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Natural Resources Wales

Chemical monitoring activity under the Water Framework Directive – Analytical challenges and solutions

Anthony Gravell

Natural Resources Wales

Llanelli laboratory

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About us

Natural Resources Wales brings together the work of the Countryside Council for Wales, Environment Agency Wales and Forestry Commission Wales, as well as some functions of Welsh Government.

Our purpose is to ensure that the natural resources of Wales are sustainably maintained, enhanced and used, now and in the future

Who we are and what we do

The principal adviser to the Welsh Government on the environment, enabling the sustainable development of Wales' natural resources for the benefit of people, the economy and wildlife

Overview

- Monitoring under the Water Framework Directive
- Passive Sampling
- HRAM Screening
- Confirmation of identity of pollutants in real life samples
- Summary

WFD

- far-reaching and complex legislation for water quality across Europe
- involves the formulation of cross border River Basin Management Plans (RBMPs)
- introduces environmental quality standards (EQS) values for priority hazardous substances

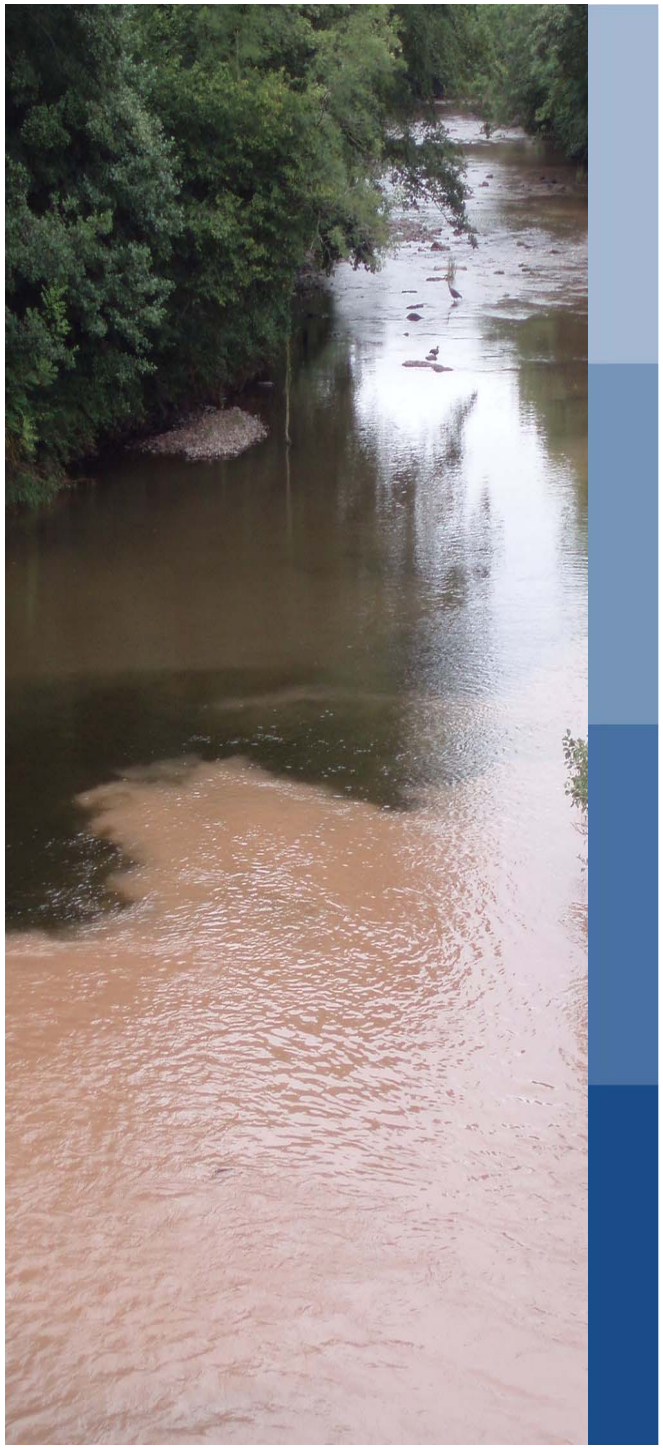
WFD challenge

- The WFD via revised Environmental Quality Standards (EQS) has driven down the required reporting limits for selected compounds to challenging concentrations analytically!

