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CHEMICALS INVESTIGATION PROGRAMME 2 - OVERVIEW

The Chemical Investigation Programme 2 (CIP2) is being driven in the UK by the requirements of the European Union (EU) Water Framework Directive (WFD). The WFD's main objective is to increase water quality within the EU. It is measured by various factors including the physical, biological and chemical quality of all ground and surface waters in the EU. The original aim was for all groundwater bodies to be classified as at least 'good' by 2015.

Introduced in 2000, the directive was implemented into UK law in 2003. Since then, River Basin Management plans (RBMP) have been developed and used as a tool to manage the 10 river basin districts within England and Wales, as well as the Solway-Tweed river basin in Scotland. These plans are jointly managed between the EA, DEFRA, local water companies, the NRW in Wales, SEPA in Scotland, and designed in consultation with as many affected parties as possible. The next sets of RBMP's are due to be finalised in June 2015, and when complete, will set out a clear program of legally enforceable measures to improve water quality in these regions. Measures may include changes to farming/pesticide use practices, reducing use of high risk compounds in certain trades/areas, reducing the impact of building developments, and in the case of the water industry, delivering improvements to water company assets which will increase removal of harmful environmental contaminants. These measures would ideally tie into the water industry Asset Management Program cycles, although the 6 yearly RBMP's do not align with the 5 yearly AMP's, so there is usually some delay in planning for these measures. The current AMP cycle running from 2015-2020, AMP6, is particularly focused in improving efficiencies while still achieving improved wastewater quality.

The outcomes of the investigations planned in CIP2 will provide a great deal of information to inform which technologies and processes provide the best contaminant removal at the most economical cost. It would be accurate to say that the law of diminishing returns particularly applies to the removal of certain compounds (such as EDC's), with a significant investment required to remove ever decreasing substance amounts. Adding this to the pressure to reduce water bills for customers (or at least not increase them by too much), it is therefore important to identify which forms of treatment perform most effectively, and at the lowest cost to the water company.

Designed by various collaborators, including UKWIR, Atkins, Brunel University and Cranfield University, the original CIP1 program ran from 2010 to 2013. CIP1 provided a large set of data by monitoring a range of substances in various stages of the water cycle. This data showed that current treatment processes actually do achieve high levels of contaminant removal. However, the stringent EU quality standards mean that discharges from some wastewater treatment works may still pose a risk to water quality in receiving rivers. Other conclusions drawn from this data included identifying sources of contamination from each substance, and more detail on the effectiveness of substance removal across various primary, secondary and tertiary treatment processes.



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Over the past few months, ALS Environmental has successfully begun sampling and analysis for a full range of determinands in support of the CIP2, which will run for a 5 year period up to 2020. We are working in partnership with various Waste Water Treatment Companies to complete the full program of analysis, across a range of matrices.

The CIP2 project has been designed to follow on from the original CIP project aims, but with a different focus. Whereas for CIP1, a relatively small subset of treatment works were sampled to get an idea of the compliance risk posed by certain substances on a national level, for CIP2, over 600 works will take part in a much more specific effluent monitoring program. This data will be used to assess compliance risk on a site by site basis, and establish which of these sites would benefit from further investment in future AMP phases.

The 600 works identified to undergo this program of Effluent screening and Upstream, Downstream River sampling, have been selected on the basis of being the highest risk works in the UK. The full set of data for each site will give a good understanding of the contribution of trace substances to the environment, as well as being able to assess compliance risks at each of these sites. Over 40 other sites will also be sampled under the C1b investigation to monitor the effectiveness of removal of certain Emerging Substances, including those on the WFD Watch List.

The substances included in these investigations include those on the current WFD Priority Substances list, the Watch List, metals, and other supporting sanitary determinands. Examples of each can be found in Table 1. There are very challenging Limits of Detection (LOD) for a number of substances in the CIP2, these have been derived from PNEC's (predicted no effect concentrations), in order for the program to produce sufficiently powerful data. The performance of the analytical methods must also be deemed suitable for use in this program; the criteria for this have been taken from the QA/QC Directive, a 'daughter' directive of the WFD. This directive lays out guidelines on methods of analysis; which states that methods should be accredited to ISO 17025, and minimum performance criteria; detailing limits of uncertainty and precision.

Other investigations will include pilot and demonstration trials of new treatment technologies, examples of these include Tertiary Nitrifying trickle filters for ammonia removal, Comag clarification systems and the Blue PRO phosphorus removal technology.

Investigation Name	Description
C1a	Effluent screening for Priority substances
C1b	Effluent screening and process investigations for Emerging Substances
C1c	Sludge Technical Investigations
C1e	U/S & D/S Surface Water sampling to support C1a
C2	Feasibility studies for technology and Catchment studies
P1	Phosphorus removal investigations



Sampling for C1a and C1e sites will continue through until March 2020, by apportioning a number of sites into tranches, with a new one beginning in each year. All other investigations will be concluded by March 2017. When completed, it is estimated that over 3million discrete determinations will have been made in support of the CIP2. The results of these investigations will feed into current and future AMP periods, and help to push innovation in contaminant removal at ever decreasing levels.

