GREENPEACE RESEARCH LABORATORIES

Innovation Centre Phase 2
University of Exeter
Rennes Drive, EX4 4RN
Exeter
01392 247920

Multiresidue analysis of pesticides in water by solid-phase extraction coupled to liquid chromatography Orbitrap mass spectrometry

JORGE CASADO AGRELO, PhD

jorge.casado@greenpeace.org

Thermo Scientific UK LC-MS User meeting

London

June 2017

OUR PEOPLE

GREENPEACE

OUR LABS

GREENPEACE

AIMS

- Short term
  - Multiresidue target analysis of pesticides in water
- Medium term
  - Extension to other matrices: sediments, soils, fruits, vegetables, cereals …
- Long term
  - Simultaneous non-target analysis for antibiotics, PFCs …

GREENPEACE

PESTICIDES

- Biocide chemical substances to control:
  - Insects (insecticides)
  - Weeds (herbicides)
  - Fungi (fungicides)

- Since 1950s extensively used in agriculture to improve production:

Although during the past 50 years the human population and global agricultural production have more than doubled, the productive arable area has increased by just 10%[1]

[1]Köhler, H. R., Triebskorn, R. (2013). Wildlife ecotoxicology of pesticides: can we track effects to the population level and beyond? Science 341: 759-765.

GREENPEACE

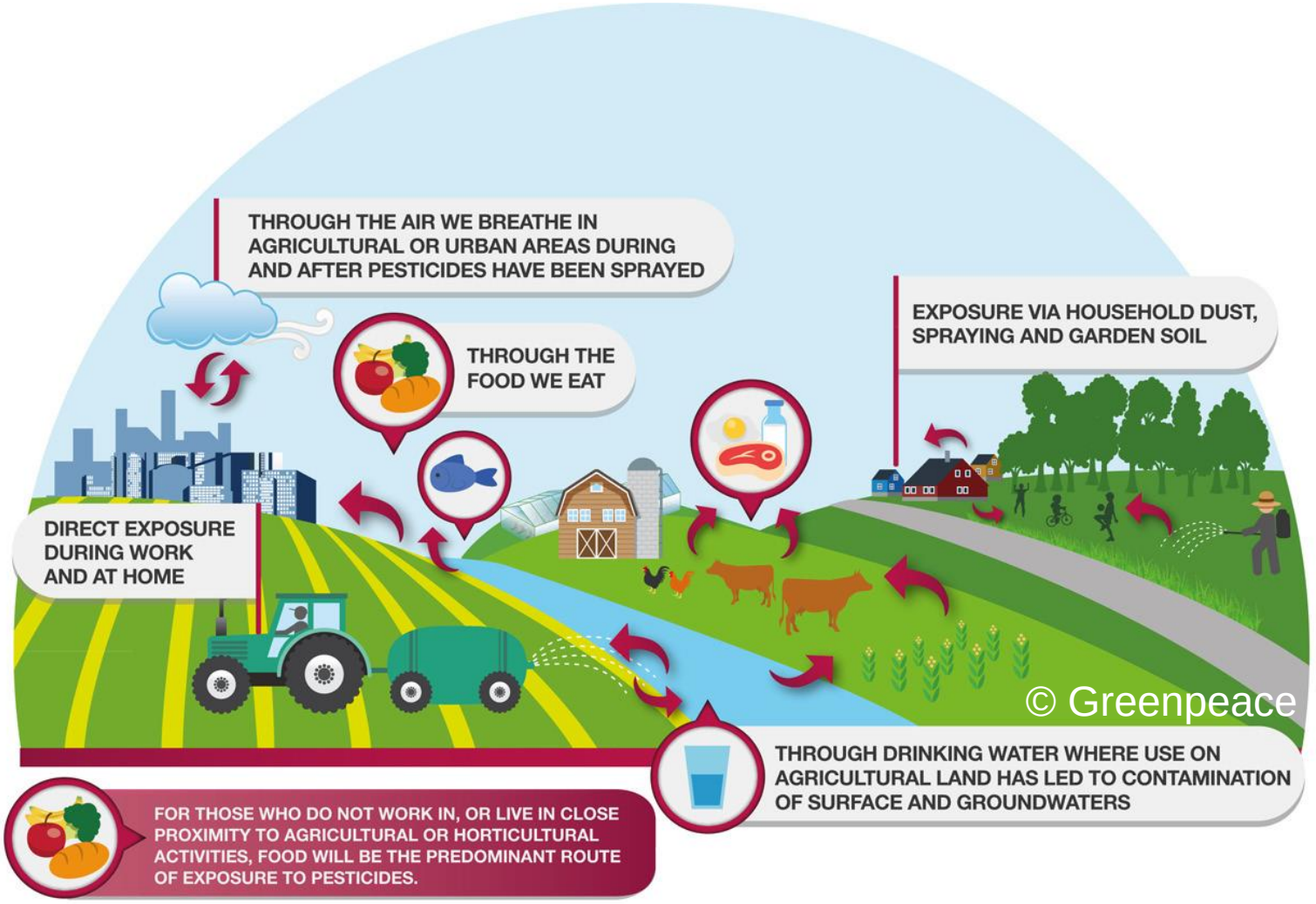
PESTICIDES

- Potential **hazards** to wildlife:
  - Reproductive failure
  - Altered behavior
  - Altered metabolism
- **Effects** on human health:
  - Developmental impairments
  - Neurological and immune disorders
  - Cancers

- **Persistence**: DDT, banned in 1972, is still being found today
- High **mobility** in water
- Poor research on pesticide **mixtures** effects
- Since 2000s EU has developed **directives** to control pesticides in surface water

GREENPEACE

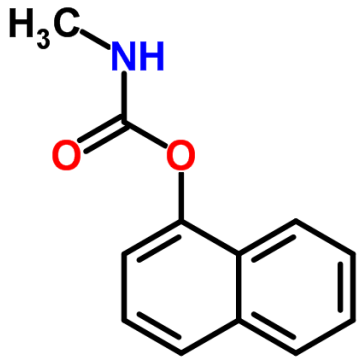
THE MEAN OF TRANSPORT: THE WATER



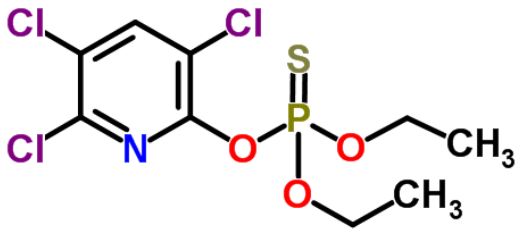
GREENPEACE

252 PESTICIDE RESIDUES

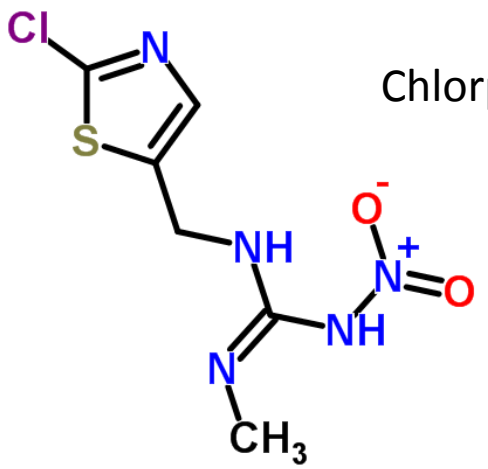
- Organophosphates**: chlrorpyrifos**, malaoxon …
- Carbamates: **carbaryl**, pirimicarb…
- Neonicotinoids: **clothianidin**, imidacloprid …
- Chloroacetamides: **alachlor**, metolachlor …
- Pyrethroids: allethrin, etofenprox …
- Azoles: difenoconazole, tebuconazole …
- Strobines: azoxystrobin, picoxystrobin …
- Anilides: boscalid, fenhexamid …
- Ureas: cycluron, diuron …
- Triazines: ametryn, trietazine …
- Pyrimidines: ancymidol, pyrimathenil …



