

Organic Contaminants of Emerging Concern in the Lake Champlain Basin: A Review of Current Knowledge, 2016

December 2016

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For:

The Lake Champlain Basin Program and
New England Interstate Water Pollution Control Commission

This report was funded and prepared under the authority of the Lake Champlain Special Designation Act of 1990, P.L. 101-596 and subsequent reauthorization in 2002 as the Daniel Patrick Moynihan Lake Champlain Basin Program Act, H. R. 1070, through the US EPA. Publication of this report does not signify that the contents necessarily reflect the views of the states of New York and Vermont, the Lake Champlain Basin Program, or the US EPA.

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December 29, 2016

Lake Champlain Basin Program Technical Report # 99.
<http://www.lcbp.org/media-center/publications-library/technical-reports/>

Funded by Lake Champlain Basin Program and NEWIPCC

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EXECUTIVE SUMMARY:

In recent years there has been increasing concern nationwide about the amount of unregulated organic pollutants entering surface waters from storm drains, wastewater treatment facilities (WWTFs), and agricultural activities. The presence, environmental fate, and effects of these Organic Contaminants of Emerging Concern (OCECs), have started to receive widespread attention in the Great Lakes, the Chesapeake Basin and elsewhere across the country. In the Lake Champlain Basin of Vermont, New York, and Québec, there have been several investigations of OCECs in the last 20-30 years. This report seeks to bring all of this information together in one place as a starting point for determining gaps in our knowledge as well as future research and management needs. The emphasis is on reporting the presence, extent, and sources of anthropogenic organic contaminants present in the water column of the Lake Champlain Basin. Summarizing effects on the people and biota of the Champlain Basin is beyond the scope of this work. Whenever possible, raw data is included in this report so that the reader can see exactly what data exists, what is missing, and draw their own conclusions about future needs.

Data is presented on pesticides, industrial wastewater contaminants, hormones, pharmaceuticals, and personal care products found in surface water, drinking water, Wastewater Treatment Facility inputs and effluents. Data has been supplied by state, provincial, university and federal researchers for research projects both recently completed and still on-going.

The Vermont Department of Environmental Conservation (VTDEC) undertook the first targeted study of OCECs in The Lake Champlain Basin in 2002, investigating six reproductive hormones and suspected endocrine disrupters in WWTF effluent. Triclocarban and 4-nonylphenol were found in all effluents, with the other four compounds detected in most samples, at low ng/L levels. The VTDEC followed up with a study in 2008 targeting WWTF effluent within the Winooski River Basin. The Essex facility dominated detections in this study, with higher levels of: triclosan, 5-methyl-1H-benzotriazole, phenol, tributylphosphate, DEET, several phenolic surfactant metabolites, triethyl citrate, and bisphenol A. These studies demonstrate that some OCECs are not being effectively removed by our WWTFs and are therefore entering our surface waters on a routine basis.

U.S. Geological Survey (USGS) and University of Vermont (UVM) researchers have investigated various OCECs and other wastewater pollutants entering and leaving WWTFs in the Champlain Basin, concentrating primarily on Burlington, Vermont. They have found that for pollutants effectively removed by the treatment process, the major sources to Lake Champlain are leaking pipes and sewage which bypasses the plant during large storm events when the

facility is over capacity (Combined Sewer Overflows, or CSOs). For those pollutants not effectively removed by the treatment process, the bulk enters the lake with effluent from routine daily operation. Therefore, for municipalities with significant amounts of leaking pipes or CSOs, even compounds well removed by the WWTF may be entering our surface waters in significant amounts. In a nationwide study, The Water Environment Research Foundation has found that in general, increasing residence time of influent in a treatment plant leads to increased removal of most OCECs.

The Vermont Agency of Agriculture, Food and Markets (VAAFM) initiated surface water monitoring for pesticides within the Champlain Basin in 2001. Targeted studies have included runoff from golf courses, railroad beds, corn fields, and tile drains into ditches, streams, and rivers, as well as ambient levels in the lake itself. These studies found that atrazine, metolachlor, and their degradates are ubiquitous in our surface waters from corn herbicide use; golf course fungicide runoff can be significant if rainstorms occur in the late fall; rail yards with multiple tracks appear to be sources of significant herbicides to nearby surface waters; and tile drainage may be a large source of herbicides and insecticides from corn fields. Pesticide concentrations were approaching or exceeding levels of concern to aquatic biota during storm events in: urban runoff, small water bodies next to railroad rights-of-way, golf course runoff in late fall, and small streams in highly agricultural areas receiving tile drain effluent. Because of their high water solubility, persistence, toxicity to aquatic insects, and rapid increase in use, neonicotinoid insecticides warrant special attention and concern.

There are twenty community/municipal water systems in New York, Québec, and Vermont which have as their source the waters of Lake Champlain. These systems supply drinking water to many of the cities along the shores of Lake Champlain such as: Rouses Point, Willsboro, and Port Kent in New York, Bedford and Philipsburg in Québec, and Burlington, Saint Albans, and Vergennes in Vermont. Therefore, the OCECs entering our surface waters from WWTF effluent, leaking sewer pipes, as well as urban and agricultural runoff are potentially ending up in the drinking water of basin residents.