ALS Environmental began the initial development plan for the CIP2 programme in January 2014 prior to the project starting in April 2015. Over this time we have been able to work closely with the CIP2 Technical Working Group (TWG) and our target has always been to send validation work to the TWG on a “right first time basis”; to date we have complied with this.

In order for ALS Environmental to prepare for the CIP2 work, a wide range of method development was undertaken. From a laboratory point of view, some of the required reporting limits for certain determinands in the priority substances list were much lower than those currently in use. The current wastewater LOD's for Cypermethrin and Tributyltin for example, were at 2ng/l and 0.2ng/l, compared to the CIP required LOD's of 0.01ng/l and 0.03ng/l respectively. Mercury in particular has been lowered by two orders of magnitude, from 100ng/l to 1ng/l. Investment in both new instrumentation and resource were made early on in the project planning process to ensure that all targets would be met, meaning that ALS would have full capability to meet all requirements of the program.

ALS Environmental were one of the first companies in Europe to take receipt of the brand new Agilent 7010 GC-MSMS, offering unparalleled sensitivity and selectivity; key requirements for analysis of this nature. In working with Anatune, our Principal Scientist (John Quick) has also utilised Gerstel dual rail systems to automate sample prep on various methods, in conjunction with running a GC-MSMS in NCI mode for greater selectivity of compounds containing electronegative compounds. Also in the Organics department, technical senior analyst Sam Towers has employed Thermo Exactives to develop brand new methods for the determination of a comprehensive Pharmaceuticals suite, and a method for the determination of DEHP, Triclosan, and the perfluorinated acids PFOS and PFOA. Control of PFOA blanks was particularly significant, as early development work suggested relatively high background levels could be found within the laboratory, and in the environment.

We have also worked with PS Analytical to improve our Atomic Fluorescence instrumentation offering, which has enabled us to offer the drastically lower Mercury reporting limits; and invested in new Agilent 7900 ICP-MS's, which has enabled precise analysis of the very low limits of detection required for the CIP metals suite. Again, tight control of blanks was also essential for the metals method, especially in elements used abundantly in industry, such as Nickel and Zinc. A new method for the analysis of Reactive Aluminium at 4ug/l was also set up on a new Konelab discrete analyser.

In addition to these new methods, various existing inorganic methods for the supporting sanitary determinands were revalidated on those different matrices that are specific to this project. Some lower LOD's were also required, and we have been able to improve methods such as those for Sulphide and Phosphorus, to report to these lower LOD's.

The development work undertaken to comply with all of the CIP2 LODs, which were lower than the current drinking water limits in most instances, in a matrix as difficult to analyse as Untreated



Sewage and even general Surface Waters has proved to be a challenge. A more complex challenge for the technical team to undertake was being able to source blanks for such low limits.

The analysis of CIP2 samples is being processed at the ALS Environmental Waste Water centre of excellence laboratory in Coventry. This laboratory has been providing water analysis for over 25 years to a range of market sectors including Waste Management, Contaminated Land and Utilities. The challenges of delivering a validated and approved CIP2 analysis suite have been numerous, and our efforts have been recognised by the CIP2 Technical Working Group. The next phase of the challenge is the successful delivery of CIP2, a challenge that all at ALS Environmental are looking forward to.....

Priority Substances	Emerging Substances	Metals	Supporting determinands
6 PBDE Congeners	Estrone (E1)	Aluminium	Phosphorus
DEHP	17-Beta-estradiol (E2)	Iron	Sulphide
Pb, Hg, Cd, Ni	17-Alpha-ethinylestradiol (EE2)		BOD
Nonylphenols and Octylphenol	Erythromycin		COD
PAH's	Trixylenyl Phosphate		Ammonia
Tributyltin			Soluble Reactive Phosphate

Table 1. An example of substances to be analysed during CIP2

Determinand	Current LoD	CIP required LoD
Cypermethrin	2ng/l	0.01ng/l
Tributyltin	20ng/l	0.03ng/l
Mercury	100ng/l	1ng/l
Copper	1.9ug/l	0.3ug/l
Zinc	14ug/l	0.8ug/l
Phosphorus	0.12ug/l	0.01ug/l

Table 2. Comparison of LOD's between existing ALS dets and new CIP dets

Determinands	LoD	Precision (against 12.5% target)
PBDE's (28, 47, 99, 100, 153, 154)	0.05ng/l	5%
Benzo (a) Pyrene	0.02ng/l	6%
17a Ethinyl oestradiol	0.03ng/l	6%
PFOS/PFOA	0.09ng/l	4%

Table 3. New method LOD's and precision achieved



References:

WFD - http://ec.europa.eu/environment/water/water-framework/index_en.html

RBMP - <https://www.gov.uk/government/collections/river-basin-management-plans>

UKWIR - <https://www.ukwir.org/content/default.asp?PageId=74343>

QA/QC Directive -

http://www.doeni.gov.uk/index/protect_the_environment/water/qaqc_directive.htm