Carbaryl



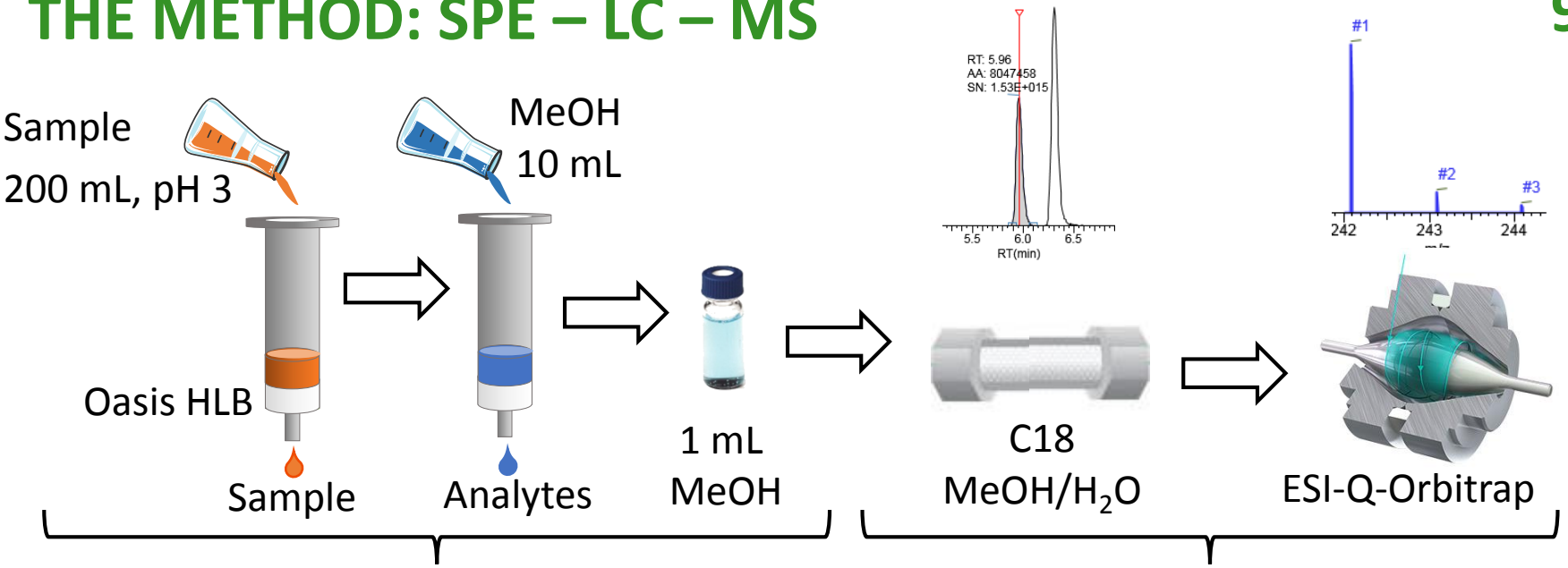
Chlorpyrifos



Clothianidin

GREENPEACE

THE METHOD: SPE – LC – MS



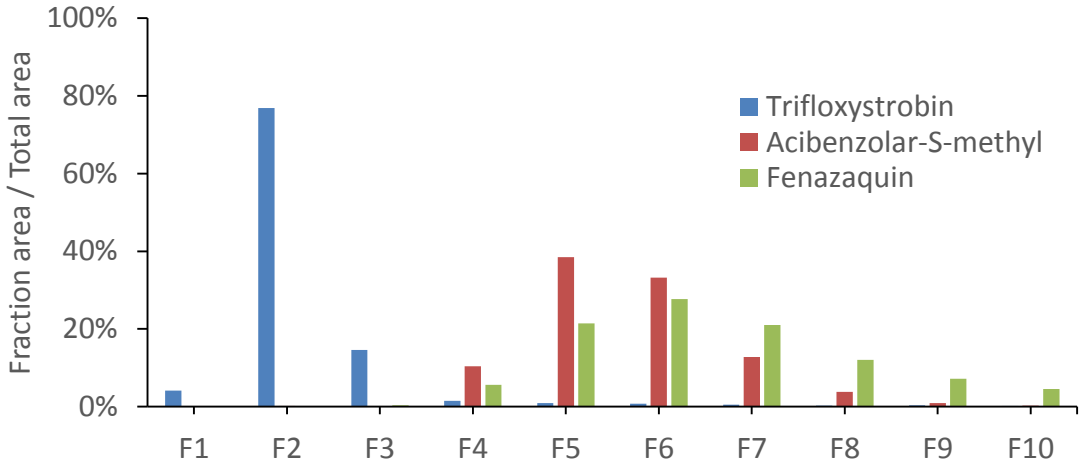
Thermo SCIENTIFIC AutoTrace SPE

Thermo SCIENTIFIC Q Exactive Focus LC-MS

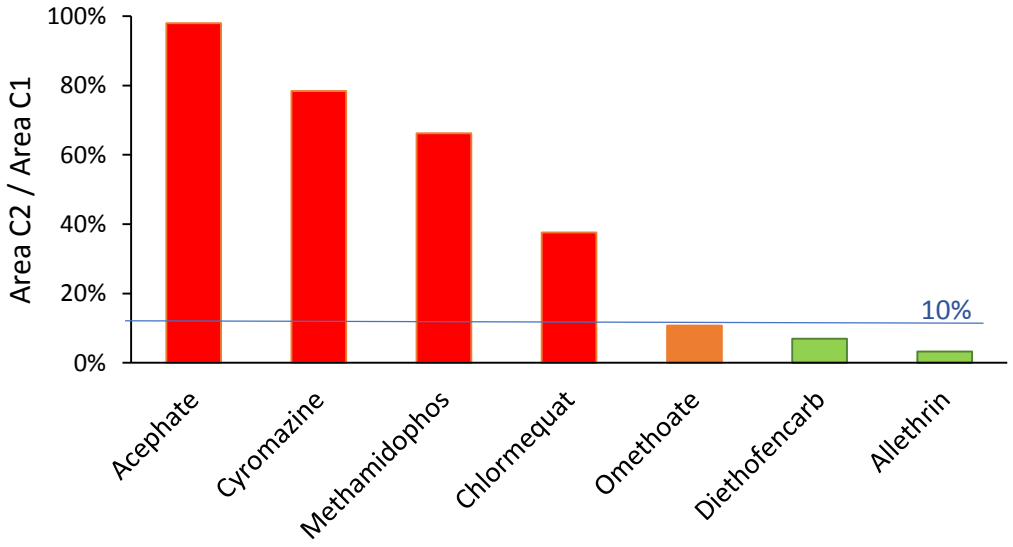
GREENPEACE

SPE OPTIMISATION

Elution volume



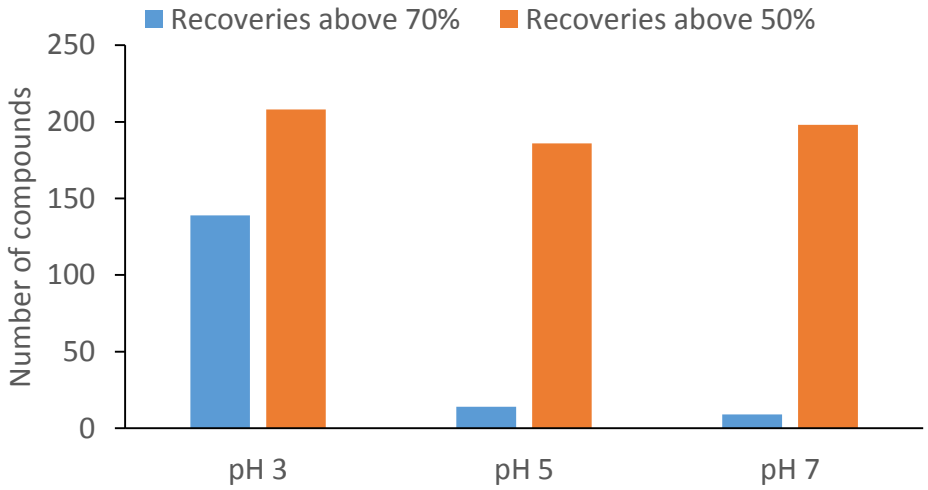
Breakthrough issues

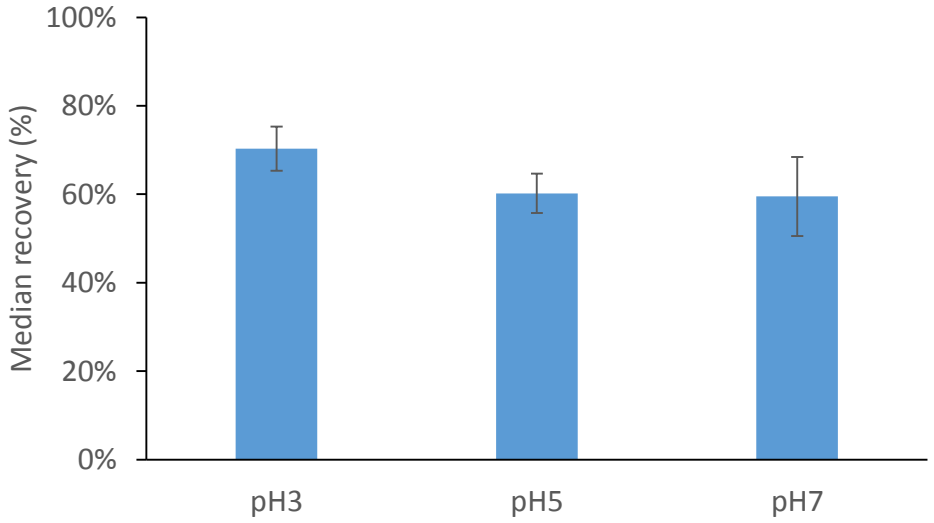


