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The list of lists – are we measuring the best PPCPs for detecting wastewater impact on a receiving water?

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Abstract

Determining an appropriate set of indicators to show that a water supply is not impacted by wastewater is critical for watershed protection and for potable reuse projects. In 2010 the California State Water Resources Control Board (CA SWRCB) Blue Ribbon Panel issued a set of recommendations for a very short list (7) of compounds to be monitored for re-use projects. In 2009/10 the Santa Ana Watershed Project Authority (SAWPA) developed a separate list of potential wastewater indicator compounds (11) based on a consensus panel, with the intention of sampling all dischargers to the Santa Ana River to determine occurrence. In 2009, the Water Research Foundation (WaterRF) funded project 4167, which examined analytical performance for 22 potential compounds of interest for assessing drinking water. In 2010, a NWRI report suggested primidone as a tracer. In 2009 Buerge *et al.* demonstrated the effectiveness of artificial sweeteners as conservative wastewater tracers. There is some overlap among these lists but there are also some potential key indicators that are only on a single proposed list and the potential that some are on 'none' of the lists.

MWH developed a direct online extraction/analysis method using LC-MS-MS for nearly 90 target analytes that covers all of the compounds listed in the projects above. This method has reporting limits for most of the analytes in the 5–10 ng/L range. In 2010 and again in 2011, this technique was used for a SAWPA effluent monitoring project to assess the relative amount of information obtained from the different lists. Samples from 17 wastewater effluents and the downstream receiving water were tested for ~90 analytes. We compared (a) frequency of detection in the effluent samples (b) concentration range and (c) variability among dischargers. Data were compared to other locations collected across the country and to municipal drinking water sources and distribution system samples to determine the most persistent compounds (and therefore best indicators). The ideal generic tracer should be relatively abundant and show minimal concentration variation.

It is apparent that none of the existing lists (SAWPA, SWRCB, WaterRF, primidone, sucralose/acesulfame-K) is a 'perfect' list and greater discerning power is obtained by looking at long lists. Specifically the SAWPA list suffers because only one compound, TCEP was detected in all effluent samples, and concentration varied by a factor of 10 among dischargers. The CA SWRCB list suffers because only sucralose was detected in all samples; iopromide was only detected in about 50% of the samples and gemfibrozil in an even smaller number of effluents. Primidone, while occurring in 100% of samples varies by five fold among local sources and thus may not be the ideal tracer. Many of the compounds in the WaterRF list are not even among the most commonly detected analytes in effluents.

Taking advantage of the power of a long list covering various classes of compounds it becomes possible to identify both generic (sucralose, acesulfame-K, TCEP, primidone) and specific (iohexal, atenolol, butalbital, caffeine degradates such as theobromine and 1, 7-dimethylxanthine, triazine and degradates) tracers to not only determine the presence of wastewater, but also potential specific primary wastewater sources. Several of the compounds seen most frequently that also have less than ten fold variation include ones not commonly measured (Dehydronifedipine, dilantin, meprobamate). Once the appropriate target analytes are identified for a given set of dischargers, future monitoring can then use a smaller set, but *a-priori* determination of a short list of indicators may eliminate significant important potential tracer compounds.

INTRODUCTION

Drinking water quality has become a focus of not just water utilities, regulators, and consumers, but also non-governmental organizations (NGOs) and the press. In 2008, the Associated Press

published a series of articles on pharmaceuticals and personal care products (PPCPs) in drinking water that captured the public's attention. These articles focused extensively on work that was done by the United States Geological Survey in the early 2000s that demonstrated the widespread occurrence of PPCPs in surface waters. As a result of this public interest, many utilities began monitoring for PPCPs to determine the extent to which their water supplies were impacted by these compounds. This is also potentially important in assessing water-reuse projects, where treated wastewater (understood to be potentially the most significant source of PPCPs to the environment) is recharged into water supplies. One of the outstanding issues in this monitoring is the choice of target analytes because EPA has not yet provided guidance on the ideal set of analytes to assess potential impact. This has led to much confusion and inconsistency among laboratories and data users. This inconsistency is also relevant for future trends towards regulating contaminants by groups, because to do such regulation requires a consistent definition of the 'group' being regulated. Were EPA to move forward on regulating PPCPs in either drinking water or wastewater this would be a critical question to address.

There have been numerous attempts to standardize lists to a meaningful number of indicator compounds. In mid 2010 the California State Water Resources Control Board (CA SWRCB) Blue Ribbon Panel (Blue Ribbon Panel) issued a set of recommendations for a very short list (7) of compounds to be monitored for re-use projects (State Water Resources Control Board 2010). Most of these were identified as 'indicator' compounds selected to determine whether a process was working correctly. In 2009 the Santa Ana Watershed Project Authority (SAWPA) developed a separate list of potential wastewater indicator compounds (11) based on a consensus panel, with the intention of sampling all dischargers to the Santa Ana River (SAR) to determine occurrence as a onetime snapshot and to subsequently monitor groundwater in the region (SAWPA 2009, 2010). In 2011 SAWPA elected to do an additional set of wastewater samples, using a slightly longer list of analytes (13) to reflect additions from the Blue Ribbon Panel List. In 2009, the Water Research Foundation (WaterRF) funded project 4167, which examined the analytical performance for 22 potential compounds of interest for assessing impacts on drinking water (Vanderford *et al*. 2011). Separately NWRI published a report in 2010 suggesting that primidone is a good generic tracer of wastewater (Guo *et al.* 2010). In 2009, Buerge *et al.* published an Environmental Science and Technology (ES&T) paper demonstrating the effectiveness of various artificial sweeteners as conservative wastewater tracers (Buerge *et al.* 2009). In 2011, Oppenheimer *et al.* demonstrated the advantages of sucralose as a wastewater indicator (Oppenheimer *et al.* 2011) and Mawhinney *et al.* (2011) recently demonstrated the preponderance of sucralose in many drinking water supplies. There is some overlap among the various lists but there are also some potential key indicators that are only on a single typical list and the potential that some good indicators are on 'none' of the lists.

Often treatment processes for generating recycled water are intensive and include everything from membrane filtration treatment (MF) through Reverse Osmosis (RO) or advanced oxidation (AOP). However in most cases not all of these processes are applied to wastewater, and when intention recycling is not planned, the treatment is typically much less intense. Tertiary wastewater undergoes indirect recycling (e.g. it is discharged to a surface water that is subsequently used as a source water for a different user). Finally, every wastewater source will be different, as a function of the industry feeding the particular discharger.

