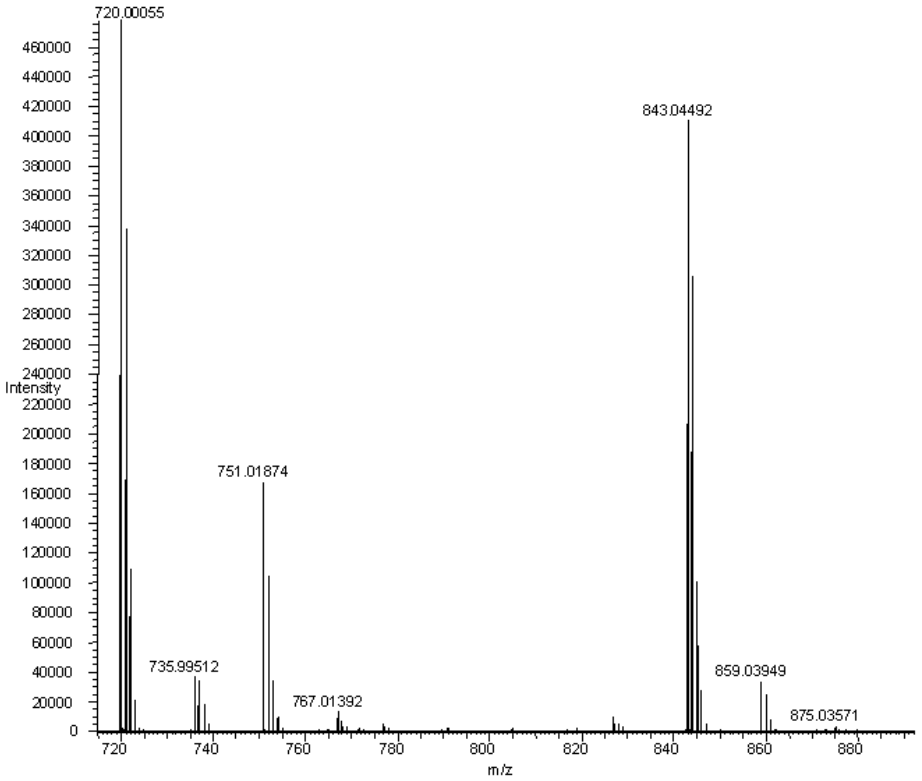
- Eluent toluene/methanol (60:40)
- c<100 µg/L → ESI/MS
- c>100 µg/L ⟶ UV