GREENPEACE

SPE OPTIMISATION

Sample pH



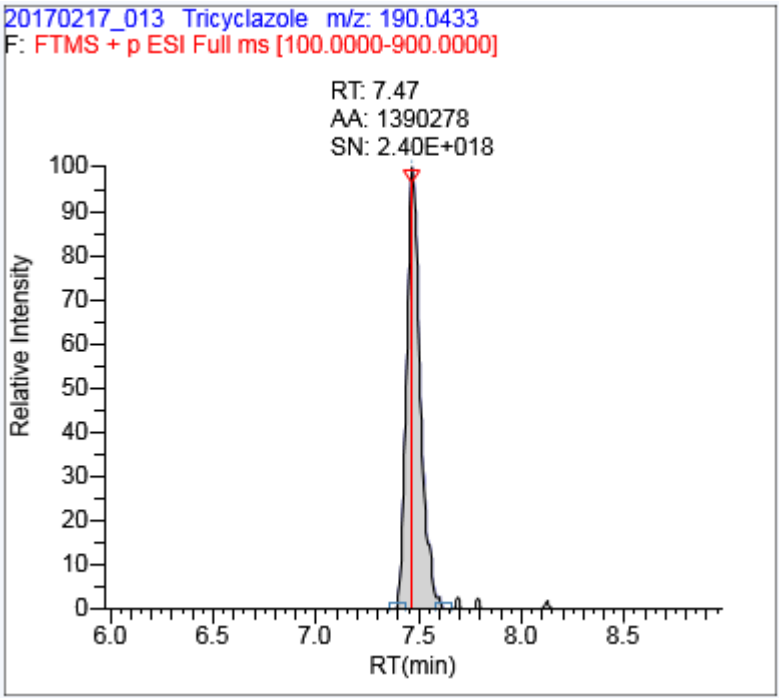


GREENPEACE

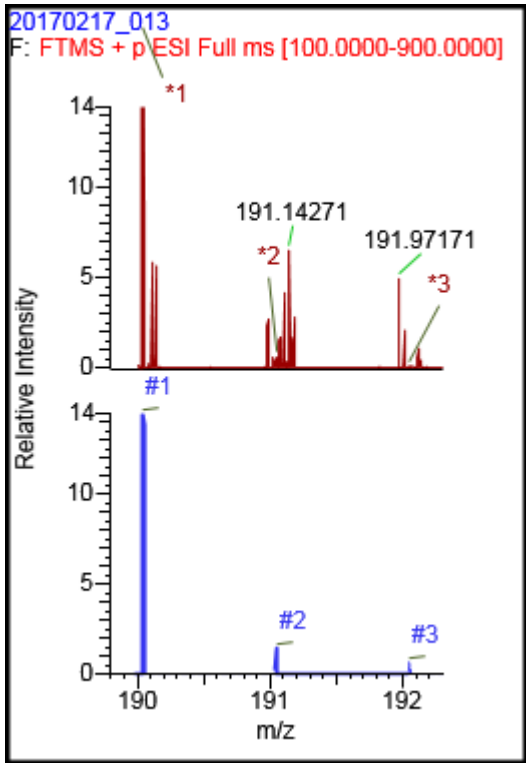
LC-MS ACQUISITION

- C18 Accucore aQ
  - Methanol/water (0.1% formic acid, 5 mM ammonium formate)
- Full scan: 70,000 resolution
  - Data-dependent MS/MS: 17,500 resolution; CE 15, 30, 45 eV

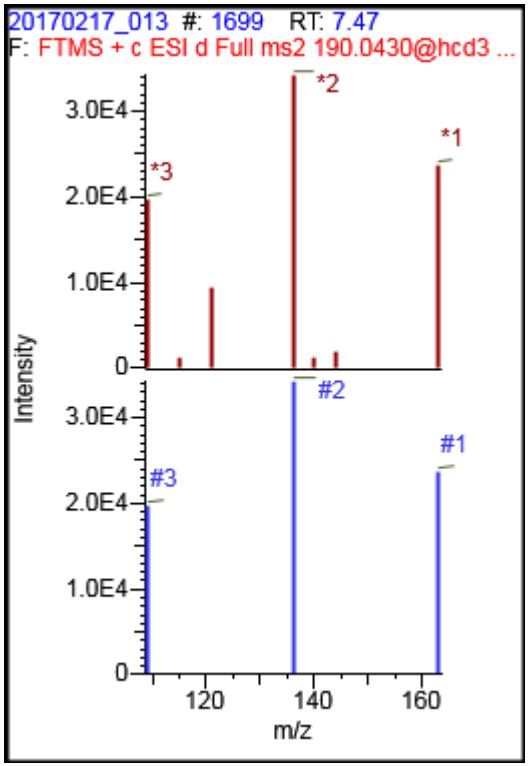
Full scan chromatogram (error: 5 ppm)