Historically assessment of the effectiveness of treatment processes for CECs such as PPCPs has been determined by using a small set of indicator PPCPs or other surrogates (Snyder *et al*. 2007; Drewes *et al*. 2008; Guo *et al.* 2010). Typically the PPCPs that have been suggested as being recalcitrant for many treatment processes have included compounds such as carbamazepine, sulfamethoxazole, primidone, TCEP, and meprobamate. The SAWPA study of numerous wastewater plants in the Santa Ana region followed this pattern and selected a suite of 11 to 13 commonly tested pharmaceutical compounds to act as indicators. Other groups (Drewes *et al*. 2010) have

recommended using indicator compounds such as TOC, TOX, UV, etc. to evaluate processes. However those indicators are difficult parameters to interpret in the receiving waters.

As noted above, most Pharmaceutical and Personal Care Product (PPCP) analytical suites have relied on relatively short lists of analytes to determine the extent to which treatment has been effective. The problem with this approach is that 'you won't find what you don't look for'. In 2008, MWH developed a direct online extraction/analysis method using LC-MS-MS for more than 90 target analytes that covers all of the compounds listed in the projects above (Haghani *et al.* 2009; Eaton *et al.* 2010; Oppenheimer *et al*. 2011). This method has reporting limits for most of the analytes in the 5–10 ng/L range. In the summer of 2010 and again in 2011 this technique was used in conjunction with the SAWPA effluent monitoring project to be able to assess the relative amount of information obtained from the different lists and to look at differences over time. In 2011, SAWPA added several analytes from the Blue Ribbon Panel list (but not all) to the testing program. Samples from 12 dischargers were tested for a full suite of analytes using the online method in 2010, and another 5 were tested only for the short list of the 11 SAWPA analytes. In 2011, MWH tested all 17 sites for the full list. Additionally the receiving water for these dischargers, the SAR itself, was sampled each year. The SAR sample represents an integrated sample of all of the dischargers after dilution and any reactions of compounds (e.g. sorption, photodegradation, etc) downstream of the discharge.

Subsequently we compared (a) the frequency of detection in the effluent samples and the SAR site (b) the concentration range over the two sampling periods and (c) the variability among dischargers. The ideal generic tracer should be relatively abundant (frequency and concentration) and should show minimal concentration variation among sources or in a single source over time.

ANALYTICAL METHODS

The method used was developed to provide quantitative precise data on over 90 PPCPs and pesticides/herbicides (Haghani *et al.* 2009; Oppenheimer *et al.* 2011) and was similar to that of Buerge *et al*. (2008), involving online preconcentration of PPCPs following direct injection. PPCPs were analyzed using an online preconcentration technique followed by LC-MS-MS with electrospray ionization (ESI) in positive and negative mode (Haghani *et al*. 2009). Instrumentation was an atmospheric pressure ionization API 5000 LC-MS-MS connected to a Dionex Ultimate 3000 HPLC system. Appropriate mass transitions for each analyte were determined by direct infusion of each analyte. Multiple mass transitions were used for each analyte (wherever there was adequate sensitivity for both transitions) to ensure unequivocal compound identification. A small sample (~2 mL) of sample is injected into the HPLC through a ten port switching valve. Analytes are concentrated onto a small Oasis HLB solid phase extraction column (Waters) and the matrix diverted to waste. The valve position is then changed and the target analytes are refocused on an analytical column and then separated and eluted into the Mass spectrometer, using an acidic eluent for positive mode and basic eluent for negative mode to gain sensitivity on the mass spectrometry. Measurement of mass intensity is determined using ESI in positive and negative mode, depending on the analyte. Because the method is an online concentration method, all standards and quality control (QC) samples are processed the same way. Results for most analytes are determined via isotope dilution, except where isotopes were unavailable.

Minimum reporting levels (MRLs) for the method range from 1 to 100 ng/L, depending on the analyte. For sucralose the MRL was 100 ng/L. For the SAWPA project all data with MRLs below 10 ng/L were censored at a reporting limit of 10 ng/L as per project specifications. MRLs are the lowest calibration point used which also corresponds to a *S/N* ratio of at least 10. Uncensored data are collected below the MRL to the MDL. Each analytical batch included numerous QC samples. Batch QC samples are summarized in Table 1.

Table 1 | Batch QC for each analytical run

QC type	Frequency	Spiking level	Acceptance criterion
Calibration curve	Each analytical batch	Minimum 5 point curve plus blank	Quadratic fit with $1/x$ weighting. Correlation coeff >0.99; back calculated to ±30% of true value (±50% at MRL level)
Method blank	Each analytical batch	0	<1/3 MRL
MRL_check	Each analytical batch	Low cal level	50–150%
Continuing calibration/ LCS	Each 10 samples	5 × MRL level	70–130%
MS/MSD (sample matrix spikes)	Each 20 samples	5 × MRL	60–140%
Closing blank (CCB) and closing standard (CCV)	At end of run	10 × MRL for CCV and 0 for CCB	70–130% for CCV, <1/3 MRL for CCB
Identification criterion	Each detect	Retention time	±1 second from determined retention time
Identification criterion	Each detect	Compound identification based on mass transitions	2 MRM transitions when available; ion ratio based on EU criteria

This method has been subjected to round-robin testing (Vanderford *et al.* 2011) for some of the target analytes in the SAWPA project. Figure 1 shows the overall performance of the method on a set of 14 PPCP analytes (including 5 of the 11 SAWPA analytes).

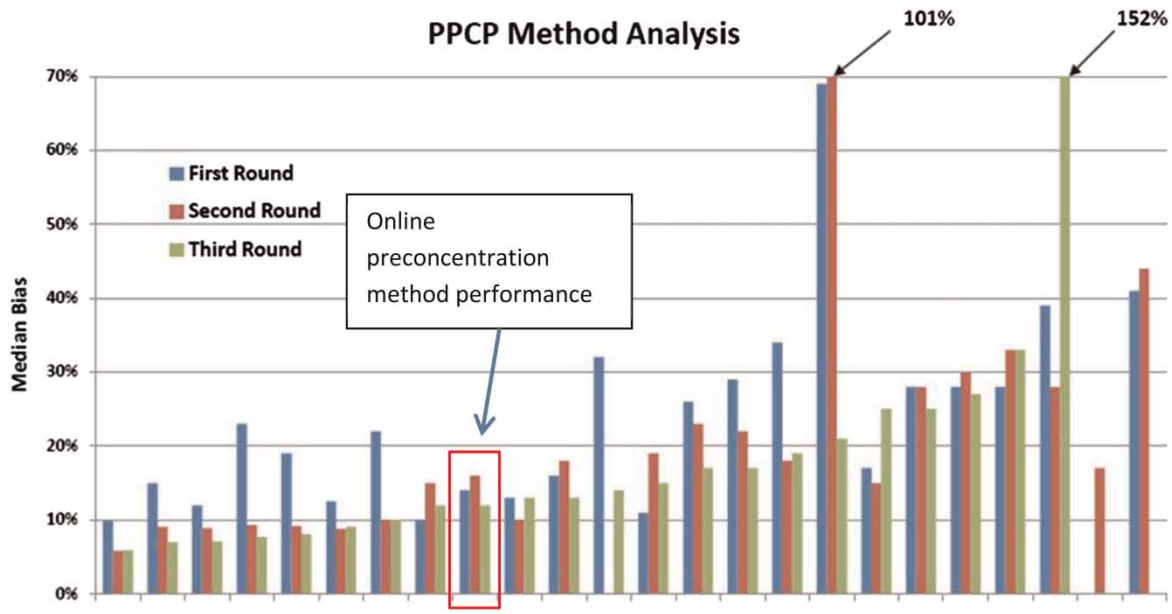

Figure 1 | Assessment of online method performance (median absolute bias) on 14 PPCP analytes compared to other tested methods (Vanderford *et al.* 2011).