3 Products formed in solvent standards (↑ storage time)

FRESH sample



OLD sample



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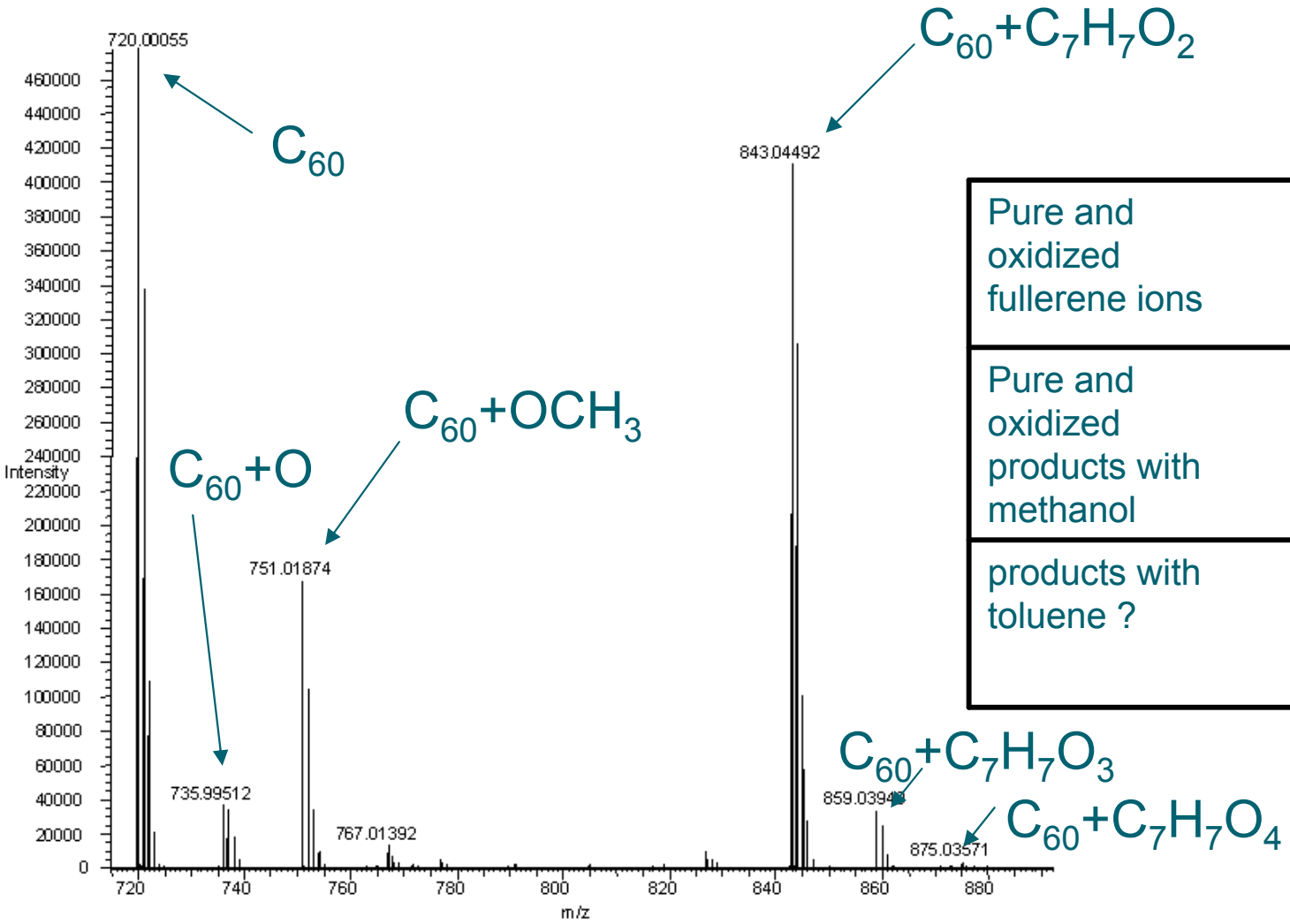
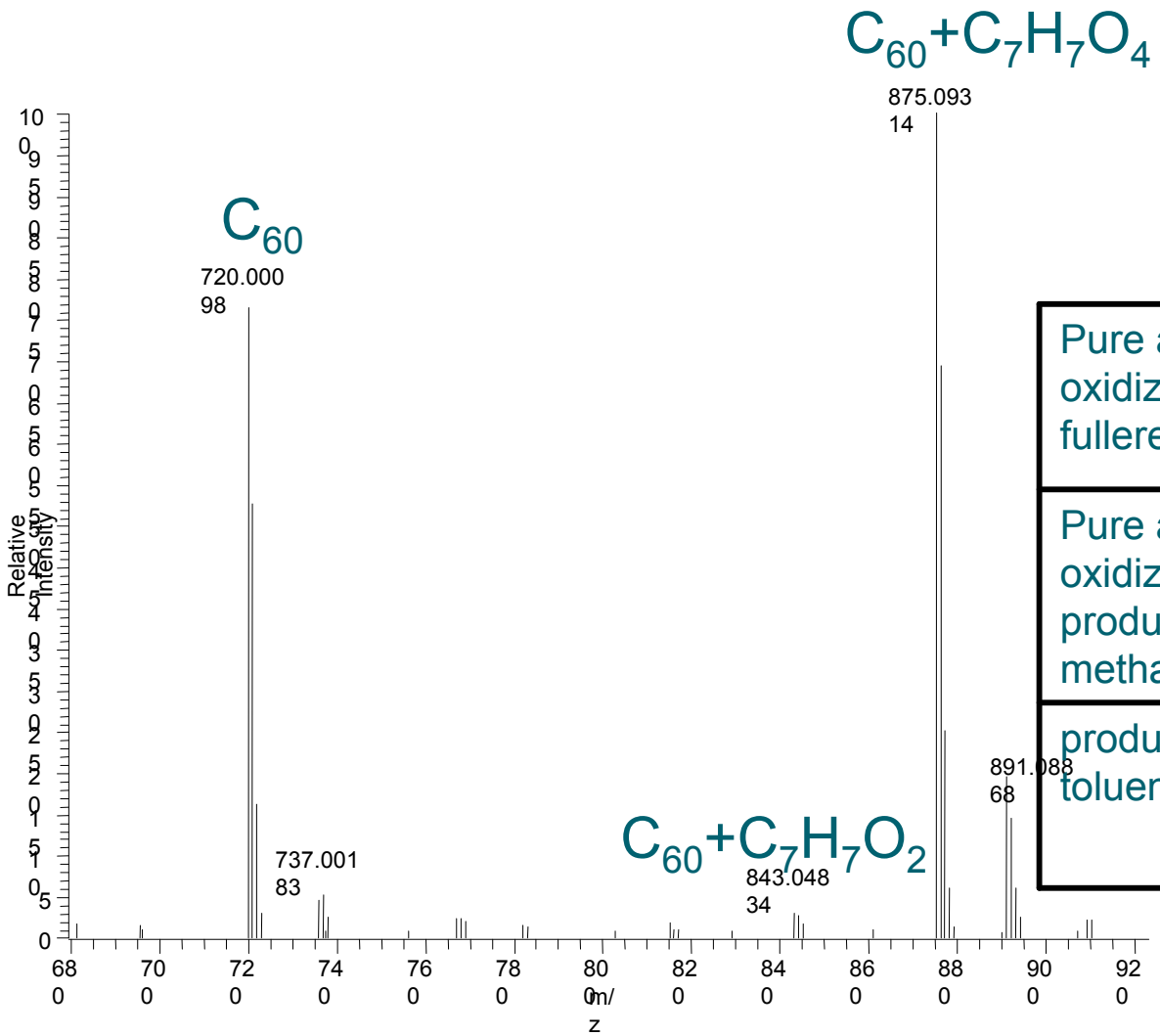