Full scan mass spectrum



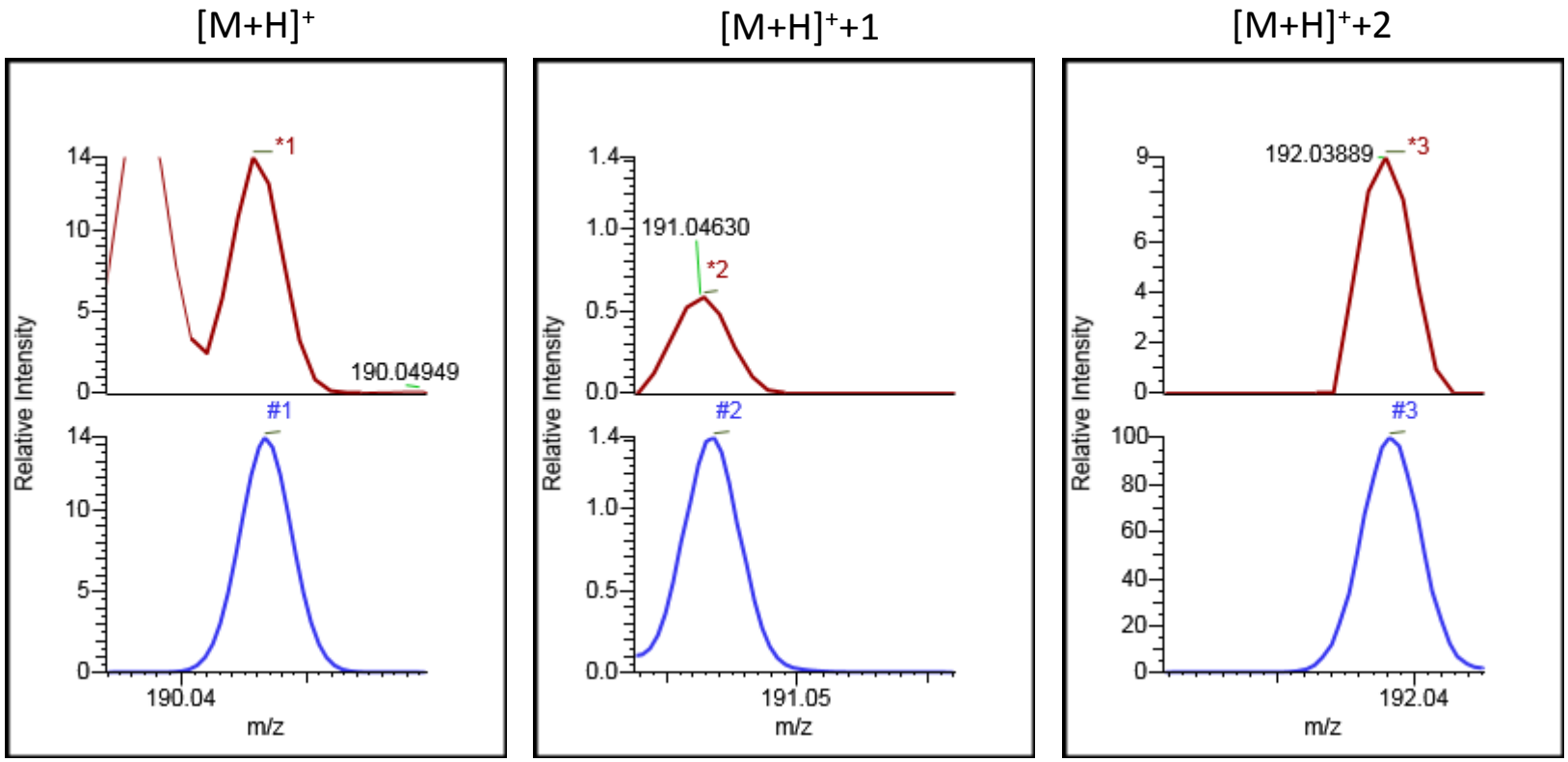
MS/MS mass spectrum



GREENPEACE

LC-MS ACQUISITION

Full scan mass spectrum



Obtained MS

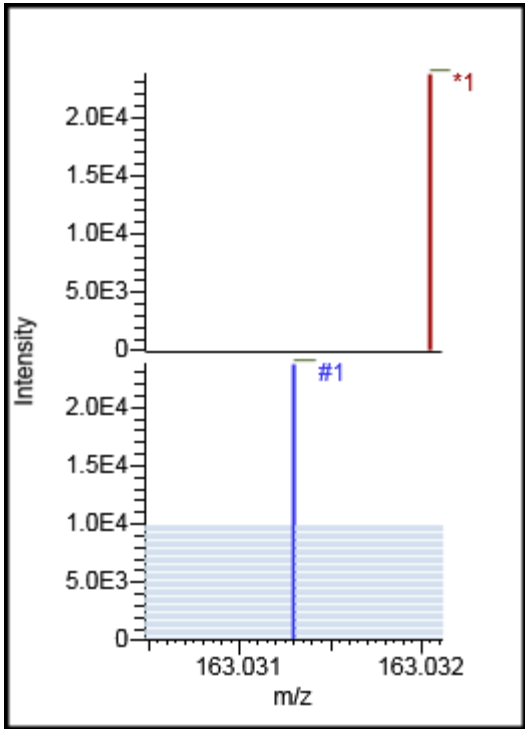
Expected MS

GREENPEACE

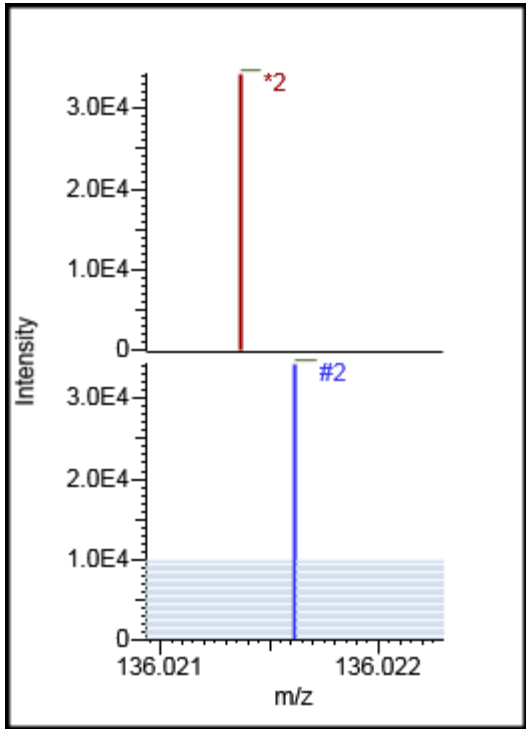
LC-MS ACQUISITION

MS/MS mass spectrum

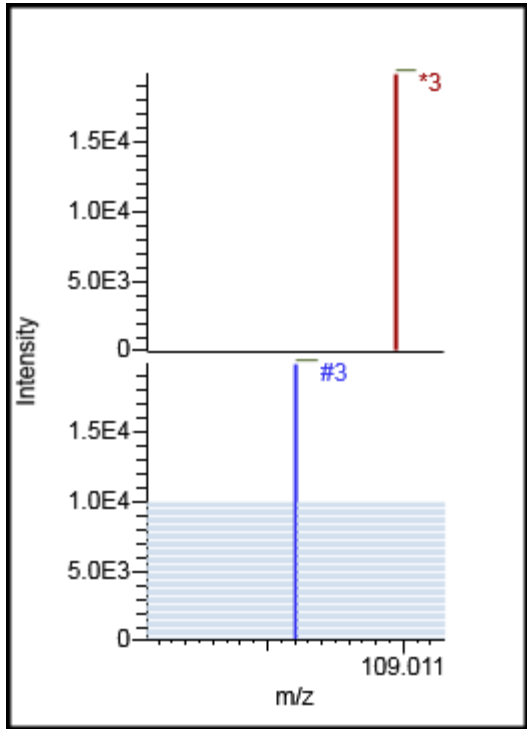
163.0313



136.0216



109.0106



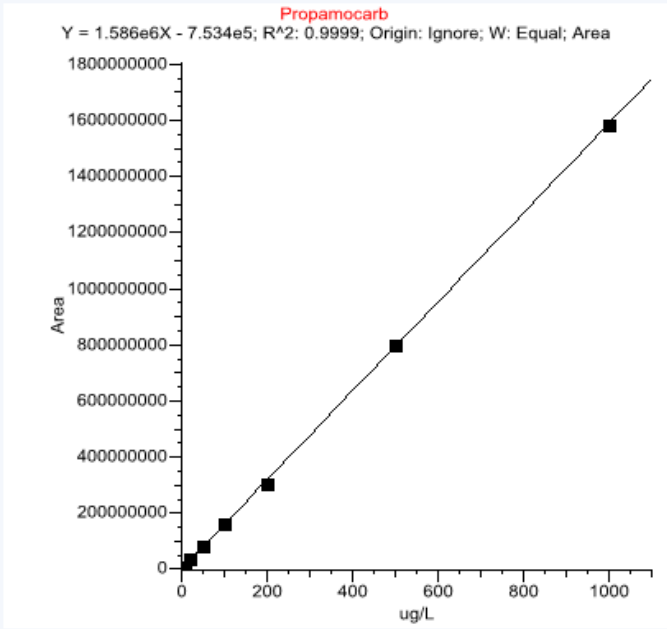
Obtained MS

Expected MS

GREENPEACE

FIGURES OF MERIT

- LOQ: 205 pesticides < 5 ng/L (ppt)
  - 0.1 – 50 ng/L (ppt)
- Linearity: R^2 > 0.99 (7-15 levels)
  - 234 pesticides LOQ - 1000 µg/L
  - 18 pesticides LOQ - 500 µg/L
- SPE yield: 229 pesticides > 70%
- ESI yield: 246 pesticides > 70%
- Inter-day repeatability: RSD < 15%



	Recoveries Surface Water		
Concentration	1 µg/L	0.2 µg/L	0.05 µg/L
Pesticides > 70%	211	217	181

GREENPEACE

I. INDUSTRIAL PARK IN CHINA

Mongolia

Beijing
北京

Qilu

Lianyungang

North Korea

Sea of Japan

Seoul
서울

South Korea

Yellow Sea

Japan

Nagoya
名古屋

Tokyo
東京

Osaka
大阪

Sapporo
札幌

China

Shanghai
上海

New Delhi

Nepal

Bhutan

Bangladesh

India

Myanmar
(Burma)