SAMPLE PRESERVATION

SAWPA discharger samples for PPCPs were collected in amber glass vials and field preserved with a combination of ascorbic acid and sodium azide (Benotti *et al.* 2009). Subsequent to this project samples have been preserved with sodium omadine/ascorbic acid (EPA 2007; Vanderford *et al.* 2011) to avoid the use of toxic sodium azide. Samples were transported on frozen blue ice and

received in the laboratory either the same day or the next day after collection and then stored refrigerated at <6 °C. Both preservatives have been shown to be effective for stabilizing many of the PPCPs for 28 days or more under refrigerated conditions. Wastewater effluent sample collection protocols followed an agreed upon protocol (SAWPA 2009) and also included a field blank for each sample site. No SAWPA target analytes were detected in field blanks.

SAMPLE LOCATIONS

For the overall project, samples were collected from 27 sites along the SAR. Twenty-three (23) of these sites represented wastewater effluents from different dischargers (Figure 2) and the others were downstream sites representing receiving water. Two different commercial labs performed testing of the dischargers and 2 utility labs analyzed the receiving water. MWH performed testing on 17 of the 23 sites in 2010 and 2011 and the data presented herein represents only those sites to avoid any issues with interlaboratory variability. It should be noted that interlab comparisons were conducted among all 4 participating labs for receiving waters and also on single blind whole volume QC samples, and although most of the SAWPA analytes showed excellent agreement among labs (<20% RSD), there were a few compounds where the receiving water samples showed major differences particularly between the two commercial labs. Because of that and the fact that only MWH conducted the 'long list' testing, the analysis shown herein is only based on MWH data. Not all of the 17 sites were tested for the entire suite of analytes in 2010, but in 2011 all 17 were tested for the extended list. In 2010, 24% were tested only for the SAWPA specified compounds.

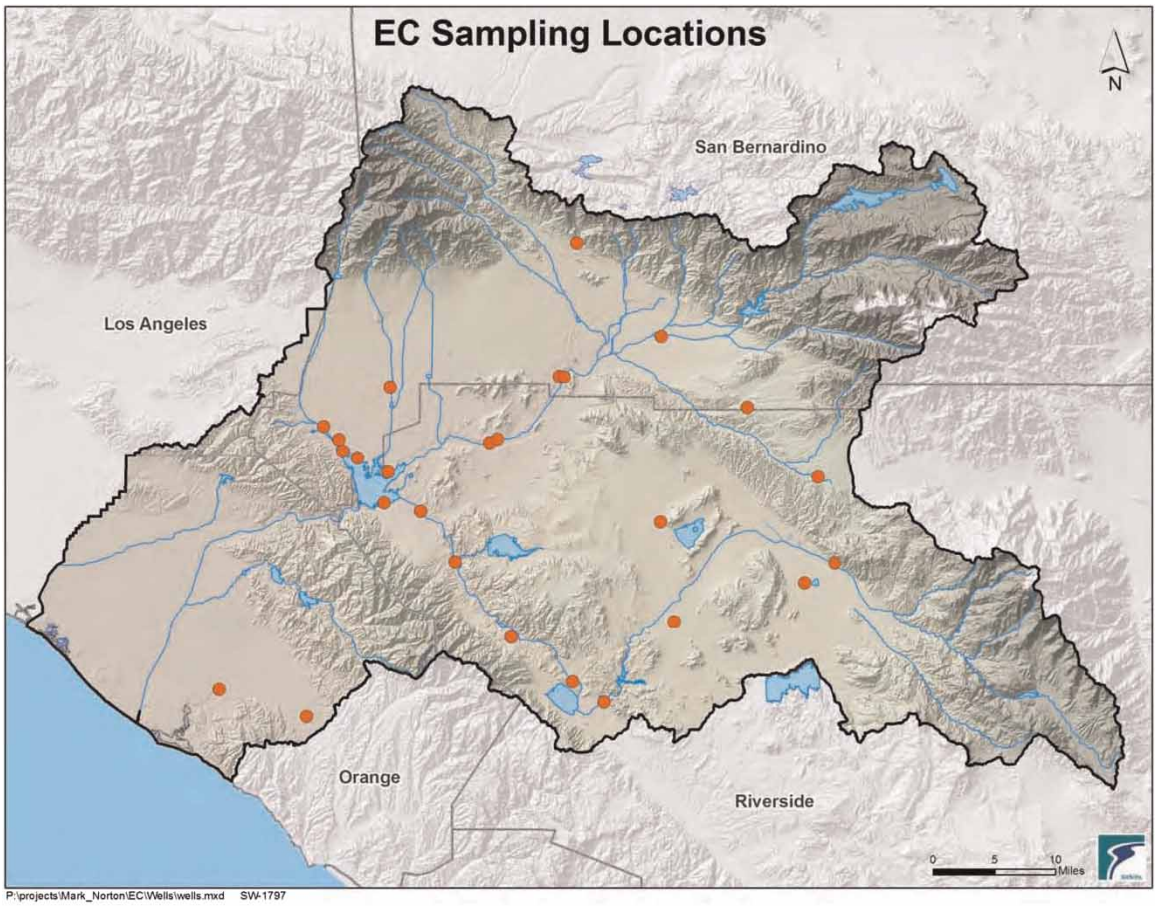

Figure 2 | PPCP sampling locations in Santa Ana Watershed.

RESULTS

Comparison of lists

As noted previously there are numerous 'lists' of analytes that have been proposed in the literature as potential good wastewater indicators. SAWPA (2009) developed a list of 11 target analytes based on a multi-year consensus process. The Blue Ribbon Panel (2010) developed a list of 7 target analytes based on both toxicity impacts (2) and potential indicators (5) as a result of an expert panel evaluation. Subsequently the California Dept of Public Health (CDPH) recommended some additions to the Blue Ribbon Panel List. NWRI (2010) conducted a statewide study of State Project Water and wastewater dischargers and recommended the use of primidone as a good wastewater indicator. The WaterRF in 2009, as part of an interlab comparison of PPCP performance established a list of 22 PPCPs that were anticipated to be good indicator compounds. This thus provides an ability to compare actual occurrence data against the various 'lists' and determine whether any of the lists are preferred. Table 2 compares the lists directly, and also includes whether the analyte is included in the MWH methodology.

