Identification of new, possible PB&T substances important in the Great Lakes region by screening of chemicals in commerce

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Summary

The goal of this study was to identify emerging contaminants and persistent, bioaccumulative, and toxic (PBT) chemicals that were not being considered in current Great Lakes contaminant measurement programs and determine how they could be chemically analyzed. We combined the Canadian DSL list totaling 11,317 compounds with the US EPA high production volume (HPV), a list of 3059 substances of "Unknown or Variable composition Complex reaction products and Biological materials" (UVCBs), the US EPA Toxic Substances Control Act (TSCA) Inventory update rule (IUR) database for years: 1986, 1990, 1994, 1998, 2002, and 2006 and 500 chemicals from the EPA's Enhanced HPV (EHPV) program, which covered substances that were not in the HPV program, but were produced in over 1 million lbs during 2002. The CAS numbers were cross-compared to remove duplicates yielding a total of 22,263. From that list 610 chemicals were identified by Structure Activity Relationships (SARs USEPA EPI Suite) and using expert judgment. Toxicity was also assessed using SARs for aquatic toxicity and cancer potential, but was not used to prioritize the chemicals. This study has yielded some interesting probable P&B substances that should be considered for further study and measurement in the Great Lakes region. Most of the 50 top priorities we identified are not currently analysed yet most are in commerce based on the 2002 and 2006 TSCA IUR information. All of the top 50 and most of the larger list of 610 could likely be analysed in environmental media although suitable analytical standards would need to be available and method testing/refinements would need to be conducted.

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Introduction

This project, funded by the US Environmental Protection Agency (EPA) Great Lakes National Program Office (GLNPO), had as its main goal to identify emerging contaminants and persistent, bioaccumulative, and toxic (PBT) chemicals that were not being considered in current Great Lakes contaminant measurement programs and determine how they could be chemically analyzed.

The goal of the initial phase of the project was to conduct a cross-comparison of the Environment Canada Domestic Substances List (DSL), the EPA high production volume (HPV) list and Enhanced HPV (EHPV) list, as well as lists of organic chemicals known as Unknown or Variable composition Complex reaction products and Biological materials (UVCBs) where information was available. The lists were to be combined and prioritized by sorting for various characteristics important in a Great Lakes context such as persistence, bioaccumulation and atmospheric transport potential. Following this the plan was to compare our top priority substances against the Toxics Release Inventory (TRI) and National Pollutants Release Inventory (NPRI), to assess whether the priority substances identified in our screening exercises will be detected by available analytical methods, and to screen a subset of the top priority chemicals (size to be determined) in terms of possible persistent/bioaccumulative degradation products.

This project is a collaboration between Derek Muir, Environment Canada, and Philip Howard, Syracuse Research Corporation (SRC). A "final" report in September 2007 listed 429 substances of which 50 top priorities were identified (Muir and Howard 2007). In this report we provide an update which includes screening for toxicity of the 429 using QSARs, the addition of another 180 substances, and revision of some of the top priorities, and additional use information on the top 50. During the course of the project four progress reports have been prepared and about 8 presentations related to the work have been given. A list of project reports and presentations is included at the end of this document.

Methods

Cross comparison of the Environment Canada and US EPA lists and development a "Great Lakes" relevant list

Full details on the preparation of our list and cross comparison of various databases are given in previous progress reports (Howard and Meylan 2007; Howard and Meylan 2008). In brief, the Canadian DSL list totaling 11,317 compounds was combined with the US EPA high production volume (HPV) list available at http://www.epa.gov/HPV/hpvchmlt.htm. After removing duplicates, the HPV list contained 3549 unique Chemical Abstracts Service (CAS) numbers. From previous work (Howard and Meylan, unpublished data), discrete, representative Simplified Molecular Line Entry System (SMILES) notations were available for 3059 substances of "Unknown or Variable composition Complex reaction products and Biological materials" (UVCBs). These 3059 substances were added to the DSL list to yield a combined list of 14,376 compounds. The list was combined with the US EPA TSCA Inventory update rule (IUR) database which contains production ranges for the following five years: 1986, 1990, 1994, 1998, and 2002 for 13,958 CAS numbers. Finally we added 500 chemicals from the EPA's Enhanced HPV (EHPV) program, which covered substances that were not in the HPV program, but were produced in over 1 million lbs during 2002. The CAS numbers were cross-compared to remove duplicates yielding a total of 22,043 chemicals. With the release of the IUR production data for 2006 the list was updated with 220 new organic chemicals reported for the first time. The combined dataset is summarized in Table 1.

Quantitative structure property/activity relationships (QSPRs/QSARs)

QSPRs and QSARs were used in screening of the thousands of chemicals and for the identification of chemicals of high priority for further assessment. Selected physical and chemical property values estimated with the QSPRs in the EPI Suite software (US EPA 2005) included octanol-water partition coefficient (log Kow) (Kowwin), BCF (Bcfwin), Henry's law constant (Henrywin), octanol-air partition coefficient (log Koa), vapor pressure (Mpbpwin), and atmospheric oxidation (Aopwin). The initial persistence and bioaccumulation criteria used for screening are listed in Table 2. These reflect thresholds used in assessmente of PB&T chemicals by the US EPA, Environment Canada, the Stockholm Convention and the EU.

QSARs, ECOSAR and Oncologic were used to predict toxicity to aquatic organisms and cancer potential respectively. ECOSAR provides estimates of potential for aquatic toxicity based upon Kow and chemical class. Over 150 QSARs have been developed for more than 50 chemical classes which predict the aquatic toxicity of chemicals (LC50, EC50, chronic, etc.) for various aquatic organisms (fish, daphnid, algae, etc.). The OncoLogic program (http://www.epa.gov/oppt/newchems/tools/oncologic.htm) assigns a baseline concern level from high to low for a chemical to have the potential to cause cancer. The chemical analog structure activity method was used with some standard exposure scenarios selected

The Identification Methodology (AIM) tool to identify close analogs that have measured data was also used. This program is designed to help identify publicly available, experimental toxicity data on closely related chemical structures. AIM database contains 31,031 potential analogs with publicly available toxicity data Experimental data sources Indexed On-Line Databases TSCATS, HSDB, IRIS, in U.S. Government Documents NTP, ATSDR, HPV Challenge Program and other sources DSSTox, RTECS, IUCLID, AEGLS.

Results and Discussion

Priority identification

The results of the screening of the 22,263 chemicals are summarized in Table 2. A significant proportion of the chemicals had predicted log Kow >5 (19%), AOt1/2 >2 days (10%) and log Kaw >-5 and <-1 (32%) when sorted by individual criteria. However, when these criteria were combined, and broadened to capture additional compounds, only 105 substances had all 3 characteristics based on BCF >1000, AOt1/2 >1 day and log Kaw >-5 and <-1 . Of these 65 were halogenated. About 2000 compounds had log Kow (~2-5) and log Koa (5-12). This categorization was investigated because some substances with lower log Kow and high log Koa may bioaccumulate in air-breathing organisms (Czub and McLachlan 2004; Kelly et al. 2007a).