- Lower detection limits for selected compounds require high specification instruments to deliver required sensitivity

- New monitoring methods and analytical techniques are now necessary

- Further requirement to undertake **investigative** monitoring in order to identify unknown non-target pollutants in water bodies with poor ecology or identified at risk



Environmental Challenge

- Achieving and maintaining a “Good Status”

Only 5 rivers in England & Wales meet the new tough standard or High ecological status, which looks at ecological, as well as chemical and other factors..

93% of rivers are currently classified as ‘good’ or ‘fair’ based on their chemistry. However, it is estimated that 95% of water bodies are at risk of failing to meet WFD ”good status”

- Identifying all of the sources of potential pollution

- Estimated that 80% of work required just to stand-still

Pressures of climate change & population growth

Current issues with investigative monitoring

- Pollutants can be below the limit of detection but high enough to have a chronic effect on aquatic organisms
- Current spot sampling techniques unable to detect transient events - only a snapshot at time of sampling
- Therefore many compounds / pollutants will remain unidentified!
- Large errors associated with calculations of mass loadings of receiving water courses

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One novel approach - Passive sampling with HRAM screening

Benefits of passive sampling

- passive (integrative) sampling concentrates trace levels of chemicals
- provides time-weighted average concentrations and gives realistic chemical loading levels
- detects transient changes in environmental contaminant concentrations (vs ‘spot’ sampling)
- applicable to almost all aqueous environmental conditions
- selectively samples residues from the dissolved (readily bio-available) phase
- allows concentration of trace, yet toxicologically relevant, contaminant mixtures over extended periods of time

Choice of sampler

Chemcatcher

Sampler on holder

PTFE sampler

SPE disks

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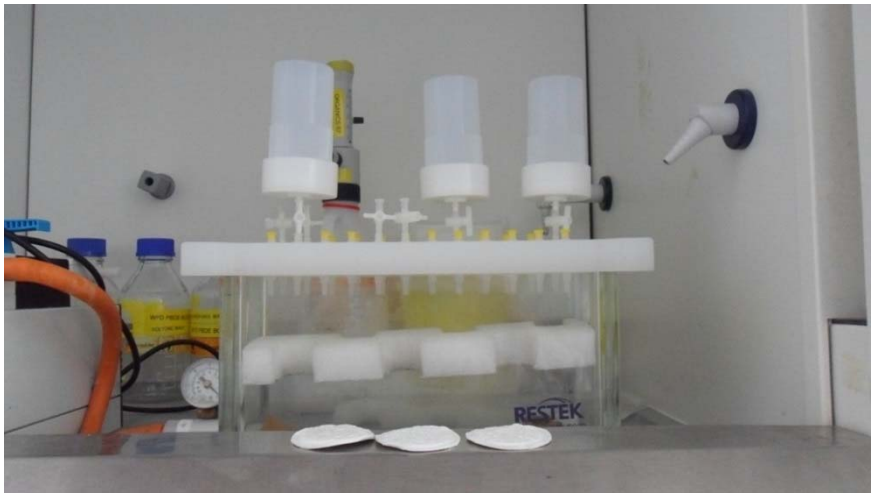
Deployment and retrieval of samplers

Housing deployed close to river bed resulting in the deposition of silt in the protective housing

POCIS samplers showing fouling after retrieval, before rinsing with distilled water

Extraction of samplers

Disks are cleaned, eluted with methanol and reduced to low volume



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Findings from a recent trial

- More than 90% of the compounds identified using a combination of passive samplers and screening methods were not identified using the routine spot sampling technique

- Also, 95% of the compounds identified using the recently developed LCMS screen were not identified using the routine GCMS Target based multi residue screen method