Laos

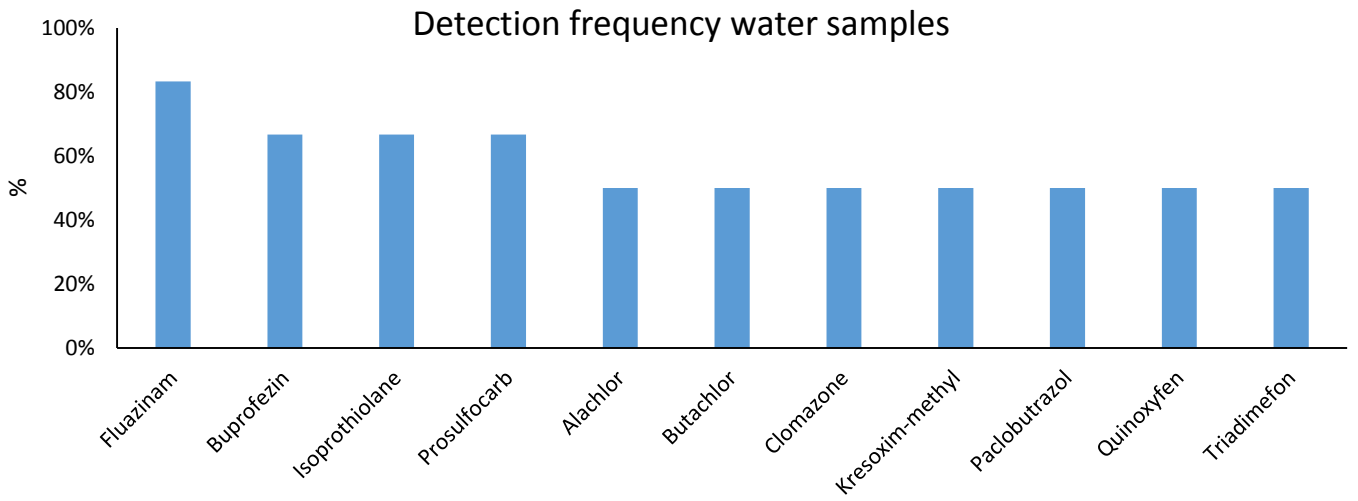
Taipei
台北

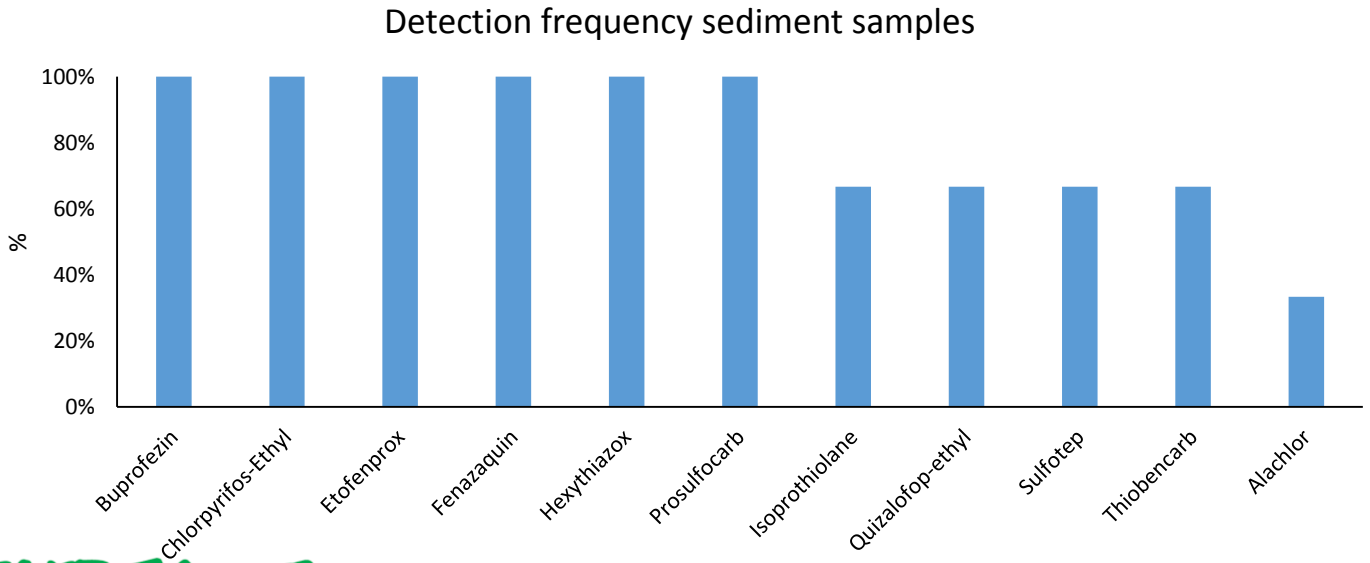
Taiwan

Hong Kong

GREENPEACE

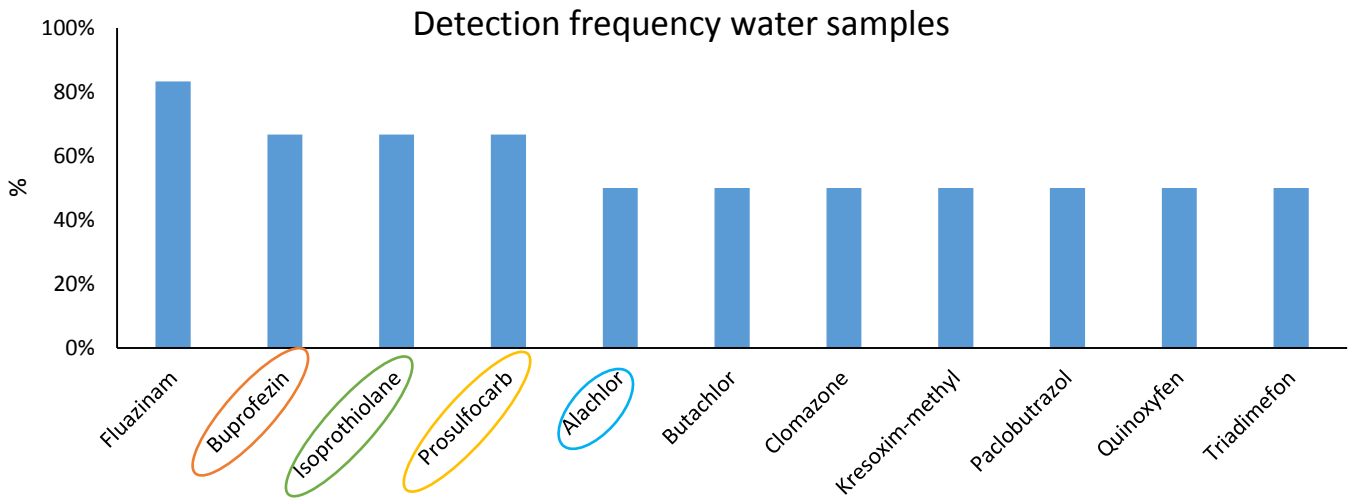
I. INDUSTRIAL PARK IN CHINA