On further evaluation some of these chemicals are not of concern as P& B chemicals and some of the criteria for selection may not be inclusive enough (Muir and Howard 2006). A recent example is Dechlorane-Plus, a dodecachlorinated flame retardant HPV chemical, which has been detected in Great Lakes air, fish, and sediments (Hoh et al. 2006). Dechlorane-Plus did not make it into the list of 105 P & B substances estimated by QSPRs because it has a predicted low BCF of 0.5 due to a very high predicted log Kow (11.3). However, it appears to be a widespread contaminant in the sediments in the Great Lakes region and may deserve further exposure and risk assessment. This illustrates the potential for some false negatives in the screening process. Of course, the combined database can also be used to identify P chemicals that have high log Kow values that may bioaccumulate like Dechlorane-Plus, but have low predicted BCF estimates.

Therefore to further refine the screening process, chemicals with high production volume were individually screened using expert judgment for persistence, persistence of potential metabolites,and bioconcentration/bioaccumulation factors (BCF/BAF) of the parent and potential metabolites. These four endpoints (P, P-Metabolite, B, B-Metabolite) were evaluated separately. Chemicals that had high log Kow values (above 8) were considered to be potential BCF/BAF chemicals unless that had very high molecular weights. In addition, chemicals with log Koa >5 had log Kow =2-5 were screened manually and 95 were selected as P and B.

All together this second selection process added another 505 chemicals. Of the 610, 62% were halogenated and 7.9 % were siloxanes, reflecting the generally higher P and B characteristics of these classes of compounds.

The full list of 610 substances is provided in an appendixed Excel Spreadsheet. Structures of 605 compounds were available as SMILES notations and molecular structures as provided in the Appendix. Eighteen were mixtures (siloxanes or perfluorinated compounds) with components not fully defined thus assignment of these SMILES notations are based on the assumed major component. Physical-chemical properties (vapor pressure, atmospheric oxidation half-life, octanol-water and octanol-air partition coefficients and bioconcentration factor for those with SMILES notations are provided in Appendix I.

Figure 1 shows the range of predicted values for air-water partition coefficient (log Kaw) versus octanol-air partition coefficient (log Koa) and log Koa versus octanol-water partition coefficient (log Kow) for the 473 neutral organic chemicals in the list in Appendix I. Dashed lines in Figure 1A group the chemicals in terms of their long range transport (LRT) potential as defined by Wania (2006). Those with log Kaw < -2 and log Koa <12 are "swimmers" i.e. due to low log Kaw tend to remain in water. Those with log Kaw >0.5 and log Koa <6 as "fliers" because of high log Kaw. Those with log Koa >12 are defined as "hoppers" and an intermediate group of "multiple hoppers" generally have log Kaw>-4 and log Koa <12. Although Wania (2006) was focusing on LRT of hypothetical nondegradable chemicals to the Arctic his categorization is useful to generally define the chemicals in the context of possible behavior in the Great Lakes region. Our selection process has identified few fliers or swimmers, most are hoppers and multihoppers, i.e. having significant transport potential from sources either directly and also on particles (for compounds with very high log Koa).

In Figure 1B, the same compounds are assessed in terms of their bioaccumulation potential following Kelly et al (2007) who concluded that compounds with log Kow = 2 to 5 and log Koa ≥ 5) constituted a little recognized group of chemicals that could be bioaccumulative particularly in food webs containing air-breathing animals. Figure 1C further examines these compounds in terms of their "Environmental Bioaccumulation Potential (EBAP)" of the neutral organics assuming humans exposed via a marine and agricultural diet (Czub and McLachlan 2004).

Monitored or analyzable?
Other characteristics on the list of 610 substances are provided in Table 3. We estimate that 101 of 610 have been measured in the Great Lakes region (as parent compound or degradation products) and about 47 (legacy organochlorines, PBDEs and perfluorinated alkyl acids) are on routine monitoring lists. Our search for measured chemicals includes environmental databases e.g. http://www.srcinc.com/what-we-do/efdb.aspx; Scopus and major journals such as Environmental Science and Technology, as well as Google (using CAS numbers), but does not include occupational exposure measurements or have unpublished measurements e.g. of various monitoring groups operating in the Great Lakes region.

Infrequently measured chemicals included several polybrominated biphenyls, tetrabromo-bisphenolA, nonyl phenol and related alkyl phenols, alkyl substituted benzenes, synthetic and aromatic musks, perfluorosulfamido alcohols and fluorotelomer alcohols. A number of these compounds are no longer in commercial production in the USA, e.g. PBBs, PBDEs, PCBs, organochlorine pesticides (OCP), PFOS related compounds, nevertheless there are major reservoirs of "in use" end use products (PBDEs, PFOS) or in the environment (PBBs, OCPs).

Given our focus on P and B chemicals it was not surprising that more than half were neutral organics. We concluded, after review of vapor pressure and structure of individual compounds, that 404 were amenable to extraction using conventional analytical methodology for POPs, PAHs and current use pesticides (i.e. neutral and moderately polar organics) and to analysis by GC-MS. By this we mean extraction and isolation steps in methods such as EPA 1613 or 1668 for PCBs/dioxins (US EPA 1999, 2000) and/or USGS methodology for pesticides and personal care products in water (Zuagg et al. 1995). Another 33 (including some alcohols, siloxanes, pigments/dyes) may be analyzable. However, there is a lot of uncertainty particularly for siloxane-related compounds, for which there is yet no concensus on analytical methodology for environmental samples. We assume that 35 of 48 silicone based products would be amenable to GC-MS analysis based on similar physical chemical properties to the cyclic siloxanes (D3-D6) for which some environmental measurements have been made (Kaj et al. 2005).

Another subset of chemicals were analyzable by LC-MS/MS. These were mainly the perfluoroalkyl acids (e.g. perfluoroalkane sulfonates, PFSA and perfluorocarboxylates PFCAs) for which LC-MS methodology is now relatively well established (Hansen et al. 2001; Martin et al. 2004). Ten other carboxylates were included in this list as "maybes".

We assessed each of the 610 for possible degradation products focusing mainly on hydrolysis products, i.e. of esters, amides and on PFSA/PFCAs. The latter group comprised 133 of the 193 compounds for which we identified possible analyzable degradation products. We did not identify any analyzable degradation products of siloxanes because of lack of information. Silanols are known atmospheric oxidation degradation products of siloxanes (Tuazon et al. 2000) but determining whether they are likely to be significant residues in Great Lakes media was a very challenging question and beyond the scope of the study.

Toxicity Screening

The AIM tool to identify close analogs that have measured data found 65% of the chemicals had analogs within 45 chemical classes with measured toxicity information (Table 4). These would be 45 chemical classes have been identified as being of potential concern for human health effects. The results from Oncologic showed 10 (6.8%) chemicals out of 146 that were within the model domain,with high to moderate concern for potential to cause cancer. The majority (54%) were categorized as "marginal" or "low" concern.