- Many of the substances identified by passive sampling are priority hazardous substances listed in Annex X of the Water Framework Directive

- Other compounds identified by passive sampling include the newly classified emerging contaminants such as triclosan, pharmaceuticals and sun-screen agents

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River Wye at Bigsweir Bridge

POCIS
Carbendazim
Metalaxyl
Ethirimol
Simazine
Isoproturon
Chlortoluron
Terbutryn
Propyzamide
Metazachlor
Phenoxyacetic acid
Flufenacet

Mixture of fungicides, herbicides identified by LCMS Screen not picked up by GC-MS Screen

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River Mersey at Woolston Weir

POCIS
Carbendazim
Thiabendazole
Metamitron
Isoproturon
Diuron
Prometryn
Terbutryn
Napropamide
Flufenacet
Phenoxyacetic acid
MCPP
Aldicarb sulfoxide

Mixture of fungicides, herbicides and insecticide metabolite identified by LCMS Screen - Not picked up by GC-MS Screen

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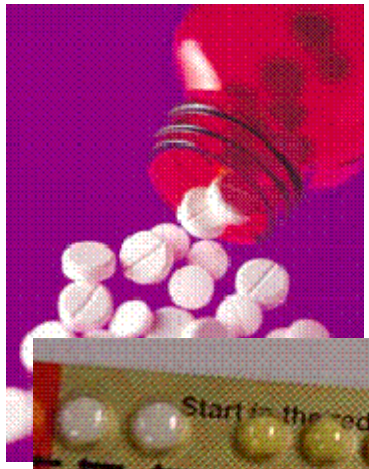
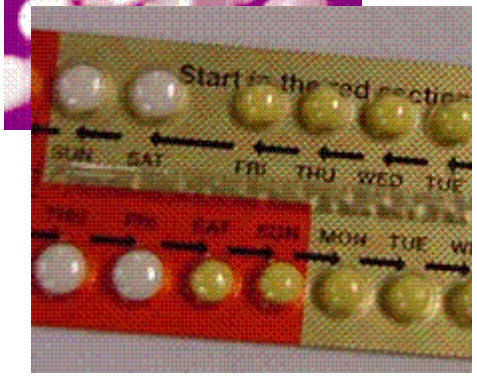
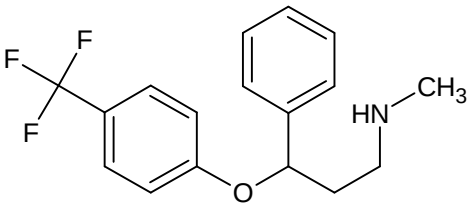
Other polar compounds found

POCIS
Carbamazepine
Sulfamethoxazole
Oxprenolol
Atenolol
Sotalol
Trimethoprim
Ibuprofen
PFHS
PFOA
PFOS

Mixture of pharmaceuticals inc. analgesics, anti-biotics, beta blockers plus persistent fluorinated compounds







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Screening for pharmaceuticals

- Pharmaceuticals now included in WFD
- Most work undertaken by LCMS QQQ
- Database of pharmaceuticals developed based on top 200 prescribed pharmaceuticals in England & Wales
- POCIS extracts run on Q-Exactive
- 39 compounds specifically interested in due to matrix interferences on lower resolution instrument

