Laboratory Analysis of EDCs and PPCPs in the Environment

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Research has been conducted for a number of years on the analysis and fate of endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in the environment, particularly in Europe (Heberer and others, 1998; Daughton and Ternes, 1999), but widespread interest on the topic was recently sparked in the United States by the publication of an article by USGS researchers Dana Kolpin and others (2002). Kolpin and colleagues used five different methods — two gas chromatography-mass spectrometry methods (GCMS) and three liquid chromatography-mass spectrometry methods (LCMS) — to screen for a large number of compounds of concern in water systems throughout the United States. This article reviews the current status of analytical methods used to detect these compounds in water and wastewater systems, with respect to standardized method availability, approximate cost, compound classes, and method sensitivity.

Two types of compounds typically are considered in the PPCP/EDC category: 1) heavy molecules such as acetaminophen or erythromycin that are insufficiently volatile to be analyzed by GCMS techniques and must be analyzed by LC-based methods; and 2) compounds that can be analyzed by GCMS but that commonly occur at such low concentrations in the environment (such as various estrogen compounds) that they are not readily detected using traditional screening techniques like EPA Method 625.

Who is Doing the Analysis?

Because of the lack of standardized methods and the high cost of the LCMS instrumentation needed to detect many of these compounds, most work on developing analytical methods in the United States continues to be conducted only in research environments such as universities, government labs, and utilities with active EDC/PPCP research programs. A number of commercial labs are investigating the feasibility of doing this type of testing, but none apparently have invested significantly in in-house testing. MWH Labs has been working on short lists from the original USGS paper using GCMS, GCMS with derivatization, and LC with UV detection.

What are the Costs?

Because of the long target lists, the difficulty of obtaining standards, and the high sensitivity required, analytical costs are relatively high. Each of the USGS-developed methods can be expected to cost between $300 and $500 per sample for small sample batches, with the LCMS-based methods costing more, so duplicating the five testing methods would cost $1,500 to $2,000 per sample. Unit costs are anticipated to come down by as much as a factor of two over the next 12 to18 months, as methods are standardized and a market is developed. Note that numerous academic research labs are using more traditional GCMS techniques (full scan or selected ion monitoring, known as SIM) following continuous liquid-liquid extraction (such as modified EPA Method 625 analysis). Most of these labs are achieving reporting limits in the 0.1 part per billion range, relatively high compared to what is needed for ambient levels. The most promising low-cost technique is a broad-scan, high-sensitivity LCMS approach being developed by Shane Snyder at Southern Nevada Water Authority, but this is still under development.

Several other factors are hindering widespread commercial availability of methods for analyzing EDCs and PPCPs:

- **Limited availability of LCMS systems in commercial labs.** LCMS instrumentation with atmospheric pressure chemical ionization (APCI) has high sensitivity but typically costs in excess of $250,000 compared to a typical GCMS system cost of less than $100,000. Most commercial labs are reluctant to invest this amount without an established set of standardized techniques and a sufficiently large market. Thus, there is a Catch-22 in the analysis of EDCs/PPCPs on a commercial basis: labs won't invest in the equipment until there is an established market, and there won't be a market until labs have the equipment and the demonstrated ability to routinely perform the tests. In spite of this limitation, many environmental labs recognize the potential for performing the analyses and are exploring options for LCMS acquisition, especially since LCMS costs have decreased rapidly over the last few years. Commercial labs also may be able to lease time on a government-owned LCMS system in order to validate methods for EDCs/PPCPs and later invest in their own LCMS once the market has grown.

- **Limited availability of standard methods for analysis of EDCs and PPCPs.** Although the USGS study used several analytical methods, only one of these was actually available as a standard method at the time of publication, and this was a GCMS method rather than one of the more sophisticated LCMS methods. The USGS only recently

Image of ICPMS torch provided by West Coast Analytical Service.

submitted details of one of the LCMS methods for publication in *Journal of Chromatography*. Without additional standardized peer-reviewed methods it is difficult for labs to know that their results are reproducible, and given the high visibility of the PPCP/EDC issue, neither labs nor utilities are likely to want to go out on a limb in reporting occurrence. Most commercial labs lack sufficient resources for comprehensive in-house method development and validation. Some compounds of concern can be analyzed with sufficient sensitivity using the more traditional GCMS methods that have been used for drinking water (caffeine can be analyzed by Method 525.2, for example), but applicability depends on the matrix being tested, and much of the interest in EDC/PPCP occurrence is focused on recycled water or wastewater matrices, which do not perform as well with solid phase extraction methods.

• **Lack of sensitivity of traditional methods, given the typical occurrence levels of EDCs and PPCPs.** Data from Kolpin et al. (2002) and others clearly show that most of the compounds of interest occur in concentrations ranging from 1 to 100 parts per trillion (ppt), except in grossly contaminated systems. Additionally, the number of potential compounds of interest could be more than 500, and more than one analytical method must usually be used if the goal is to achieve broad spectrum monitoring. While many compounds identified in the USGS study can be analyzed by traditional full-scan GCMS techniques, utilities may not benefit from using such methods if they are truly interested in investigating the possibility of low-level occurrence.

What Compounds CAN be Analyzed?

Most of the drugs reported in the Kolpin study are still not readily analyzed by commercial labs, for the reasons cited above. However, compounds such as caffeine, cotinine, phthalates, and various pesticides are readily analyzed by a wide variety of labs, using solid phase extraction or liquid-liquid extraction followed by GCMS SIM. With solid phase extraction methods in particular, one can increase sensitivity by processing larger volumes of water, in the absence of matrix issues. Many compounds of concern are highly reactive with surfaces, and special preparations are typically required to prevent loss of the compounds onto the sample bottle walls. Steroids and hormones are not yet typically analyzed by most commercial labs, principally due to the high sensitivity of the required methods, which necessitate the extraction and chemical preparation of samples before analysis.

MWH Labs has developed an LC-UV detection method (modified from USGS Method 2) with a sensitivity of 10 to 20 ppt for three compounds — acetaminophen, caffeine, and cotinine (a nicotine metabolite) — with a cost per sample of $150 to $250, depending on the number of samples being tested. However, in general, use of UV detectors has limited applicability because of sensitivity and because only MS-based techniques can be used to separate and identify co-eluting compounds when screening for large numbers of compounds.

What Does the Future Hold?

We anticipate there will continue to be significant developments in this area over the coming 12 to 18 months. As the target list of analytes is refined, there will be sufficient incentive for labs to begin developing standardized methods. In the meantime, any measured results should be considered semi-quantitative in nature. However, utilities are encouraged to remain aware of these compounds and to consider possibilities and methods of testing for them.

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