ECOSAR was applied to 603 chemicals, i.e. all for which SMILES notations were available (Table 4). Model output was limited to either 96 hr LC50s for freshwater fish or for mysid shrimp. Results for all substances are given in Appendix II. About half of the chemicals (54%) were classified as neutral organics by the program. Esters and phenols represented the next largest groups (7% each). ECOSAR includes separate QSARs for each group. For neutral organics and esters the predicted 96 hr LC50 mysid shrimp (freshwater) was used as the endpoint for this class because it was generally the most sensitive organism (other options were daphnia, or saltwater fish (no species)). For all other chemical groups a 96 hr LC50 for freshwater fish was used because other QSARs did not provide predictions for mysids (freshwater). About 60 (10%) of the chemicals had relatively high predicted aquatic toxicity based on low 96 h LC50s

(<0.001 ug/L) in either mysids or fish, while the majority were between 1 and 1000 ug/L (47%). Many of the chemicals, particularly neutral organics with high log Kows, were outside the model domain which is log Kow = <5 for ECOSAR's 96 hr acute toxicity test. ECOSAR output also includes chronic aquatic toxicity values which actually may have greater relevance for many of the chemicals in the list, however, the predicted acute values were judged easier for broad comparisons among chemicals. It should be noted that degradation products were not assessed by ECOSAR.

Top 10 priorities
To reduce the list of 610 so that a more manageable number could be identified, we selected our top 10 priorities from each chemical group in Appendix I, i.e. from brominated, chlorinated, fluorinated, silicone, non-halogenated. The fluoro siloxanes (2 compounds) were assigned to the fluorinated group and chloro/bromos (1) to brominated. These are presented in Tables 4 to 8 along with estimated properties, information on analyzability and on quantity in commerce in the 1990s to 2006. The major criteria used to select the top 10 were production volume, BCF, and persistence (AO t1/2). We also sought to identify representatives of important classes of compounds such as TBBPA derivatives, cyclic siloxanes, chlorinated pyridines and cyclopentane/enes. We omitted most chemicals for which there were already measurements e.g. PBDEs, synthetic musks, triaryl phosphates, haloalkyl phosphates.

Brominated:
Our selection of 10 brominated was designed to reflect important classes of compounds that could be penta-. octa-BDE and decabromodiphenyl ether (decaBDE) replacements as well as some more volatile compounds that have LRT potential (Table 4). In this group there are 3, CAS# 87843, 3322938 and 30554724 which are single ring compounds and likely analyzable along with PBDEs and chlorobenzenes. Likely Penta- and octa-BDE replacements in the list are CAS#26040517 (a tetrabromophthalic acid ester, TBP-BEHE) and #37853591, bis(tribromophenoxy ethane (BTBPE)) and #032588-76-4 (ethylene bis(tetrabromophthalimide, EBTBP)). Both THP-BEHE and EBTBP are on the EU list of PB& T substances (Pavan and Worth 2008) but EBTBP has recently been de-listed according to the manufacturer (Albemarle Corp. 2007). These three are representative of a much larger group (see Appendix) which are all esters. They have low predicted BCFs due to a combination of high log Kow (7.6-12) and potential for ester hydrolysis.

Three highly brominated compounds were included #155613937, an octabromoindane, #58965665, a 14 bromine containing compound with significant production in 2002 (1-10M lbs) and decabromodiphenyl ethane (DBDPE). All three are possible replacements for decaBDE. As highly brominated compounds they are likely to have relatively low bioavailability but high persistence and therefore would be good candidates for survey of Great Lakes sediment. They could also debrominate to more bioavailable compounds. DBDPE is listed as LPV chemical in Europe but is not listed on EPA IUR or Canada's DSL yet is has been increasing in Great Lakes herring gull eggs over the past decade (Gauthier et al. 2009).

Finally, #128632, a tetrabromopyrene, is not a flame retardant but apparently has been used as a chemical intermediate for production of monomers used in electroluminescent (EL) displays (Mikroyannidis 2005). It is unclear if it would be released during use but relatively high use (500K-1 M lbs in 2002; 30-500K lbs in 2006) suggests that it could be. It had a somewhat higher predicted BCF than most of the other brominated compounds although not above the BCF criteria for POPs of 5000 (UNEP 2001). All 10 brominated compounds in Table 4 appear to be

amenable to analysis by GC-MS using conventional techniques for extraction and isolation that are used for the PBDEs. Thus many in this group could possibly be retrospectively analysed in existing extracts.

Chlorinated:

Our selection of 10 chlorinated (from 116 in the Appendix) reflects mainly AOt1/2 and production criteria. Nine of 10 compounds have AOt1/2 values of >2 days, a POPs LRT criteria (UNEP 2001). We included Declorane Plus® (DP) because of its large production volume and predicted persistence which appears to have been confirmed by measurements in Great Lakes sediments (Hoh et al. 2006). However, it has a low predicted BCF due to high log Kow value (and molecular size). Similarly, bis(chlorphenyl)sulfone (BCPS, CAS# 80079), an HPV chemical which is used in production of thermostable plastics (Norström et al. 2004) is included despite relatively low predicted BCF, because of detection in Great Lakes herring gull eggs (Letcher et al. 1995) and presence of high levels in guillemot eggs in the Baltic Sea (Jörundsdöttir et al. 2006). The molecular structure of BCPS also resembles the PCB methyl sulfone metabolites which are known to be very bioaccumulative (Letcher et al. 2000). The microbicide triclocarban (#101202) was included because of its large production (although lower in 2006 than previous years) and relatively high predicted BCF (1187). Several other microbicides are also found in the Appendix e.g. triclosan (#3380345), tribromsalan (#87105) and tetrachlorosalicylanilide (#1154592) although their production is much lower than triclobarban as of 2006. Triclosan can be considered a well monitored chemical and was therefore not included.

Along with DP, the list contains 3 other cyclopentane based compounds. Hexachloro-cyclopentadiene has previously been used as a biocide (DHHS/ATSDR 1999) but is mainly used as a reactive intermediate and in manufacture of DP as well as the preparation of chlorendic anhydride (Mack 2004). HCCP has been detected in the Great Lakes atmosphere above Great Lakes (Vernier and Hites 2008). The chlorinated cyclopentanes are all chemical intermediates probably used in the production of HCCP (Cheung 2001).

All 10 chlorinated compounds should be readily analyzable by gas chromatography and to be amenable to extraction by conventional techniques that are used for other chlorinated organics such as PCBs and chlorobenzenes. Thus this group could possibly be retrospectively analysed in existing extracts. However a search of analytical standards suppliers (Sigma-Aldrich; Supelco; Accustandard) and using the CAS number in a Google search revealed no suppliers for the cyclopentane/enes, possibly because they are chemical intermediates and have not been synthesized for other uses.