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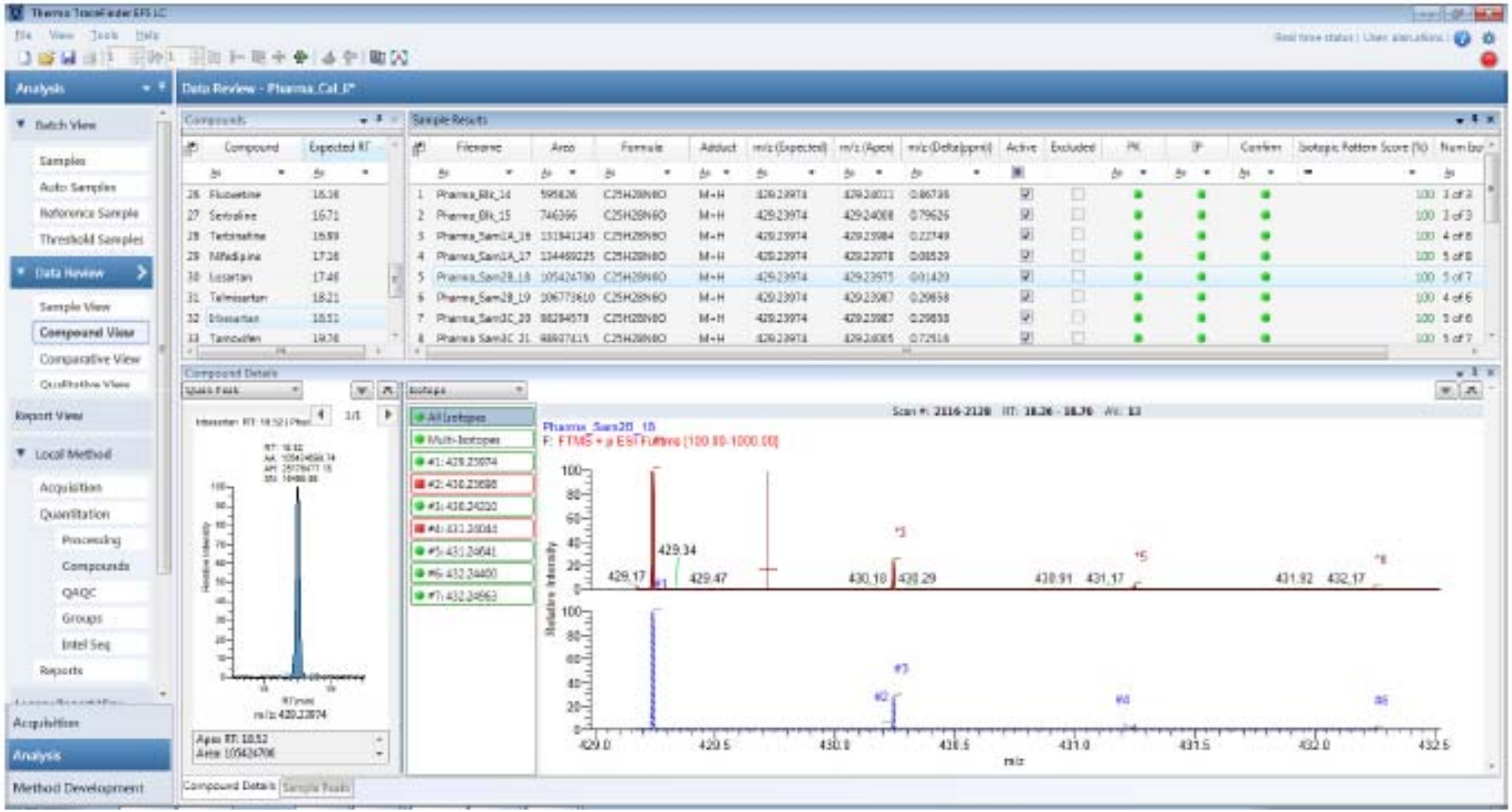
Irbesartan in sample extract