	Ion	m/z
Pure and oxidized fullerene ions	$[C_{60}]^-$	720,00055
	$[C_{60}+O]^-$	735,99545
	$[C_{60}+OH]^-$	737,00328
Pure and oxidized products with methanol	$[C_{60}+OCH_3]^-$	751,01893
	$[C_{60}+OCH_3+O]^-$	767,01383
	$[C_{60}+OCH_3+OH]^-$	768,02165
products with toluene ?	$[C_{60}+C_7H_7O_2]^-$	843,04513
	$[C_{60}+C_7H_7O_3]^-$	859,04003
	$[C_{60}+C_7H_7O_4]^-$	875,03493

3 Products formed in water? (↑ storage time 1 wk, room temp, light)



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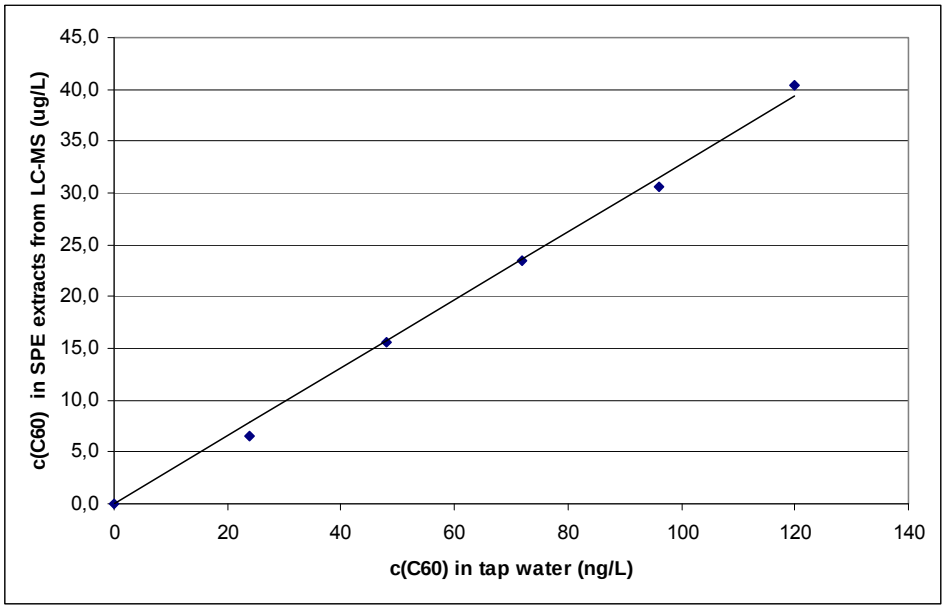
Results: Analysis of spiked water samples