Fluorinated:

The selection of fluorinated compounds was challenging because a large number on the list were actually chemical intermediates, e.g. telomere iodides, sulfonyl fluorides, used in production of fluoropolymers containing fluorotelomer or fluoroalkylsulfonate moieties. Also the phase out of the perfluorooctanesulfonate (PFOS) related products may make many chemicals on the list of lower priority. Thus our selection (Table 6) includes chemicals that we believe are currently in use and actually replacements in some cases, e.g. fluorotelomer acrylates (#17527296, 2144538) and perfluorobutane sulfonamide- (#s 34449893, 67584558, 67584592) based chemistries. These compounds are likely to yield perfluorocarboxylates (PFCAs) and perfluorobutane sulfonates (PFBS) in the atmosphere (Ellis et al. 2004; D'Eon et al. 2006) and in sewage treatment plants (Dinglasan et al. 2004; Wang et al. 2005). Overall about 73% of the 183 fluorinated compounds likely give rise to PFCA or PFSAs.

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Also included are several compounds trifluoromethyl-substituted compounds (#328847, 393759 and 50594779) which have relatively long AOt1/2 and significant production (1-10M lbs for 2 of 3 in 2002; 500K-1M lbs in 2006). However none of the three meet the POPs log Kow=5 criteria and may therefore not be very bioaccumulative. They could, however, fit into the class of chemicals with relatively high predicted biomagnification in air breathing animals due to intermediate Kow and relatively high log Koa (Kelly et al. 2007) and therefore deserve further study.

The fluorinated phosphonate (#68412680; PFPA) was included because of the high predicted BCF (19510) for the mono-substituted compound along with high AOt1/2. Several other related phosphates with perfluorinated substituents are also found in Appendix I (#2965528, 67939973, 67969691, 68412691, 74499448, 148240851, 148240873 and 148240895). The phosphates are amenable to LC-MS/MS analysis as with other perfluoroalkyl acids (Hansen et al. 2001) and the first measurements of C6, C8 and C10 PFPAs in the Great Lakes region have recently been made (D'eon et al. 2009).

Several relatively volatile compounds are included in Table 4. The fluorinated cyclic siloxane, # 2374143, is very interesting because it is a fluorinated siloxanes and combines relatively high AOt1/2 with large production (1-10 M lbs in 2002; 500K-1M lbs in 2006). Due to relatively high log Kow (8.66) this compound has low predicted BCF (343). Nevertheless other siloxanes have high predicted (and in some cases measured) BCFs as discussed below. Perfluoroperhydrophenanthrene represents a class of perfluorinated cyclics (see also # 306945 in Appendix I) which are likely very persistent but have low predicted bioaccumulation due to their very high log Kow. These compounds have many applications in the electronics industry, including as a fluid for vapour phase soldering, condensation inert heating, fluid for testing and direct contact cooling (Siegemund et al. 2000). They are most likely emitted directly to the atmosphere given their volatility.

Unlike the chlorinated and brominated compounds, the 10 fluorinated compounds in Table 6 are more of a challenge to analyse by existing methodology. The trifluoromethyl-substituted compounds (#328847, 393759 and 50594779) and Perfluoroper-hydrophenanthrene appear to be amenable to analysis by GC-MS using conventional techniques for extraction and isolation of PCB/chlorobenzenes although methods would need modification to avoid volatilization losses due to high volatility. Most others are more likely analysed by LC-MS as degradation products i.e. perfluoroalkyl acids or directly in the case of PFPA.

Nonhalogenated:
The selection of chemicals from this large group (totaling 165 in the Appendix) was based mainly on predicted BCF and production volume. All ten were produced in the range of 1-10M lbs to up to 50-100 M lbs in 2002 and most continue to be HPV in 2006 (Table 7). AOt1/2 values for these 10 and indeed most non-halogenated compounds, were <2 days reflecting much greater reactivity with hydroxyl radical, especially for aromatic hydrocarbons. Triphenyl phosphite and triphenyl phosphine were included (#101020, 603350) because of their high predicted BCFs (25170 and 4801 respectively). Several related triaryl phosphate, e.g. TTBPP (#31570044) and trihaloalkyl phosphates (e.g. tris(2-chloropropyl)phosphate # 6145739) are also in the list of 610 compounds but were not included because of low predicted BCFs. Nevertheless, there is evidence for environmental contamination by these compounds in the Great Lakes (Scott et al. 1996; Andresen et al. 2007) and some tris-(chloroalkyl) phosphates may be replacements for Penta-BDEs (U.S. EPA 2005) so we could see increased use. Several other compounds in Table 7 have high predicted BCF including #25973551 (10350), #1742149 (15170), #69009901

(27240) and the synthetic musk, galoxide #1222055 (13200). All are characterized by optimum log Kow (6-7) and substitution on aromatic rings in the para-position which may limit biodegradation. There are generally no experimental BCFs to confirm these predictions. All 10 compounds appear to be amenable to analysis by GC-MS using conventional techniques for extraction and isolation.

Silicone related compounds:
Selection of the top 10 from this group (totaling 48 in the Appendix) was based on high predicted BCFs (8 of 10 are >5000) and AOt1/2 (9 of 10 are >2 days) as well as production volume. Dimethyl cyclic siloxanes with 4 to 6 siloxane groups appear to be particularly bioaccumulative and recent laboratory measurements confirm this (Drottar et al. 2007). Environmental measurements in Scandinavia show that the cyclic siloxanes are the major siloxanes found in environmental media despite wide use of both linear and cyclic products (Kaj et al. 2005). Unlike the other groups, the analytical methodology for determining silicones (a generic term) or siloxanes (refers to Si-O with substituents (usually alkyl) on the Si (Silicon, Oxygen, and alkane) is not well established. The Nordic group responsible for most of the measurements to date has not published method details. Nevertheless all 10 compounds on the list are likely to be amendable to extraction and isolation methods similar to those currently used for the cyclic siloxanes (Kaj et al. 2005). They probably cannot be determined, however, in existing extracts developed for analysis of halogenated organics or PAH/hydrocarbons due to background contamination issues. The wide use of the linear and cyclic siloxanes (note that "D4" #556672 had production in the range of 100-500 M lbs in 2002) including in personal care products, combined with high volatility (most have VPs>1 Pa) means that they are widespread contaminants in laboratories. Also they may contaminate laboratory reagents. Thus minimizing contamination during sample collection and storage, as well as during analysis is a major challenge. Several laboratories in the Great Lakes region are currently developing methods to analyse siloxanes but it may be several years before the full picture of whether predicted BCFs and long persistence of these compounds is confirmed. We therefore refrained from identification of sources of analytical standards for this group.

Conclusions
This study has yielded some interesting probable P, B and T substances that should be considered for further study and measurement in the Great Lakes region. Most of the 50 top priorities we identified are not currently analysed yet most are in commerce based on the 2002 and 2006 TSCA IUR information. All of the top 50 and most of the larger list of 610 could likely be analysed in environmental media although suitable analytical standards would need to be available and method testing/refinements would need to be conducted.