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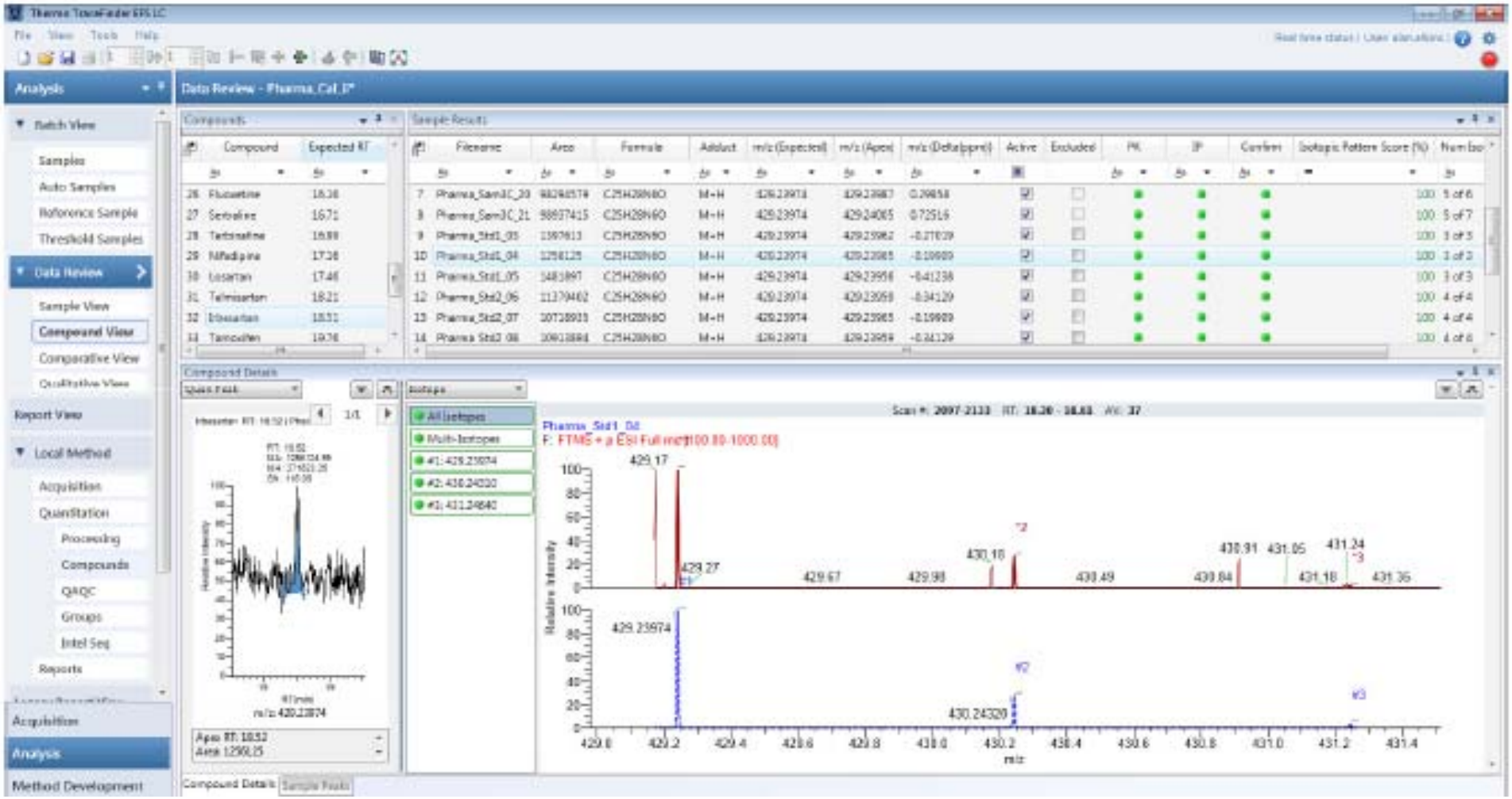
Irbesartan std at 40ppt