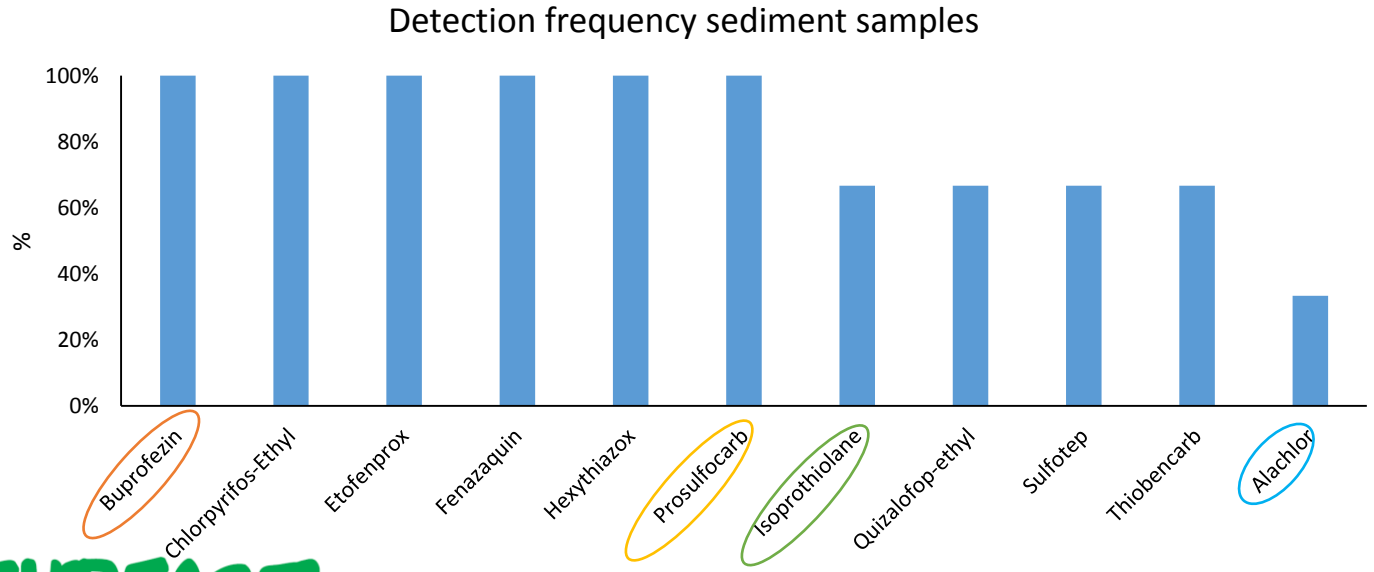




GREENPEACE

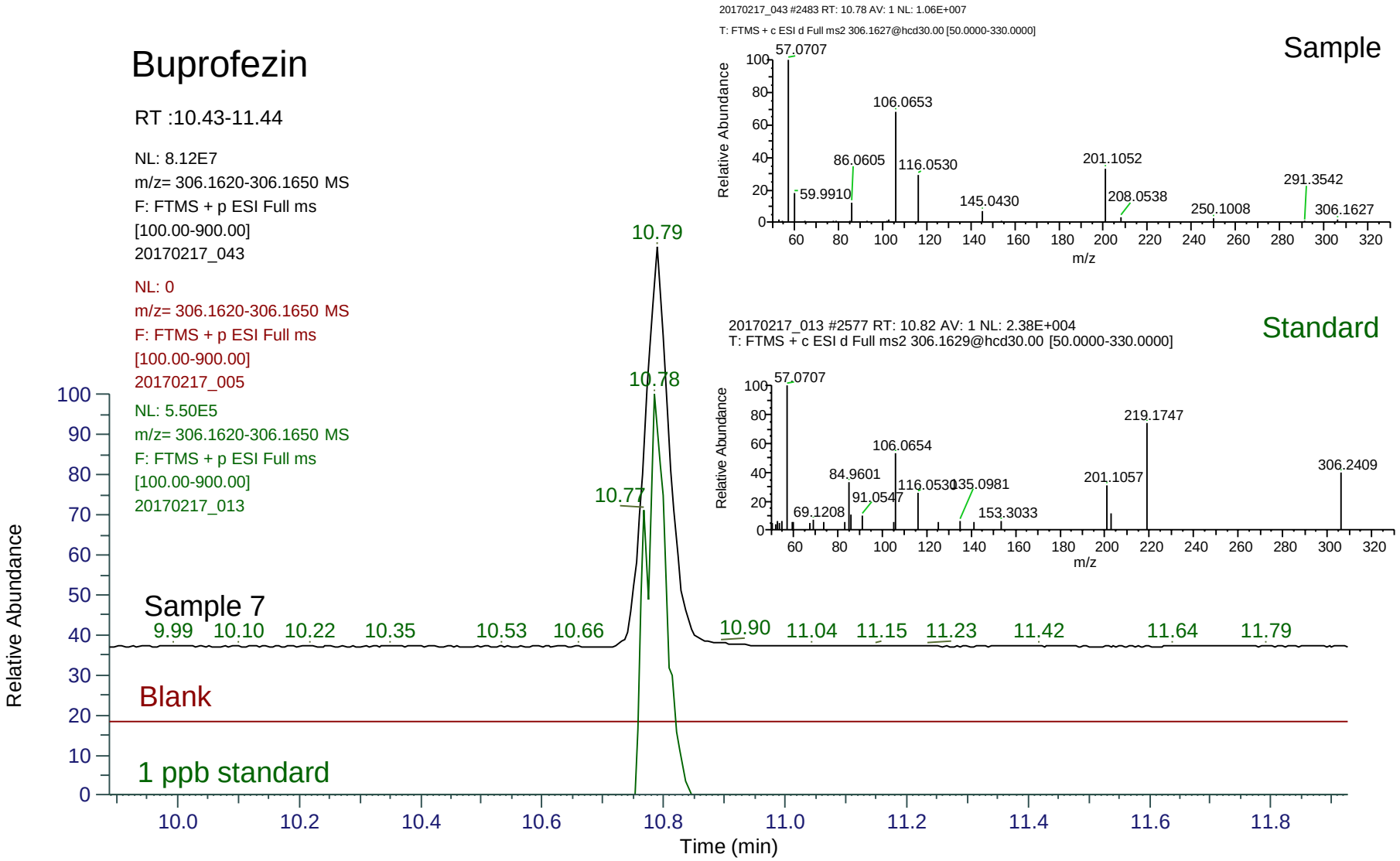
I. INDUSTRIAL PARK IN CHINA





GREENPEACE

I. INDUSTRIAL PARK IN CHINA

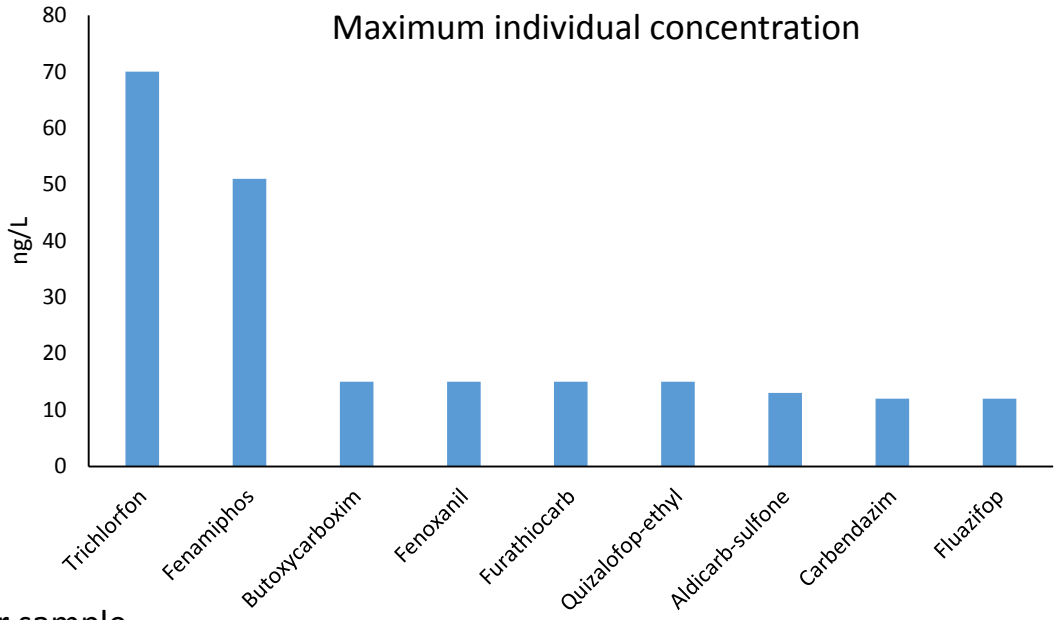