We have been flexible with the definition of P, B and T chemicals and this could be criticized. However most assessments of P and B characteristics have faced a similar challenge. Indeed, a report prepared for the POPs Review Committee of the Stockholm Convention noted that 5 of 10 substances proposed for addition to the POPs list were concluded to fulfil the screening criteria for classification as POPs despite their low BCF (<5,000) (Kitano 2007). Other assessments of the 610, or the 22,263, could take a different approach, for e.g.. simply identifying the top 50 chemicals without categorizing them first as halogenated or non-halogenated, and this might yield a quite different list for the top 50.

Shortly after our first report on this study (Sept 2007), Brown and Wania (2008) identified 120 chemicals as potential Arctic contaminants based on persistence, long range

transport and bioaccumulation potential. They also used the EPI Suite software to estimate properties for 105,584 individual chemicals on the CAS/SMILES string database of the EPISuite software. In addition they used a novel selection algorithm based on structural resemblance to a list of 86 known Arctic contaminants. Comparing lists, 110 of these are in our 22,000 chemical DSL/IUR database. The other ten are pesticides (e.g. endosulfan, chlorothalonil, picloram etc). Current use pesticides were not included in the present study. Altogether there are 86 chemicals in their 110 industrial chemicals that are in our 610 chemical list indicating good agreement between studies. Their use of a much larger list increased the number of compounds which had molecular structures similar to know P and B chemicals but also introduced many that are possibly not in commerce or used in low amounts. Of the 24 in their list that are not in ours (Appendix II) many are not good potential PBT chemicals due to high reactivity, e.g. alpha-aminonitriles, isocyanates, diesters.

Another alternative would be to classify by toxicity first and then examine P and B characteristics. However, the model domains for most ECOSAR QSARs are generally for substances with log Kow <6 and there are other limitations such as the compound cannot be a solid. Therefore a large number of potentially P and B chemicals would be missed with that approach if the model domain criteria were strictly followed. For e.g., 4 brominated compounds in the top 50 priorities also had high predicted aquatic toxicity (LC50s <0.001 ug/L). However all four substances had high log Kow (>5) and thus the prediction for neutral organics was outside the model domain. On the other hand screening substances with intermediate or low log Kow by toxicity first might be an approach for prioritizing chemicals of concern which may not meet P and B criteria but are pseudo-persistent i.e. continually infused to the aquatic environment essentially become "persistent" pollutants even if their half-lives are short (Daughton 2005).

Thus, while we have taken into account aquatic toxicity information on the chemicals this information was not used for identifying the top 50 priorities. Previous experience in the Great Lakes region indicates that some chemicals become concerns because of widespread detection, biomagnification, increasing trends, and high persistence e.g. PBDEs, (decabromodiphenyl ether, toxaphene) and not because much is known about toxicity. We subscribe to this view and have selected priority chemicals with this in mind particularly for the halogenated compounds. However, for the non-halogenated and siloxanes-related substances, we relied mainly on POPs criteria for BCF and atmospheric oxidation half-life as well as production volume.

Further work should be done with the list of 610 chemicals and with the larger list of 22,263 chemicals in commerce. Information on uses and releases is critical to proper assessment and prioritization. Some compounds may have very high release potential, e.g., plasticizers, hydraulic fluids, or solvents, fire fighting surfactants and other defoaming agents, fragrances, auto wax products, soil repellants. Others are degraded during use such as antioxidants, vulcanizing agents, UV stabilizers, polymer initiators, and may not be released into the environment.

A variety of pollution prevention and "green chemistry" approaches could also be considered as part of the assessment of each substances, depending upon the use and chemical properties required for the application. For example for known synthetic intermediate: development of different synthetic route; solvent: examining physical properties (vapor pressure, solubility) and identifying substitutes; surfactant: same surfactant properties but more biodegradable; Flame retardants: evaluating use phosphate based organics rather than halogenated.

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Tables and Figures

Table 1. Development of a combined Canadian and US database of chemicals in commerce

Source	# substances	Reporting threshold	Reporting date
US EPA High production volume (HPV) and EHPV program	4049	10^6 lbs/yr (454 t/yr)	IUR reporting years; 1990, 1994, and 2002
US EPA TSCA Inventory update rule (IUR)	13,958	$>10^4$ lbs/yr (4540 kg/yr)	IUR reporting years; 1986 to 2002
Canadian DSL categorization	11,317 organics	>100 kg	Mid-1980s
UVCBs	3059 organics	>100 kg	Mid-1980s
IUR 2006 update	220 organics	>25,000 lbs/yr	Reporting year 2006
Total (after duplicates removed)	22,263		

Table 2. Persistence and Bioaccumulation Characteristics of the 22,263 Chemicals

Characteristics*	#	%	Notes
log Kow > 5	4239	19	Indicates tendency to adsorb to sediments and to bioaccumulate
BCF > 2000	924	4.6	BCF is an estimate of bioaccumulation
BCF > 5000	566	2.8	potential
BCF > 50000	19	0.1	
AO t1/2 > 2 day	1973	10	AO half-life indicates stability to atmospheric
AO t1/2 > 10 day	840	4	oxidation
log Kaw > -5 <u>and</u> log Kaw < -1	6515	32	Kaw describes air-water partitioning. Compounds with log Kaw >-5 & <-1 have long range transport potential
Combined BCF > 2000, AO t1/2 >1 d and log Kaw > -5 and <-1	105	0.5	The number of substances with all 3 characteristics combined is much smaller
Combined BCF > 2000, AO t1/2 >1 d and log Kaw > -5 and <-1	79	0.4	
log Kow 2-5 and high log Koa 5-12	2000	10%	Biomagnification in air breathing organisms

Table 3. Information on measurement and analyzability of the 610 substances in Appendix I

Analysable	Well monitored in the GL region (ie. programs such as IADN & fish monitoring)	All chemical that may have been analysed in any GL measurement studies	Analysable using existing methods for neutral POPs or other neutrals such as pesticides	Phenols or carboxylates analyzable after derivatization or by LC-MS	Analysable by LC-MS/MS ESI mode (anionic) or positive CI mode (cation)	Analysable degradation product
Yes	47	101	404	70	43	193
% Yes	7.7	16.5	66.2	11.5	7.0	31.6
No	563	509	167			
Maybe			39	8	24	4

[1] ESI = electrospray ionization, CI = chemical ionization

Table 4. Results of toxicity screening of 610 chemicals using QSARs

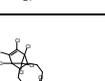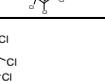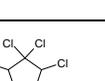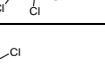| QSAR	Number of chemicals tested or within model domain	Endpoints	Results	Number	%
AIM tool	429	close analogs that have measured toxicity data	Included in 45 classes	277	65
ECOSAR	603	Predicted 96 hr EC50 in freshwater fish or in mysid shrimp	<0.001 ug/L = >0.001 – 1 ug/L = >1-1000 ug/L = >1000 ug/L	60 107 282 155	10 18 47 26
OncoLogic	146	Cancer potential	High High-moderate Moderate Low-Moderate Marginal Low	0 10 24 34 29 49	0 6.8 16 23 20 34