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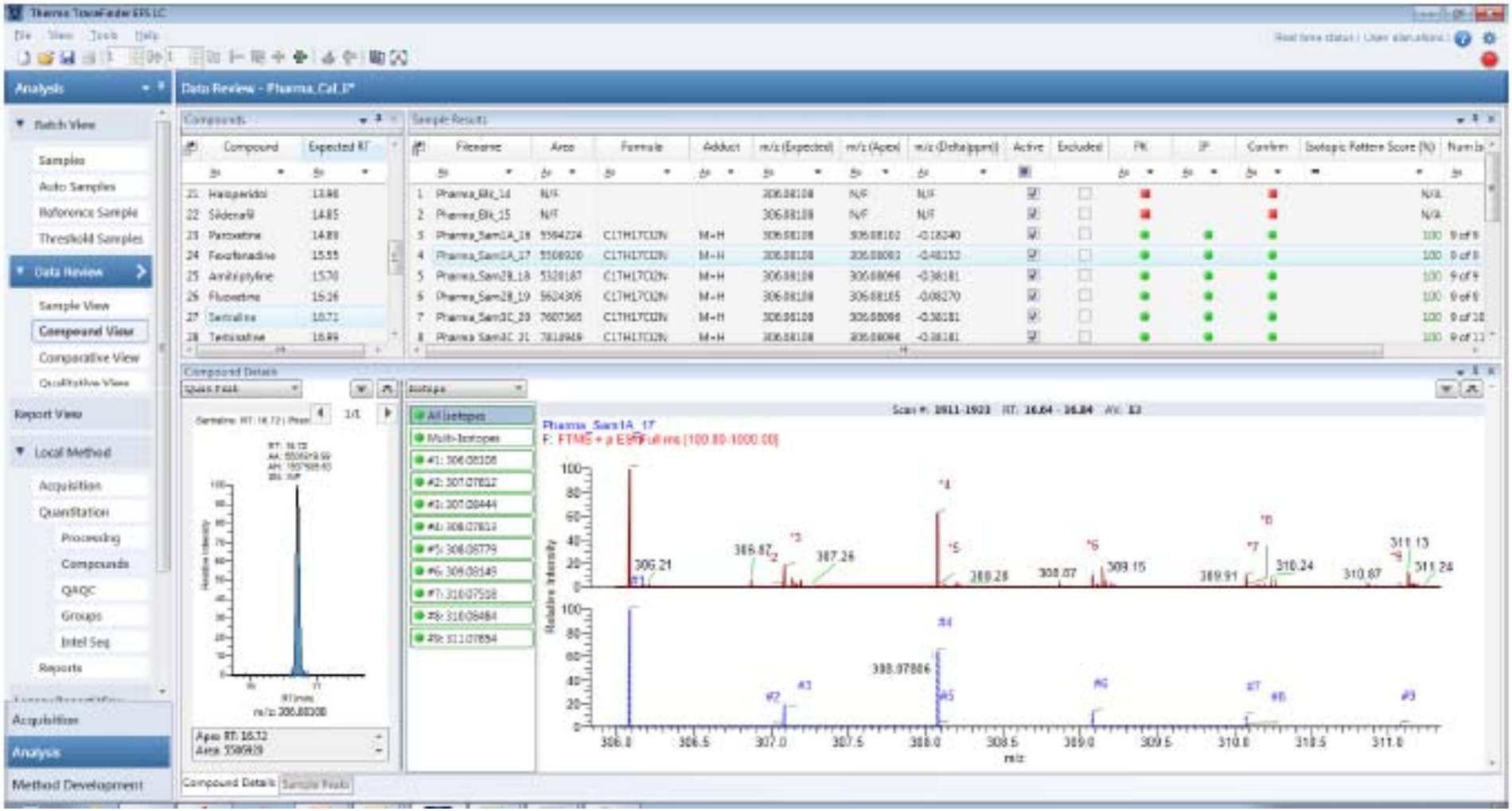
Sertraline in sample extract