Table 2 | Comparison of target compounds in various lists

Compound	SAWPA	SWRCB	NWRI	WaterRF 4167	MWH
Acetaminophen	Yes	No	No	Yes	Yes
BPA	Yes	No	No	Yes	Yes
Caffeine	Yes	Yes	No	Yes	Yes
Carbamazepine	Yes	No	No	Yes	Yes
DEET	Yes	Yes	No	No	Yes
Diuron	Yes	No	No	No	Yes
Estradiol	Yes (2011)	Yes	No	Yes	Yes
Ethinyl Estradiol - 17 alpha	Yes	No	No	Yes	Yes
Gemfibrozil	Yes	Yes	No	Yes	Yes
Ibuprofen	Yes	No	No	Yes	Yes
Iopromide	No	Yes	No	No	Yes
Primidone	No	No	Yes	Yes	Yes
Sucralose	No	Yes	No	No	Yes
Sulfamethoxazole	Yes	No	No	Yes	Yes
TCEP	Yes	No	No	No	Yes
Triclosan	Yes (2011)	Yes	No	Yes	Yes

Results of testing

Numerous target analytes from the PPCP method were detected in more than 90% of SAWPA wastewater effluents that were tested as shown in Table 3. Compounds that were detected frequently in wastewater had concentrations ranging from levels of 10 ng/L (ppt) or less to concentrations of more than 30 μg/L (ppb). The table also includes the ratio of the 90th percentile to 10th percentile concentration in 2010 and 2011. In the event that a compound was not detected in 100% of samples, the 10th percentile concentration was set at the reporting limit for purposes of this table. It is also worth noting that even for some of the frequently detected compounds, the 90th percentile concentration was still less than 50 ng/L, indicating that the analyte is not likely to be a good indicator due to low concentrations, decreasing the precision and accuracy of analysis.

Table 3 | Comparison of frequency of detection of SAWPA and SWRCB and NWRI recommended analytes in SAWPA effluents N/A – could not be calculated. ND – not detected.

Count of Sites Tested 2010	Count of Sites Tested 2011	compound	Ratio 90th/ 10th percentile 2010	Ratio 90th/ 10th percentile 2011	90th percentile conc2010	90th percentile conc 2011	Frequency of detection 2010	Frequency of detection 2011
17	17	Acetaminophen	9	2	34	17	88%	50%
17	17	BPA	N/A	6	16	63	18%	39%
17	17	Caffeine	29	14	288	137	53%	67%
17	17	Carbamazepine	12	11	358	343	88%	94%
17	17	DEET	10	32	304	320	94%	61%
17	17	Diuron	20	8	76	106	88%	100%
13	17	Estradiol	N/A	N/A	ND	ND	0%	0%
17	17	Ethinyl Estradiol - 17 alpha	N/A	N/A	ND	ND	0%	0%
17	17	Gemfibrozil	82	199	818	1990	47%	72%
17	17	Ibuprofen	11	16	112	156	59%	67%
13	17	Iopromide	31	42	311	420	60%	56%
13	17	Primidone	3	2	214	216	100%	100%
13	17	Sucralose	2	13	29300	43000	100%	100%
17	17	Sulfamethoxazole	66	116	664	1160	65%	72%
17	17	TCEP	6	3	448	333	100%	100%
13	17	Triclosan	N/A	5	62	53	70%	28%

Figure 3 shows the same data in graphical form, demonstrating clearly that most of the SAWPA analytes are detected with a high frequency (>50% of field samples), but not all of them. This is not unexpected, because the workgroup relied on extensive experience to recommend the list of analytes to be tested. Compounds detected frequently in 2010 were again detected frequently in 2011.

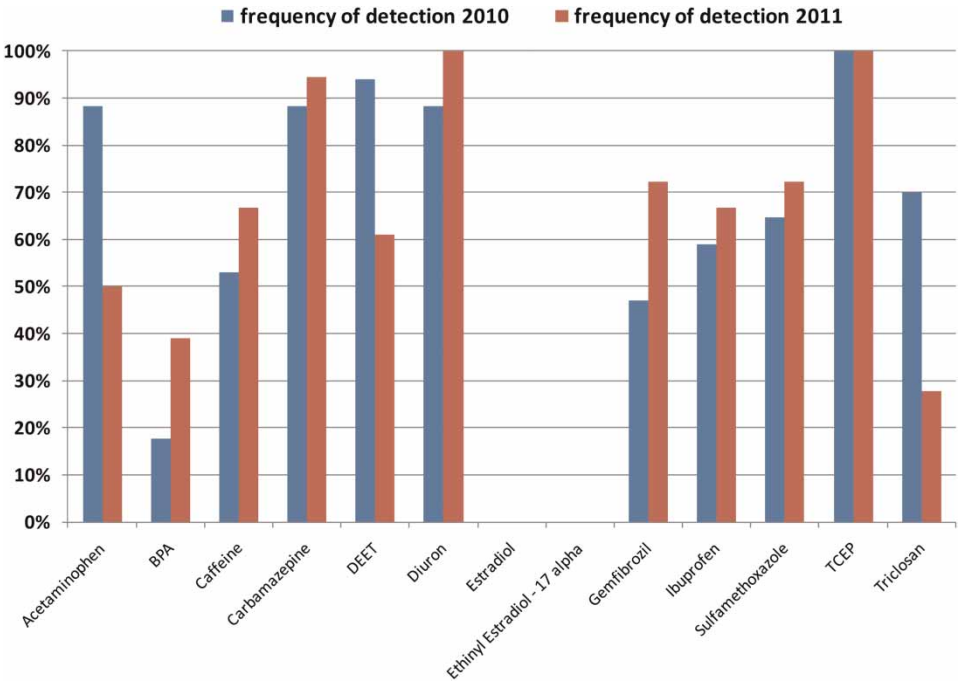

Figure 3 | Frequency of detection of SAWPA list analytes in effluents.

The other critical factor noted in Table 3 is the range of concentration that occurred among the various wastewater plants, particularly considering that the samples represented a snapshot in time. Figure 4 illustrates that even for the SAWPA analytes detected in 100% of samples there are very large differences in concentration both from year to year and from plant to plant. It is thus apparent that the SAWPA list may not be adequate for a careful analysis of occurrence of indicator compounds.