Table 5. Top ten brominated compounds from the list of 610 substances

CAS # without hyphens	Molstructure	Class	VP est (Pa)	Atmos Oxid'n t1/2 (days)	Log Kaw	log Kow	Log Koa	BCF	Chemical intermediate?	Currently analysed in environmental monitoring or research programs in the Great Lakes	Analysable using existing methods for neutral POPs or other neutrals such as pesticides, i.e. no derivatization	Probable degradation product	Analysable degradation product	Pdt'n range (M lbs) 86 b	Pdt'n range (M lbs) 90	Pdt'n range (M lbs) 94	Pdt'n range (M lbs) 98	Pdt'n range (M lbs) 02	Pdt'n range (M lbs) 06	Likely source of analytical standards
87843	(structure)	Br	4.61E-04	15.71	-4.41	4.71	9.12	860	N	N	Y						0.5	0.5	–	Accustandard
128632	(structure)	Br	5.41E-08	6.57	-5.07	8.49	13.56	2424	Y	N	Y			0.5	1	10		1	0.5	Wellington Labs
3194556	(structure)	Br	2.24E-06	2.13	-4.15	7.74	11.89	6211	N	Y	Y			10	10	50	50	50	50	Wellington Labs
3322938	(structure)	Br	1.40E-02	2.20	-2.77	5.24	8.01	2153	N	Y	Y			0.5	0.5	0.5	0.5	0.5	–	Wellington Labs
26040517	(structure)	Br	2.28E-09	0.49	-4.91	11.95	16.86	3	N	N	Y	tetrabromophthalic acid	Y	10	10	10	10	10	10	Wellington Labs
30554724	(structure)	Br	1.12E-03	16.36	-3.92	4.62	8.54	716	N	N	Y			0.5	0.5	0.5	0.5		–	No source identified
32588764	(structure)	Br	3.39E-20	0.27	-18.83	9.80	28.63	10	N	N	Y	tetrabromophthalic acid	Y	10	1	10	50	10	10	SAYTEX® BT-93W
84852539	(structure)	Br	2.53E-11	4.50	-5.92	13.64	19.56	3	N	Y	Y								–	Wellington Labs
37853591	(structure)	Br	3.17E-08	0.72	-6.52	9.15	15.67	74	N	Y	Y	Tribromophenol	Y	50	50	50	10	10	10	Wellington Labs
58965665	(structure)	Br	4.91E-18	195.93	-9.57	16.89	26.46	3	N	N	Y				1	1	10	10	–	SAYTEX® 120
155613937	(structure)	Br	1.64E-10	6.20	-6.91	11.80	18.71	1	N	N	Y						10	0.5	–	Wellington Labs
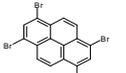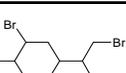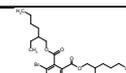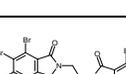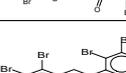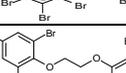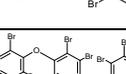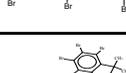
a. All physical-chemical property estimations using EPISuite ver 3.12 VP = vapor pressure; Atmos. Oxid'n= atmospheric oxidation half-life (12 hr day at 1.5x106 H/cm3)
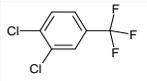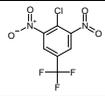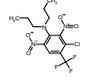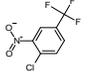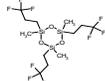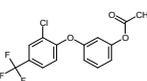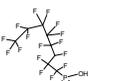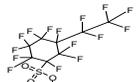b. Production values from TSCA IUR for the five reporting years to 2002. Values refer to millions of lbs: (0.5 = 10-500 K; 1 = 500 K-1 M; 10 = 1-10 M; 50 = 10-50 M; 100 = 50-100 M; 500 = 100-500 M; 1000 = 500-1000 M lbs for the reporting year).

Table 6. Top ten chlorinated compounds from the list of 610 substances

CAS # without hyphens	Molstructure	Class	VP est (Pa)	Atmos Oxidation t1/2	LogKaw	logKow	Log Koa	BCF	Chemical intermediate?	Currently analysed in environmental monitoring or research programs in the Great Lakes	Analysable using existing methods for neutral POPs or other neutrals such as pesticides, i.e. no derivatization	Probable degradation product	Analysable degradation product	Pdt'n range (M lbs) 86 b	Pdt'n range (M lbs) 90	Pdt'n range (M lbs) 94	Pdt'n range (M lbs) 98	Pdt'n range (M lbs) 02	Pdt'n range (M lbs) 06	Likely stand
77474		Cl	6.51E+00	26.99	-1.06	4.63	5.69	1516	Y	N	Y			50	50	50	50	50	50	Aldri
101202		Cl	4.81E-07	0.50	-8.73	4.90	13.63	1187	N	N	Y			0.5	10	10	1	10	0.5	Aldri
80079		Cl	0.00010786	218.8586	-5.2519	3.9	5.757563	199.5	Y	N	Y			10	10	50	50	50	50	Aldri
133493		Cl	2.49E-02	76.72	-2.32	5.91	8.23	7066	Y?	N	Y			1	1	1	0.5	0.5	–	Supe
1770805		Cl	1.627E-05	320.20	6.28	7.25	0.97	29340	Y	N	Y	hexachlorocyclopentadiene-phthalate						0.5	0.5	–	Dow
1737935		Cl	2.08E+02	172.54	-4.60	2.69	7.29	24	Y	N	Y						0.5	10	10	Sigma
13560899		Cl	9.41E-08	160.10	-3.52	11.27	14.79	1	N	Y	Y			10	10	10	10	10	10	Welli
62111471		Cl	6.76E-01	2.66	-1.99	4.44	6.43	521	Y	N	Y					10	10	10	–	No so
68258902		Cl	3.39E-01	93.49	-2.56	4.03	6.59	253	Y	N	Y					50	500	50	–	No so
68412408		Cl	1.05E-01	974.13	-0.59	4.03	4.62	104	Y	N	Y			10	10	10	10	10	10	Aldri
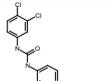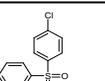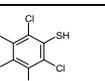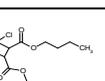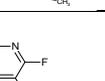
a. All physical-chemical property estimations using EPISuite ver 3.12 VP = vapor pressure; Atmos. Oxid'n= atmospheric oxidation half-life (12 hr day at 1.5×10^6 OH/cm^3)

b Production values from TSCA IUR for the five reporting years to 2002. Values refer to millions of lbs: (0.5 = 10-500 K; 1 = 500 K-1 M; 10 = 1-10 M; 50 = 10-50 M; 100 = 50-100 M; 500 = 100-500 M; 1000 = 500-1000 M lbs for the reporting year).
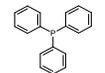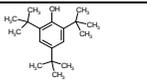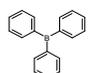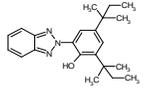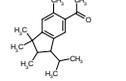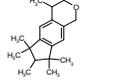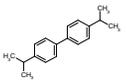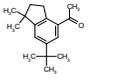
Table 7. Top ten fluorinated compounds from the list of 610 substances