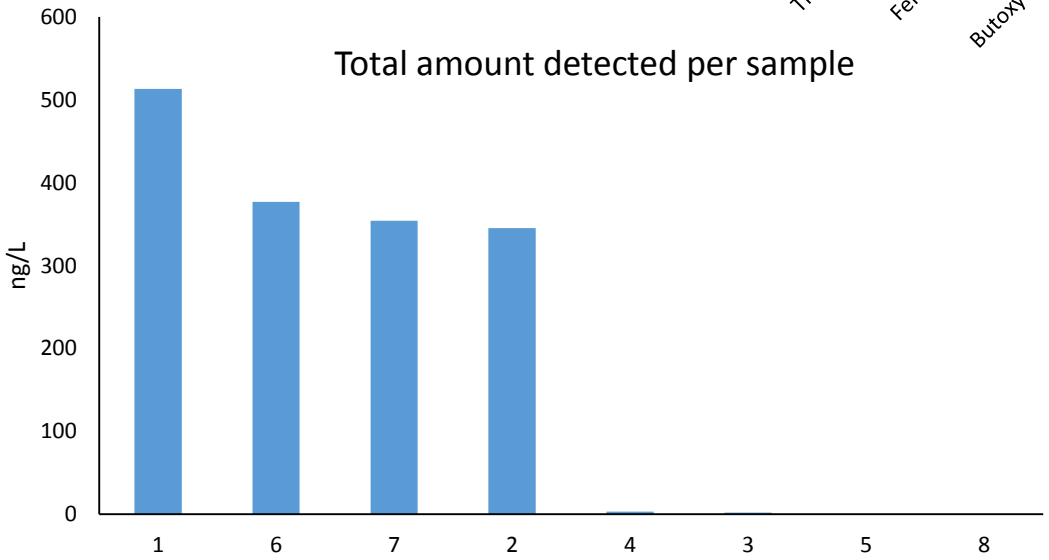
GREENPEACE

II. LAKE VICTORIA

Detection frequency (> LOQ):

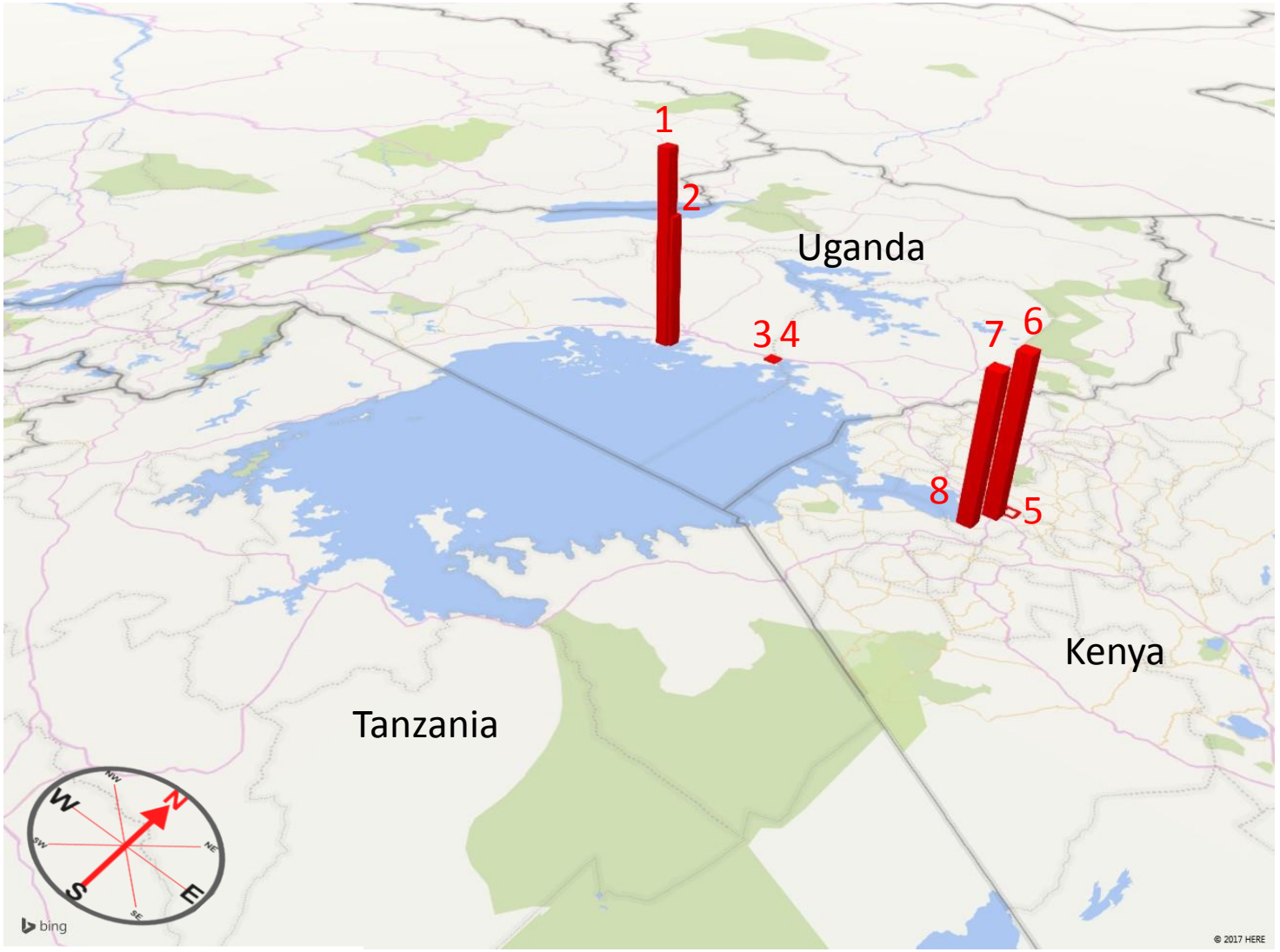
- 75% Schradan
- 63% Mexacarbate
- 50% Another 43 pesticides