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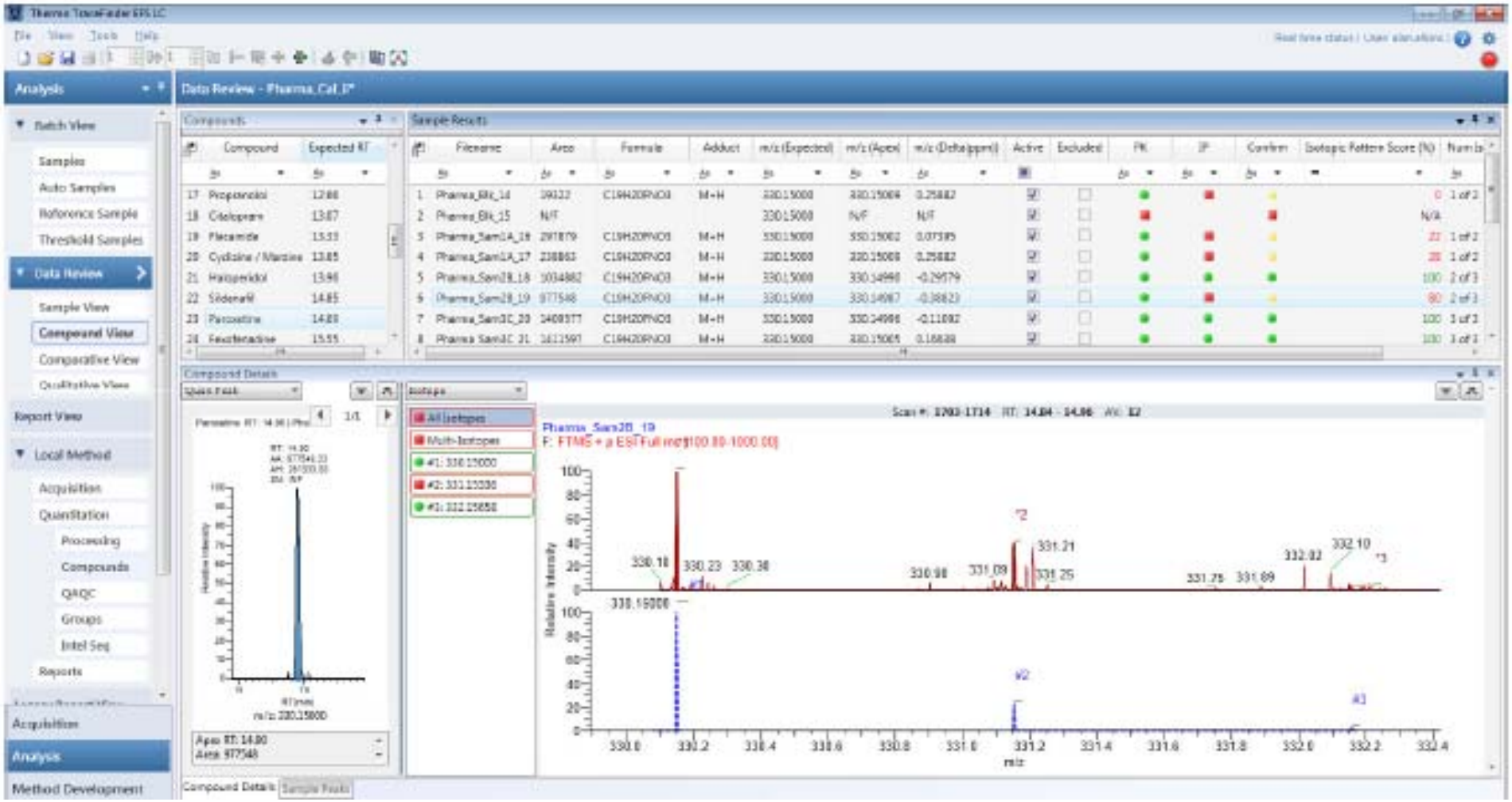
Paroxetine in sample extract