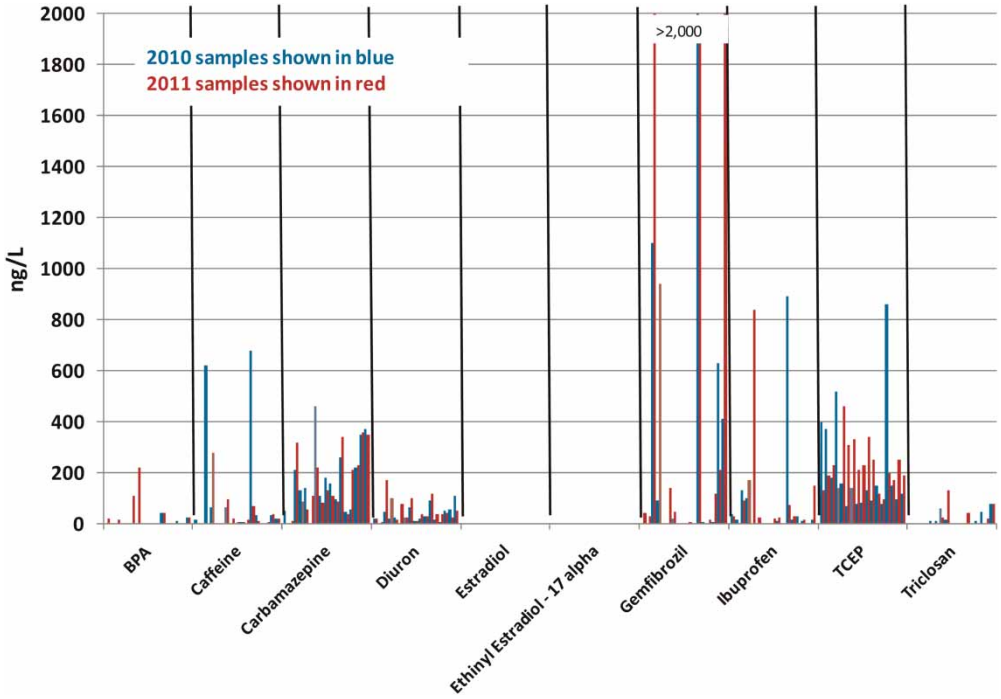

Figure 4 | Concentration range observed in 17 wastewater effluents for SAWPA constituents Samples are shown as paired concentrations (2011 adjacent to 2010).

In Figure 5, we compare the 2010 and 2011 average concentration of the SAWPA (2011) list of analytes for all plants. It is apparent that the average concentration (with the exception of gemfibrozil) is not noticeably different for these plants. For gemfibrozil there are several plants with much higher concentrations in 2011 than in 2010, likely reflecting large variations in use of this compound over time.

However, if the 'test list' is expanded to include a greater number of analytes and one re-examines the most frequently detected compounds in these wastewaters, it is clear that the vast majority of analytes that were detected all of the time are not on either the SAWPA list or the Blue Ribbon Panel List (Figure 6). In many cases there are 'non-standard' compounds (atenolol, carisoprodol, dehydronifedipine, dilantin, iohexal, meprobamate, theobromine) that all occur at concentrations in excess of nearly all of the SAWPA and Blue Ribbon Panel lists (Figure 7) and the average concentration (except for fluoxetine) is not significantly different in 2011 compared to 2010. Furthermore some of these show very small variation in concentration among samples, meaning that they should potentially be excellent indicators of wastewater on a receiving water.

A direct comparison of the 'SAWPA' list versus the 'Blue Ribbon Panel' list is shown in Figure 7. In this case it is apparent that only a few of the Blue Ribbon Panel analytes are actually detected with any significant frequency. The SAWPA detection frequency demonstrates that the SAWPA analytes are more prevalent, but as noted in Table 5, with the exception of TCEP there is nothing that is detected with a frequency approaching 100% (essential for a broad based indicator).

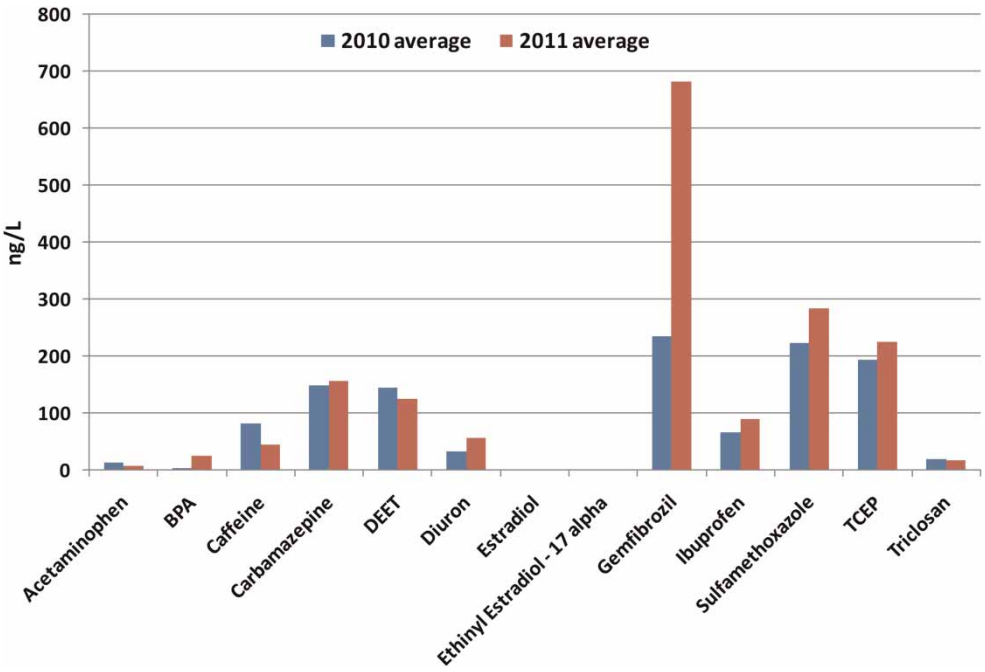

Figure 5 | Comparison of average concentrations of SAWPA analytes for two sampling rounds for up to 17 plants in two snapshot sampling rounds (2010 and 2011).