CAS # without hyphens	Molstructure	Class	VP est (Pa)	Atmos Oxidation t1/2	LogKaw	logKow	Log Koa	BCF	Chemical intermediate?	Currently analysed in environmental monitoring or research programs in the Great Lakes	Analysable using existing methods for neutral POPs or other neutrals such as pesticides, i.e. no derivatization	Probable degradation product	Analysable degradation product	Pdt'n range (M lbs) 86 b	Pdt'n range (M lbs) 90	Pdt'n range (M lbs) 94	Pdt'n range (M lbs) 98	Pdt'n range (M lbs) 02	Pdt'n range (M lbs) 06	Likely source standard
328847		F	1.76E+02	132.87	0.02	4.24	4.22	370	Y	N	Y			10	10	10	10	10	0.5	Aldrich 2
393759		F	5.08E-02	16206.04	-4.66	3.24	7.90	17	Y	N	Y				1	10	10		0.5	Aldrich 1
29091201		F	4.69E-05	5.35	-2.19	5.96	4.76	7688	Y?	N	Y			0.5		1	1		–	No sourc
121175		F	15.73	3724.92	-2.25	3.42	2.28	86	Y	N	Y			0.5	0.5			0.5	–	Aldrich C
306912		F	42.80	very long	8.78	9.58	-2.60	19	N	N	Y			0.5	0.5		0.5		–	www.flu
2374143		F	40.40	2.39	3.84	8.66	4.82	343	N	N	Y			10	1	1	10	10	0.5	http://ww
344047		F	971.92	1025.74	-0.72	3.88	1.21	196	Y	N	Y						0.5		–	Aldrich E
50594779		F	1.88E-03	2.56	-3.43	4.41	7.84	500	N?	N	Y	halogenated diphenyl(ol)	Y	1	10		10	10	–	http://ww tm
68412680		F	6.95E-02	38.20	-3.36	6.48	9.84	19510	N	N	N	PFOA/PFNA	Y				0.5	0.5	–	Mason C
67584423		F	2.09E-07	very long	-9.83	0.47	10.30	3	N	N	N		Y				0.5	0.5	–	MIC Spe

a. All physical-chemical property estimations using EPISuite ver 3.12 VP = vapor pressure; Atmos. Oxid'n= atmospheric oxidation half-life (12 hr day at 1.5×10^6 OH/cm^3)

b Production values from TSCA IUR for the five reporting years to 2002. Values refer to millions of lbs: (0.5 = 10-500 K; 1 = 500 K-1 M; 10 = 1-10 M; 50 = 10-50 M; 100 = 50-100 M; 500 = 100-500 M; 1000 = 500-1000 M lbs for the reporting year).
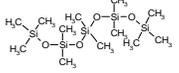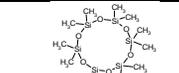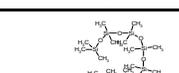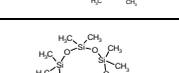
Table 8. Top ten non-halogenated compounds from the list of 610 substances

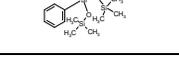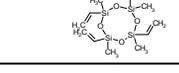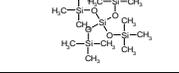| CAS # without hyphens	Molstructure	Class	VP est (Pa)	Atmos Oxidation t1/2	LogKaw	logKow	Log Koa	BCF	Chemical intermediate?	Currently analysed in environmental monitoring or research programs in the Great Lakes	Analysable using existing methods for neutral POPs or other neutrals such as pesticides, i.e. no derivatization	Probable degradation product	Analysable degradation product	Pdt'n range (M lbs) 86 b	Pdt'n range (M lbs) 90	Pdt'n range (M lbs) 94	Pdt'n range (M lbs) 98	Pdt'n range (M lbs) 02	Pdt'n range (M lbs) 06	Likely source standards
101020		Non-halo	1.02E-02	0.99	-4.66	6.62	11.28	25170	Y	N	Y	Triphenyl phosphate?	Y	50	50	50	50	50	50	Aldrich T84
603350		Non-halo	1.36E-03	1.83	-6.03	5.02	11.05	4801	Y	N	Y			1	10	10	10	10	1	Sigma-Aldr
732263		Non-halo	2.67E-02	0.67	-3.40	6.39	9.79	3282	Y	N	N			10	10	10	10	50	50	Aldrich T49
960714		Non-halo	3.29E-03	1.83	-3.00	5.52	8.52	3558	Y	N	?			10	10	10	50	10	10	Fluka 9298
1742149		Non-halo	9.67E-03	0.33	-1.41	6.34	7.75	15170	N	N	Y						10	10	10	– http://www. cc000b.htm
25973551		Non-halo	2.57E-08	0.68	-10.57	7.25	17.82	10350	N	N	N			10	10	10	10	10	10	Aldrich 422
68140487		Non-halo	9.11E-03	0.55	-2.76	6.31	9.07	2080	N	Y	Y			0.5	0.5	0.5	0.5	0.5	0.5	Promocher
1222055		Non-halo	1.17E-02	0.28	-2.27	6.26	8.53	13200	N	Y	Y			1	10	10	10	10	10	Aldrich W5
69009901		Non-halo	9.80E-03	0.84	-1.20	6.67	7.87	27240	N	N	Y					10	10	10	10	No source
13171001		Non-halo	1.92E-02	1.44	-2.75	5.93	8.68	1057	N	N	Y			0.5	0.5	0.5	0.5	0.5	-	Promocher

a. All physical-chemical property estimations using EPISuite ver 3.12 VP = vapor pressure; Atmos. Oxid'n= atmospheric oxidation half-life (12 hr day at 1.5×10^6 OH/cm^3)

b Production values from TSCA IUR for the five reporting years to 2002. Values refer to millions of lbs: (0.5 = 10-500 K; 1 = 500 K-1 M; 10 = 1-10 M; 50 = 10-50 M; 100 = 50-100 M; 500 = 100-500 M; 1000 = 500-1000 M lbs for the reporting year).