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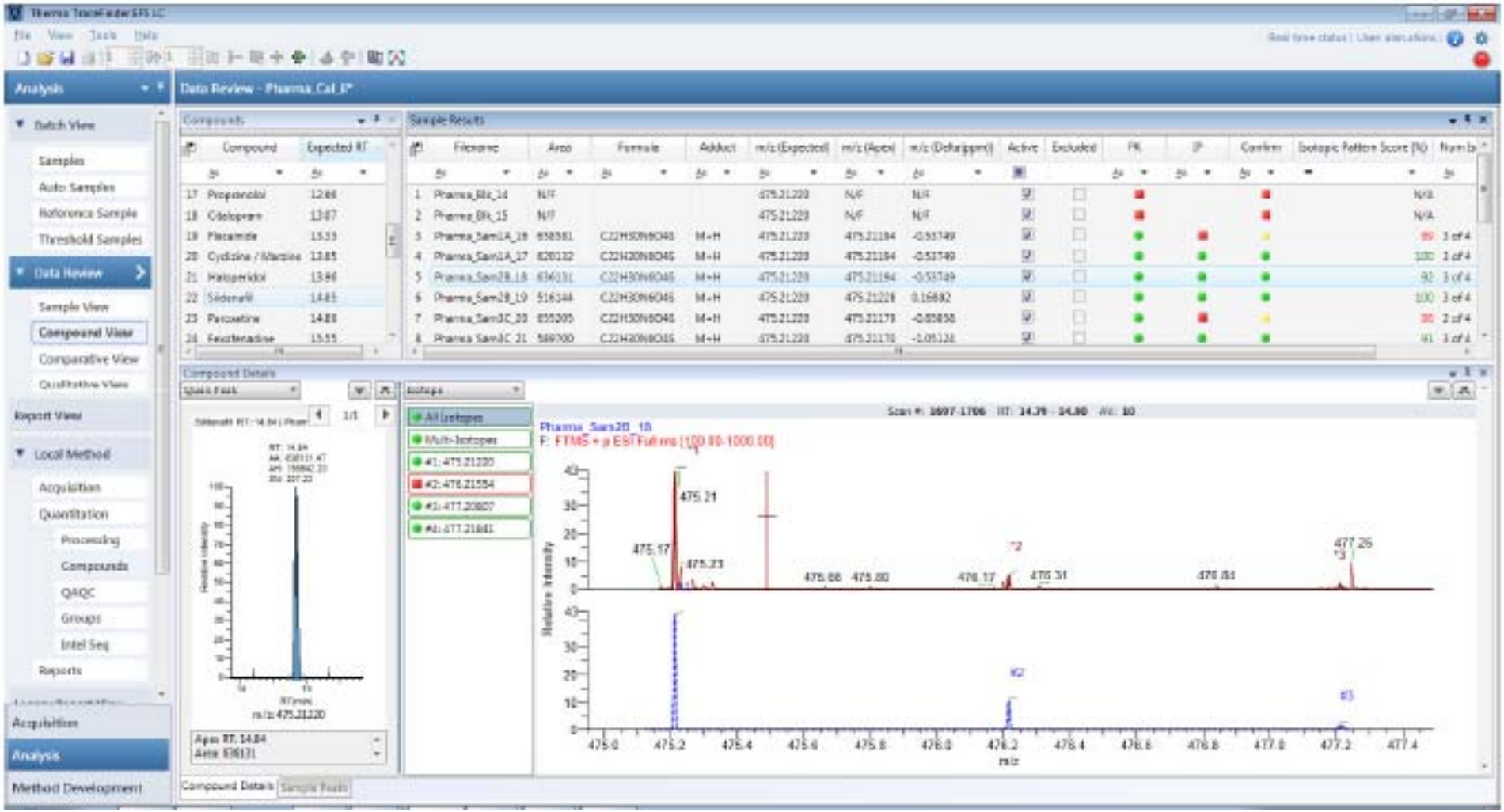
Sildenafil in sample extract



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Results from Q-Exactive screening

- Chromatographic peaks and isotopic pattern matches have been reported for all 39 compounds, in both matrix samples and standard solutions
- Mass accuracy was excellent, typically < 1ppm and the maximum error observed was 2.25pm. This was using no lock mass.
- By using high resolution (140,000 @ m/z 200) the fine isotopic structure could be observed to further confirm identification.
- High resolution also resolved isobaric species in the background, maintaining the excellent mass accuracy

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Summary & Conclusions

- Passive samplers are an effective investigative tool
- Detects episodic changes in environmental contaminant concentrations often missed with spot sampling
- Proven to accumulate a wide variety of polar pesticides
- TWA estimates of concentration obtained from calibration
- Use of Q-Exactive resulted in increased sensitivity & confidence in identification of pharmaceutical residues

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Thank you for listening