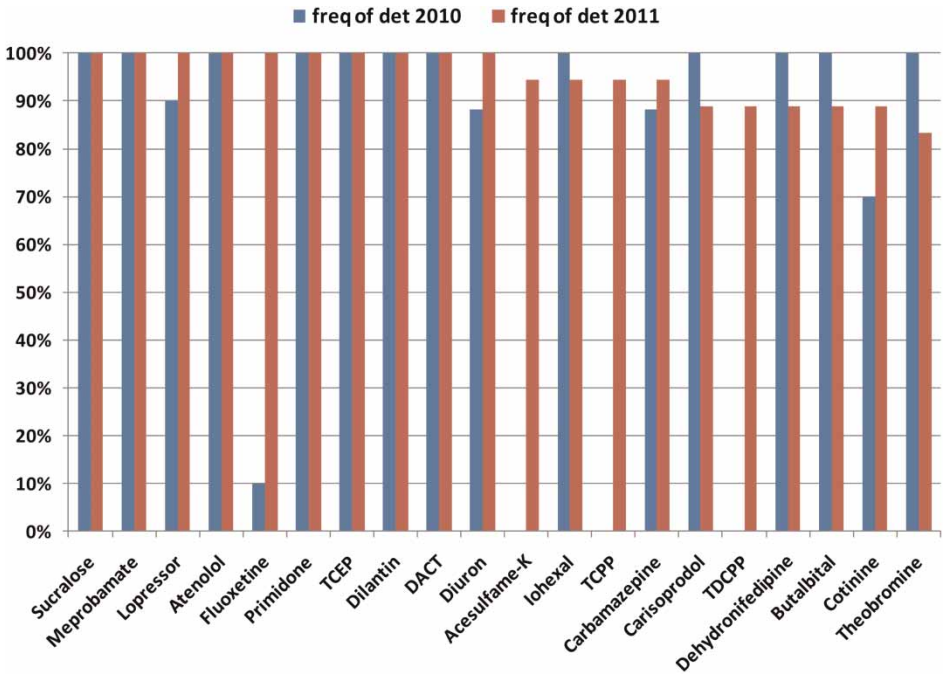

Figure 6 | Comparison of frequency of detection for top 20 detections in 2011. Several of the compounds detected in 2011 (Acesulfame-K, TCPP, TDCPP) were not included in the expanded test list in 2010 but added in 2011.

The other important factor in assessing the utility of an indicator is by comparison of concentration range amongst effluents. As noted in the introduction, the ideal tracer will have only a small variation in concentration among sources (and ideally also only a small variation over time, although that was not assessed as part of this project except through two annual snapshots. Figure 8, a box and whisker plot of concentration for the top 20 compounds, along with Figure 9, a plot of the ratio of 90th percentile to 10th percentile concentration, demonstrates that a large number of the analytes detected in

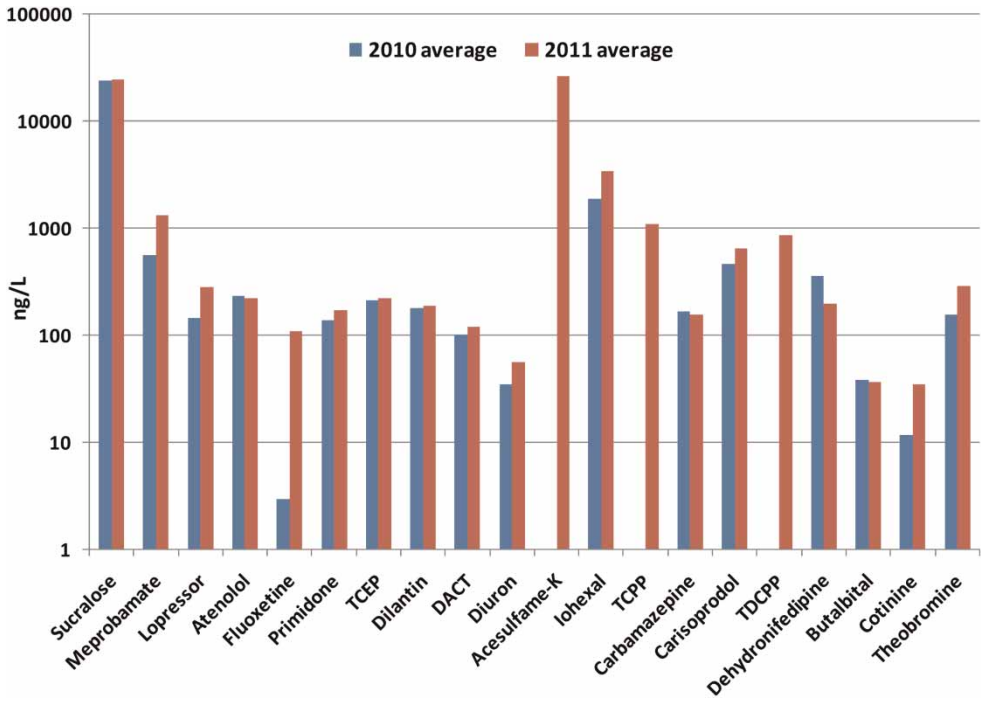

Figure 7 | Comparison of average concentration in 2010 vs 2011 for the most frequently detected compounds. Of the SAWPA or Blue Ribbon Panel analytes, only sucralose, TCEP, diuron, and carbamazepine are detected frequently in samples.

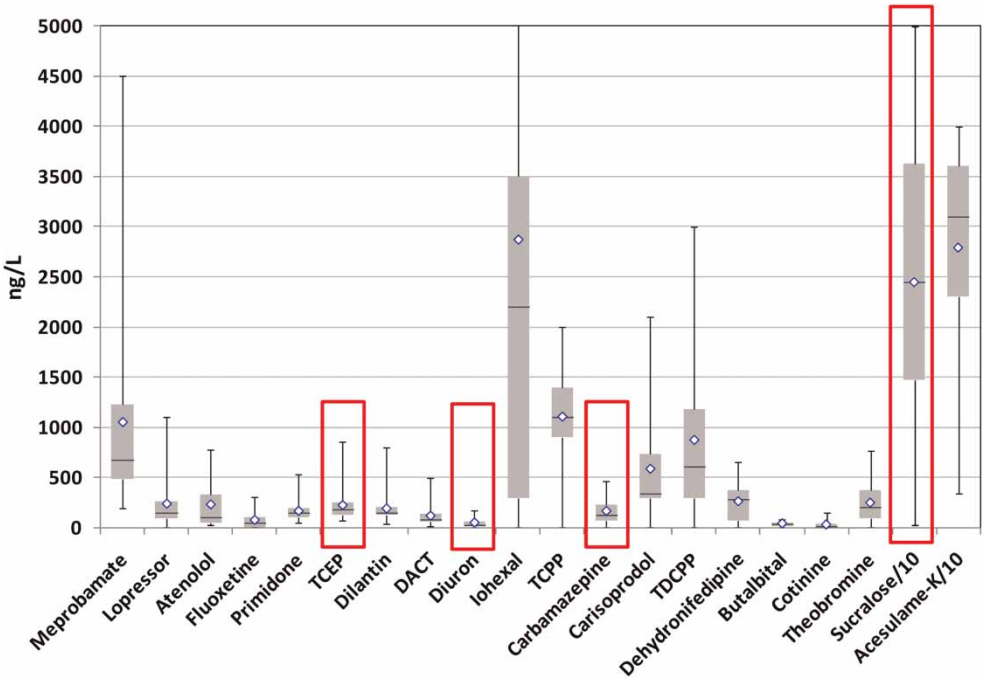

Figure 8 | Box and Whisker plot of concentration range for top 20 most frequently detected analytes in SAWPA effluents (sucralose and acesulfame-K results divided by 10 for readability).

most samples have relatively small variation among plants and over time, making them likely generic indicators. Out of the SAWPA and Blue Ribbon Panel analytes, only sucralose and TCEP fit this category, while primidone (NWRI proposal) is also in the group. However out of the 'least variable' seven (7), four (4) are not on any of the aforementioned lists. The very high concentration range of several of the others (atenolol and iohexal) may indicate that they are very good specific indicators. It is worth noting that even though iopromide was recommended by the Blue Ribbon Panel as an