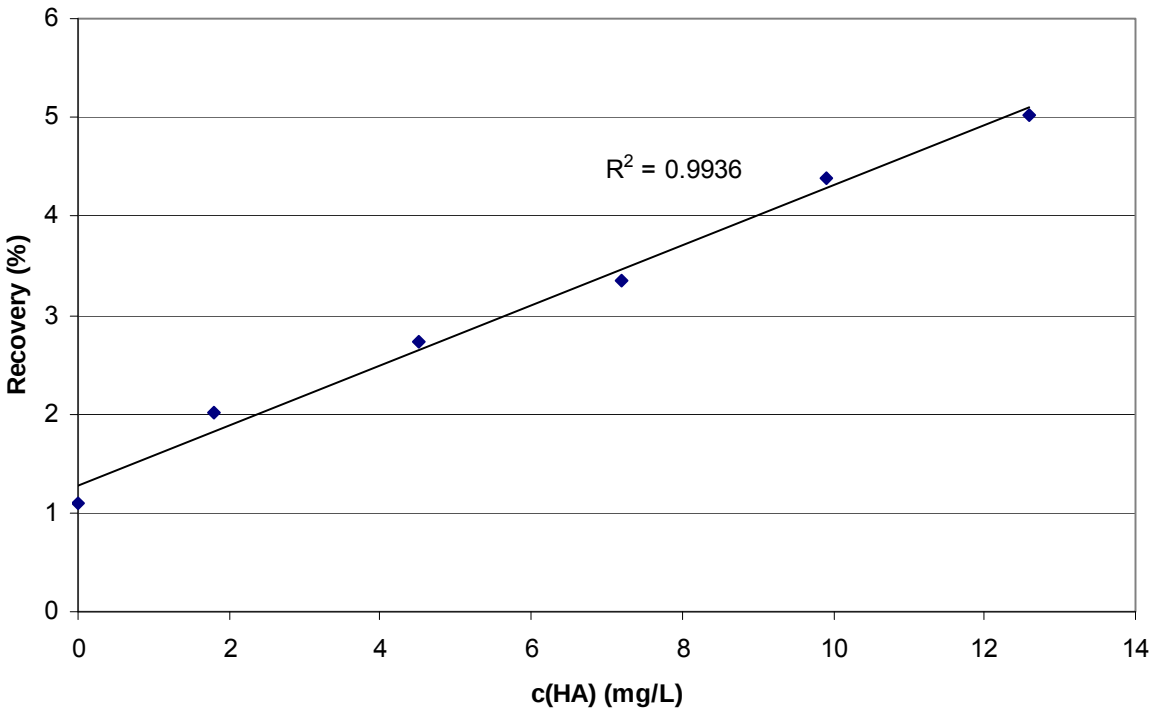
Recovery in tap water : 32 ± 2 %
Recovery in surface waters 26 ± 4 %
Recovery in ultrapure water < 3%
Recovery in (ultrapure) HA solutions 1-5%



Samples	recovery (%)
Lekchannel / Vork	28
Rhine / Lobith	32
Meuse / Brakel	23
Meuse / Esloo (before plant)	26
Meuse / Obbich (after plant)	27
Dommel / Boxtel	20
Dommel boven Eindhoven	28
Drentsche Aa	21
Rotterdam harbor	27

Results: Analysis of spiked water samples

Recovery in Fluca HA solutions
dissolved in millipore water = 1-5%



Recoveries

Influence HA on extraction efficiency?

Influence of salt content on extraction efficiency?

Recoveries

Influence HA on stability aggregates, and thereby on extraction efficiency?

Influence of salt content on stability aggregates, and thereby on extraction efficiency with SPE! [1,2,3]

Various studies have observed similar [1,2] or higher [1,4,5] recoveries in various aquoeus matrices. Nevertheless the low variation allows accurate analysis

1 Chen et al 2008, ETC 1852-1859
2 Chen et al 2010, Env Chem 10-27
3 Espinasse et al 2007, EST 7396-7402
4 Bouchard et al 2008, J Chom A 153-159
5 Farre et al 2010, J Hydrol 44-51

Hardly any quantitative monitoring data of NPs in surface water environment[1,2]

[1]Klaine et al. 2008, ET&C 27:1825-1851
2 Barcelo et al, talk of yesterday

Results: Analysis of surface water samples

µg/L

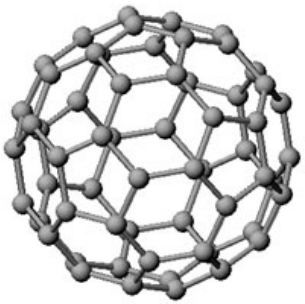
Modelled SW concentrations (excluding sedimentation)[1]

Detection limits in (surface) water <5 ng/L

ng/L

Modelled SW concentrations[1]

pg/L



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Rotterdam harbor

[1]Boxall et al. 2008, Defra
2 Gottschalk et al. 2009 EST

Results: Analysis of surface water samples

µg/L

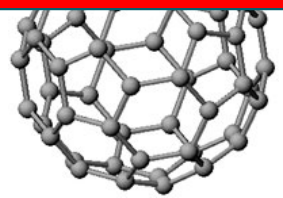
Modelled SW concentrations excluding sedimentation/sorption

Detection limits in (surface) water <5 ng/L

ng/L

No C_{60} detected in SW samples

pg/L



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[1]Boxall et al. 2008, Defra

Conclusion / Future research

- Low detection limit: <5 ng/L
- Accurate MS: identification of the products formed in water and solvent
- Analysis method applicable for accidental release, specific contaminated sites
- More sensitive analysis necessary for monitoring the aqueous environment

- Planned activities within HTS&M FES