GREENPEACE

II. LAKE VICTORIA



GREENPEACE

II. LAKE VICTORIA

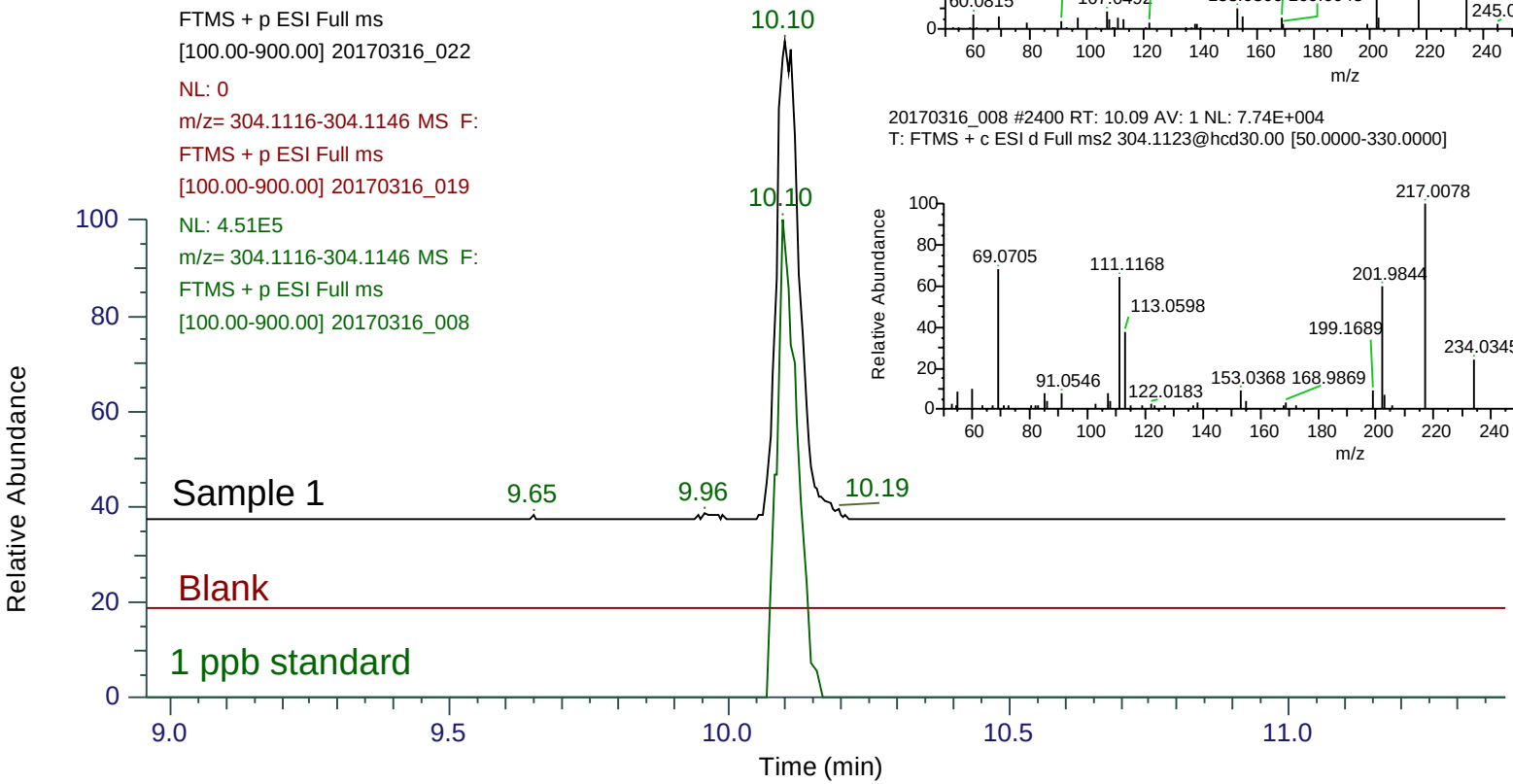
Fenamiphos

RT :8.96-11.39

NL: 5.66E6
m/z= 304.1116-304.1146 MS F:
FTMS + p ESI Full ms
[100.00-900.00] 20170316_022

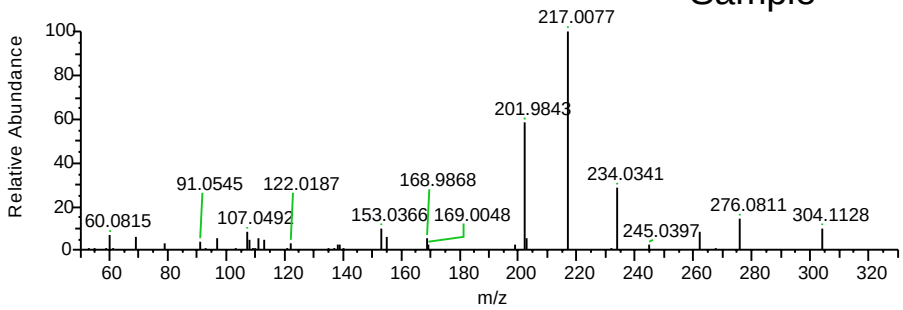
NL: 0
m/z= 304.1116-304.1146 MS F:
FTMS + p ESI Full ms
[100.00-900.00] 20170316_019

NL: 4.51E5
m/z= 304.1116-304.1146 MS F:
FTMS + p ESI Full ms
[100.00-900.00] 20170316_008



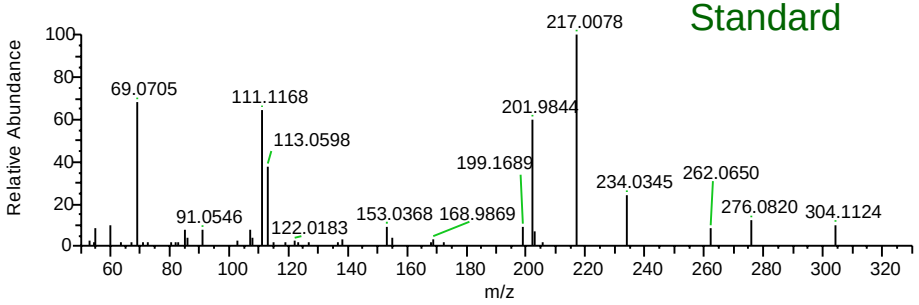
20170316_022 #2338 RT: 10.12 AV: 1 NL: 8.23E+005
T: FTMS + c ESI d Full ms2 304.1122@hcd30.00 [50.0000-330.0000]

Sample



20170316_008 #2400 RT: 10.09 AV: 1 NL: 7.74E+004
T: FTMS + c ESI d Full ms2 304.1123@hcd30.00 [50.0000-330.0000]

Standard



GREENPEACE

CONCLUSIONS

- LOQs far below current European legislation
- Quantification of 252 pesticides in 12 minutes
- Analysis of surface water
  - Low individual concentrations
  - Risk of mixtures at high concentration
  - Legislation only establishes individual MRLs ignoring cocktails of pesticides
- Possible solution: ecological farming[2] + local production/consumption

[2] http://www.greenpeace.to/greenpeace/wp-content/uploads/2015/05/Food-and-Farming-Vision.pdf

GREENPEACE

ACKNOWLEDGEMENTS

UNIVERSITY OF EXETER

Thermo SCIENTIFIC

THANKS FOR YOUR ATTENTION

jorge.casado@greenpeace.org

GREENPEACE