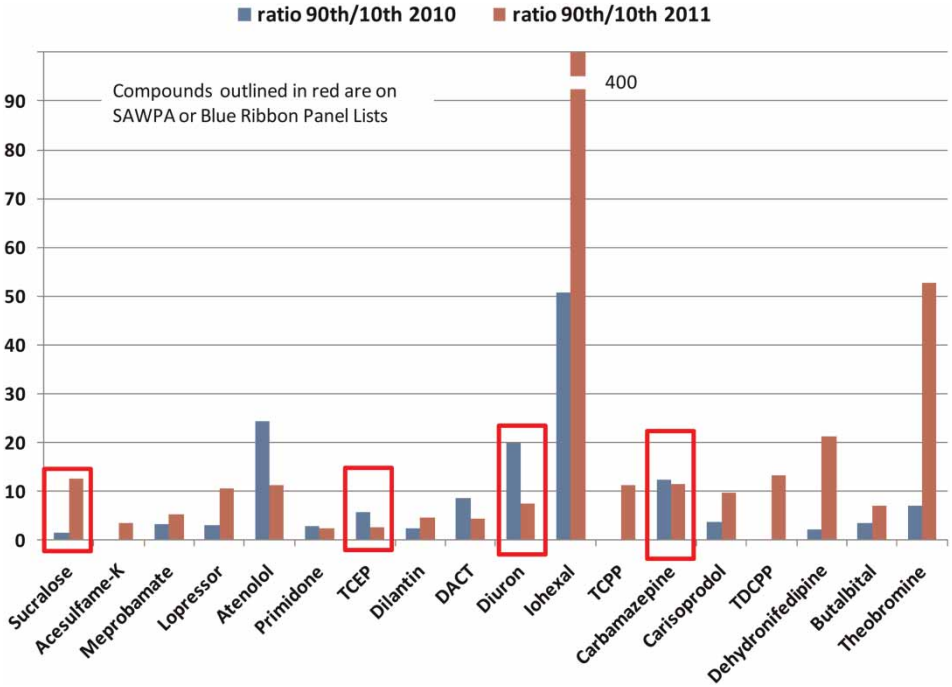

Figure 9 | Concentration ratio of 90th percentile/10th percentile for most frequently detected compounds. Most of the frequently occurring and least variable concentration compounds are not on any of the suggested 'lists' as indicators.

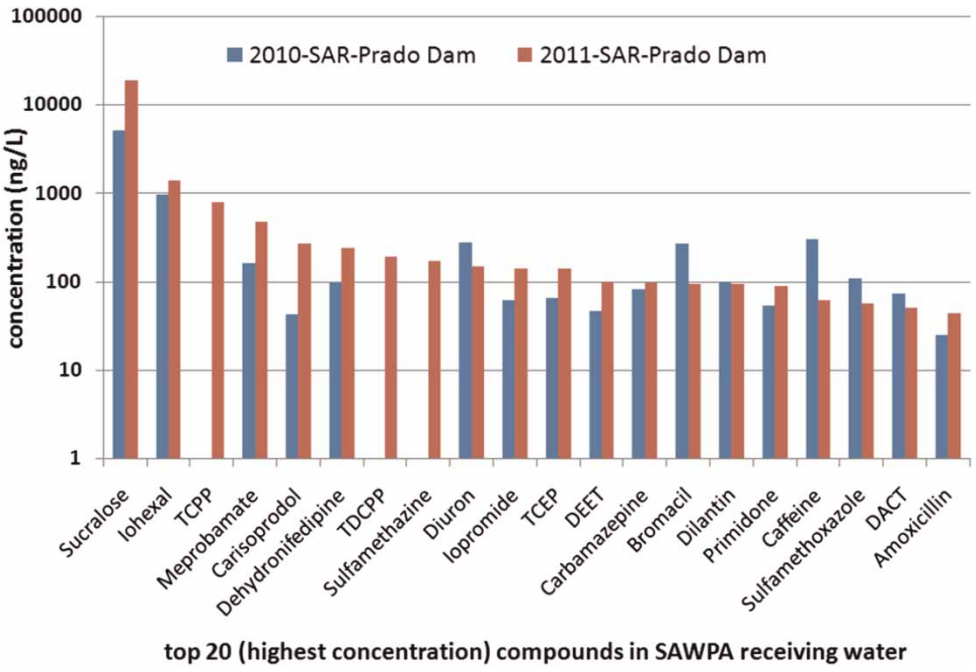

Figure 10 | SAR sample results for 2010 and 2011.

indicator, it does not appear in the top detection frequency whereas iohexal, another contrast agent, does. Although there were a large number of pharmaceuticals detected in wastewater effluents, there were also a large number of personal care products (e.g. over the counter products or food additives) and a number of pesticides and herbicides and their degradation products. This distribution of analytes suggests that there is a need to use multiple indicators of wastewater influence on receiving waters. The advantage of a broad spectrum method with rugged analytical methods is that one can

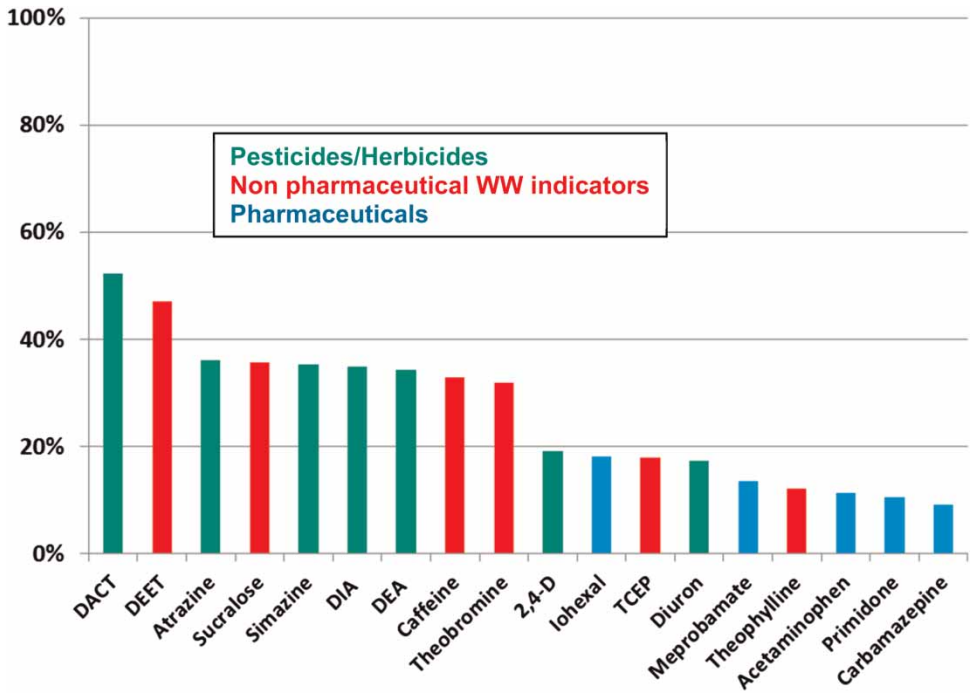

Figure 11 | Frequency of occurrence of PPCPs and Pesticides/Herbicides in 230 finished drinking waters from across the United States. Pesticides and herbicides are shown in green, non pharmaceutical WW indicators are shown in red and pharmaceuticals are shown in blue.

detect multiple indicators at one time. By using multiple indicators it may be possible to not only determine whether there is a wastewater influence, but also the nature of the wastewater source (e.g. municipal, industrial, hospital, septic, etc).