Table 9. Top ten siloxanes related compounds from the list of 610 substances

CAS # without hyphens	Molstructure	Class	VP est (Pa)	Atmos Oxidation t1/2	LogKaw	logKow	Log Koa	BCF		Currently analysed in environmental monitoring or research programs in the Great Lakes	Analysable using existing methods for neutral POPs or other neutrals such as pesticides, i.e. no derivatization	Probable degradation product	Analysable degradation product	Pdt'n range (M lbs) 86 b	Pdt'n range (M lbs) 90	Pdt'n range (M lbs) 94	Pdt'n range (M lbs) 98	Pdt'n range (M lbs) 02	Pdt'n range (M lbs) 06	Likely source standards
141639		Si	9.39E+00	5.96	1.51	6.52	5.01	8318	N	N	Y			0.5	0.5	0.5	0.5	0.5		Not determ
540976		Si	4.73E+00	5.96	0.83	6.33	5.50	14890	N	Y	Y			0.5	10	10	10	50		Not determ
541015		Si	1.23E+00	4.47	0.78	7.69	6.91	34360	N	Y	Y							0.5		Not determ
541026		Si	2.91E+01	7.15	0.69	5.71	5.02	2014	N	Y	Y			50	50	50	100	500		Not determ
556672		Si	1.57E+02	8.94	0.55	5.09	4.54	1687	N	Y	Y			500	500	500	500	500		Not determ
556694		Si	1.39E+00	3.97	0.92	8.28	7.36	7096	N	N	Y							0.5		Not determ
2116849		Si	3.13E-01	3.24	0.16	7.15	6.99	40260	N	N	Y			0.5	0.5	1	0.5			Not determ
2554065		Si	1.43E+01	0.10	0.56	6.51	5.95	20410	N	N	Y?			0.5	0.5	0.5	0.5	0.5		Not determ
3555473		Si	2.01E+01	5.96	1.51	6.52	5.01	20860	N	N	Y									Not determ
10448096		Si	3.41E-01	3.57	-0.66	6.30	6.96	14260	N	N	Y									Not determ
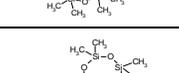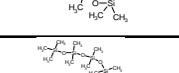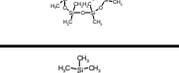
a. All physical-chemical property estimations using EPISuite ver 3.12 VP = vapor pressure; Atmos. Oxid'n= atmospheric oxidation half-life (12 hr day at 1.5×10^6 OH/cm^3)
b Production values from TSCA IUR for the five reporting years to 2002. Values refer to millions of lbs: (0.5 = 10-500 K; 1 = 500 K-1 M; 10 = 1-10 M; 50 = 10-50 M; 100 = 50-100 M; 500 = 100-500 M; 1000 = 500-1000 M lbs for the reporting year).

Figure 1.
Range of values of (A) air-water partition coefficient (log Kaw) versus octanol-air partition coefficient (log Koa) and (B) log Koa versus octanol-water partition coefficient (log Kow) for 475 neutral organics and (C) Environmental Bioaccumulation Potential (EBAP) of the neutral organics assuming humans exposed via a marine and agricultural diet (Czub and McLachlan 2004). Lines in A indicate "fliers" (upper left), "swimmers", lower left, and hoppers (log Koa >~12) (from Wania 2006). Dashed line in B indicates compounds of intermediate to low log Kow and high log Koa identified by Kelly et al (2007b). Lines in C outline the most chemicals that are most bioaccumulative in humans assuming contamination of the marine and agricultural food web.

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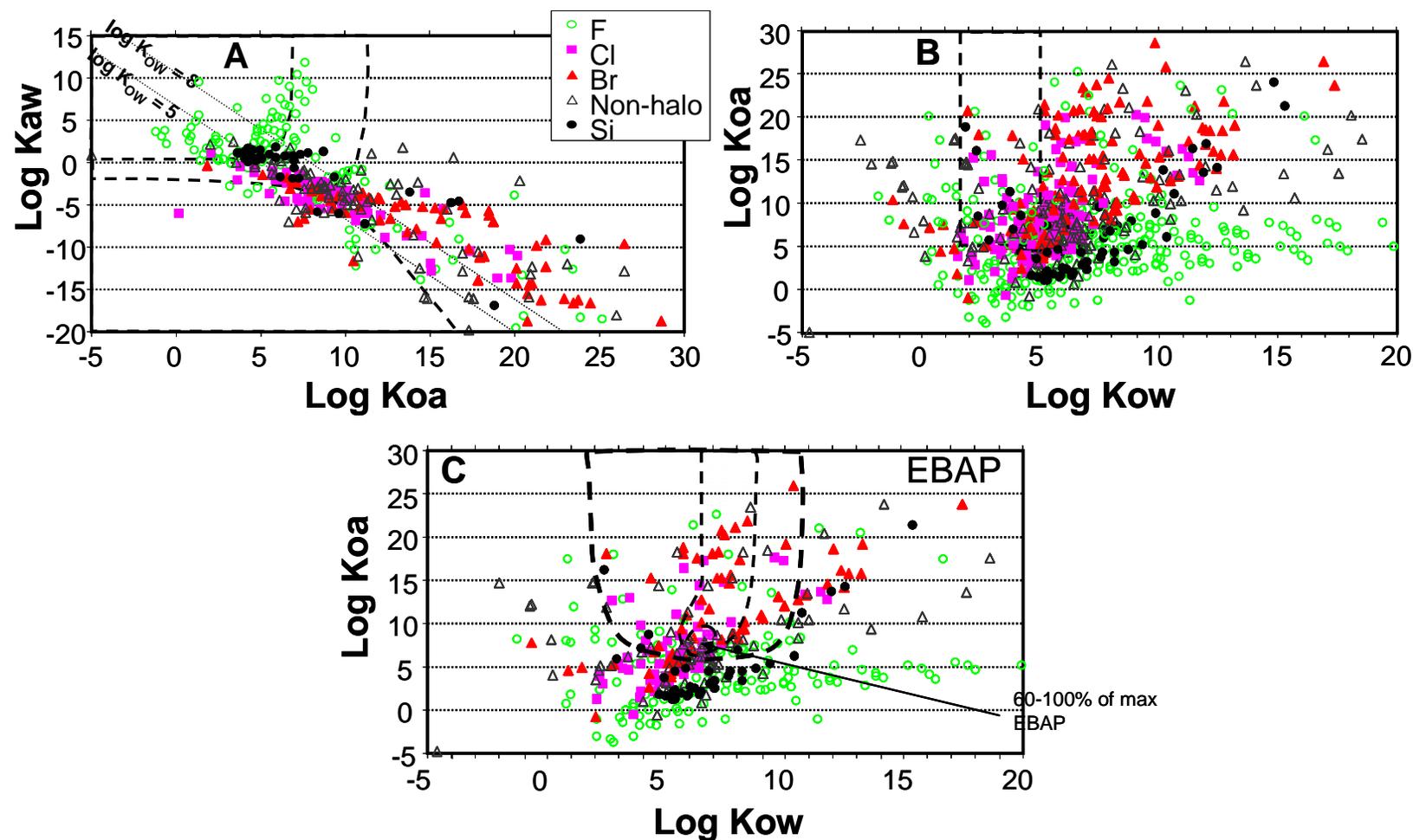
Appendices (available in a separate Excel spreadsheet "EPA Report Table Appendix")

Appendix I. "610 chemicals"
CAS numbers, structures and predicted properties of all 610 chemicals

Appendix II "ECOSAR"
Results for predicted aquatic toxicity for all 610 chemicals.

Appendix III "Brown and Wania"
List of 24 compounds identified with Persistence, Bioaccumulation and long range transport potential that were not identified in this study