If one switches focus from the direct effluent samples to the receiving water (SAR) as shown in Figure 10, it becomes even more apparent that the SAWPA or Blue Ribbon Panel list (as currently proposed) are inadequate to assess receiving water impact. The SAR is well documented to be heavily wastewater impacted throughout most of the year.

However only 7 of the top 20 compounds detected in SAR were on the SAWPA or SWRCB lists (sucralose, diuron, TCEP, Deet, Carbamazepine, Caffeine, and sulfamethoxazole) and several of the analytes that were detected frequently in the effluents (even non-SAWPA analytes) such as theobromine, lopressor, and atenolol, were not detected in the SAR samples. Even sucralose concentrations varied by over a factor of two between the two sampling events, whereas several of the other highest concentration compounds had much less variability. It is also of note that several of the high concentration target analytes in the SAR site are pesticides/herbicides or their degradates (bromacil, DACT), indicating potential multiple influences on the receiving water.

A broader analysis of more than 200 finished drinking water samples for the long list of compounds (Figure 11) shows that (a) very few PPCPs show up with any degree of frequency (e.g. >20%) in most finished drinking waters, with pesticides and herbicides detected much more frequently than PPCPs and (b) the PPCP compounds that do show up with any degree of frequency are not the ones on the most common analyte lists. This suggests that it is important to expand the testing lists used when assessing PPCP impact on potable water sources.

CONCLUSIONS

Based on this analysis it is apparent that none of the existing short lists (SAWPA, SWRCB Blue Ribbon Panel, WaterRF, primidone, sucralose/acesulfame-K) provides a 'perfect' indicator and

much greater discerning power is obtained by looking at a long list. Specifically the SAWPA list suffers because only one compound, TCEP was detected in all effluent samples, and for that analyte concentration varied by a factor of 10 among dischargers. The CA SWRCB Blue Ribbon Panel list suffers because only sucralose was detected in all samples; iopromide was only detected in about 50% of the samples and gemfibrozil in an even smaller number of effluents. Neither of these two latter analytes was detected at a significant concentration in the SAR sample. Other analytes in the Blue Ribbon Panel list were included in the list due to toxicity, so their low frequency of detection does not impact this data assessment. Primidone, while occurring in 100% of samples varies by five fold among local sources and thus may not be the ideal tracer to assess the percent of wastewater influence on its own. Many of the compounds in the WaterRF list are not even among the most commonly detected analytes. Data from 2011, when additional analytes were added to the long list (TCDPP and Acesulfame-K) demonstrates unequivocally that the more you look for, the more you find. In 2011 some of the compounds that were not measured in 2010 were the most frequently detected analytes in both the effluents and the river water.

Taking advantage of the power of a long list covering various classes of compounds it becomes possible to identify both more generic (sucralose, acesulfame-K, TCEP, primidone) and specific (iohexal, atenolol, butalbital, caffeine degradates such as theobromine and 1,7-dimethylxanthine, flame retardants such as TDCPP, and triazines and their degradates) tracers to not only determine the presence of wastewater, but also potentially specific primary wastewater sources. Several of the compounds seen most frequently that also have less than ten fold variation include ones not commonly measured (Dehydronifedipine, dilantin, meprobamate, and TDCPP). Having a relatively low cost broad spectrum analytical method allows leveraging of this monitoring to gain much greater information on potential indicators.

REFERENCES

Benotti, M., Trenholm, R., Vanderford, B., Holaday, J., Stanford, B. & Snyder, S. 2009 Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ. Sci. Technol.* **43** (3), 597–603.

Buerge, I., Kahle, M. *et al.* 2008 Nicotine derivatives in wastewater and surface waters: application as chemical markers for domestic wastewater environ. *Sci. Technol.* **42**, 6354–6360.

Buerge, I., Rudolf Buser, H. *et al.* 2009 Ubiquitous occurrence of the artificial sweetener acesulfame in the aquatic environment: an ideal chemical marker of domestic wastewater in groundwater environ. *Sci. Technol.* **43**, 4381–4385.

Drewes, J. E., Sedlak, D. *et al.* 2008 *Development of Indicators and Surrogates for Chemical Contaminant Removal during Wastewater Treatment and Reclamation*. WateReuse Foundation, WRF-03-014.

Eaton, A., Haghani, A. *et al.* 2010 On the use of Multiple Indicators for Impaired Waters 25th Annual Water Reuse Association Conference, Washington, DC. September 2010.

Guo,, Y. C., Krasner, Y. S. *et al.* 2010 Source, Fate, and Transport of Endocrine Disruptors, Pharmaceuticals, and Personal Care Products in Drinking Water Sources in California final Project Report May 2010. NWRI.

Haghani, A. W., Eaton, A., Wan, J. & Cha, Y. Y. 2009 Multi-residue analysis for emerging contaminants using direct online injection. 2009 AWWA Research Symposium: Emerging Organic Contaminants, Austin, Texas, February 12–13, 2009.

Mawhinney, D., Young, R. B., Vanderford, B. J., Borch, T. & Snyder, S. A. 2011 The artificial sweetener sucralose in U.S. *Drinking Water Syst. Env. Sci Tech.* in press.

Oppenheimer, J., Eaton, A., Badruzzaman, M., Haghani, A. & Jacangelo, J. 2011 Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. *Water Res.* **45**, 4019–4027.

Santa Ana Watershed Project Authority. 2009 Phase-II Report of the Emerging Constituents Workgroup December 2009.

Santa Ana Watershed Project Authority. 2010 Phase-II Report of the Emerging Constituents Workgroup December 2010.

State Water Resources Control Board. 2010 Final Report Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water Recommendations of a Science Advisory Panel June 25, 2010. ppp. 220.

Snyder, S. A., Wert, E. C. *et al.* 2007 *Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes*. AWWA Research Foundation, Denver, CO.

Vanderford, B., Snyder, S., Eaton, A., Guo, C., Ternes, T., Drewes, J. & Wood, C. 2011 Seventh Periodic Report for 'Evaluation of Analytical Methods for EDCs and PPCPs via Interlaboratory Comparison' WaterRF Project 4167, January 16, 2011.