Finally, a scoping process is outlined with the goal of producing prioritized lists of compounds of concern within the water, sediment and biota of the Champlain basin and leading to development of a long-term monitoring program for OCECs in the basin. The scoping process would be coordinated by the LCBP Toxics Workgroup, and would include a one day conference bringing together researchers, regulators, and other interested parties to review current knowledge and prioritize areas of concern in water, sediment, and biota. Results from this conference would be developed by the Toxics Workgroup into proposals to fill data gaps in specific environmental compartments, narrow down the scope of any proposed monitoring efforts, and propose a sustainable long-term monitoring program for OCECs in water, sediment, and biota of the Lake Champlain Basin.

INTRODUCTION:

In recent years there has been increasing concern nationwide about the amount of unregulated organic pollutants entering surface waters from storm drains, wastewater treatment facilities (WWTFs), and agricultural activities. The presence, environmental fate, and effects of these Organic Contaminants of Emerging Concern (OCECs) have received widespread attention in the Great Lakes, the Chesapeake Basin and elsewhere across the country. In the Lake Champlain Basin of Vermont, New York, and Québec, there have been several investigations of certain classes of OCECs in the last 20 years or so. This report seeks to bring all of this information together into a synoptic review in order to determine if there are gaps in our knowledge. The emphasis of this report is on the presence, extent, and sources of anthropogenic organic contaminants present in the water column of the Lake Champlain Basin. For many OCECs found at trace levels in surface waters, little is known as to whether the concentrations found have effects on fish, insects, plants or microbial life in the receiving waters. The emphasis of this report is presence/absence, not effects on the

biota. Whenever possible, raw data is included in this report so that the reader can see exactly what data exists, what is missing, and draw his or her own conclusions about future needs.

This report is divided into four sections. The first section describes the characteristics of the Lake Champlain Basin, and likely sources of OCECs in the basin. The second section gives background information on the emerging contaminant problem, and major groups of OCECs as investigated worldwide. The third section summarizes what we know about OCECs in the Lake Champlain Basin (LCB) and what gaps there are in our current knowledge. The final section will discuss efforts of prioritization and a suggested scoping process for prioritizing which gaps in our knowledge are of most concern, if and how to move forward on collecting data to fill these gaps.

1.0 THE LAKE CHAMPLAIN BASIN and LAKE CHAMPLAIN BASIN PROGRAM.

Lake Champlain is a large lake forming much of the boundary between New York and Vermont, and extending into Québec, Canada. It is approximately 120 miles long and 12 miles wide at the widest. It is up to 400 feet deep and the flow of water is south to north to the Richelieu River which flows to the St. Lawrence River in Canada. The lake contains approximately 6.8 trillion gallons of water, but has a residence time of less than three years, so water soluble pollutants are not likely to accumulate. With an area of 435 square miles and a drainage basin of approximately 8,234 square miles Lake Champlain has a very large drainage basin for its size. Fifty-six percent of the basin is in Vermont, 37% in New York, and 7% in Québec. About 570,000 people live within the basin, about 200,000 of whom use the lake as source of their drinking water (1).

Because Lake Champlain falls under the jurisdiction of New York, Québec, and Vermont, a joint management plan has been negotiated between these three governments, with the assistance of the U.S.E.P.A. and the New England Interstate Water Pollution Control Commission. The Lake Champlain Basin Program (LCBP) was created in 1990 to administer this management plan (2), which is entitled “OPPORTUNITIES FOR ACTION” (OFA). OFA was updated most recently in 2010 and can be found on the LCBP website: <http://plan.lcbp.org/>. This plan contains eight goals for maintaining and improving water quality and natural and cultural resources. One of these goals is to: “Reduce contaminants that pose a risk to public health and the Lake Champlain ecosystem”. This chapter of the OFA discusses both manmade and natural contaminants which may pose a risk to the Lake Champlain ecosystem. Included in this are inorganic contaminants such as mercury and road salt, as well as natural organic contaminants such as cyanobacterial toxins. A major emphasis is on organic compounds currently in common use and termed in OFA as “new generation contaminants”. Generally included in this category are: pharmaceuticals, natural and synthetic hormones, pesticides, personal care products, plasticizers, surfactants, and various other organic compounds in current use by humans which are unregulated or poorly regulated.

As part of the 2010 revision of OFA, a LCBP Toxics Management Workgroup was tasked with developing a Lake Champlain Toxics Management Strategy (3). This document was completed and published in September 2012 and is available here: http://www.lcbp.org/wp-content/uploads/2012/11/69_Toxics_Strategy_September2012.pdf This strategy is based on The Precautionary Principle, defined as: “...when there are suspected health or environmental concerns, preventative actions should be taken even when there is not a scientific certainty that harm will ensue.” The Toxics Management Strategy discusses general classes of toxins such as: pesticides, mercury, PCBs and dioxins, cyanotoxins, road salt, minerals, as well as pharmaceuticals and personal care products (PPCPs). The management strategy also discusses possible areas for research, management, and minimization of toxins in the basin. One goal of the strategy is to develop a list of PPCP compounds of concern to aid in identifying and prioritizing management and reduction strategies. This paper is a first step in creating a prioritized list of OCECs in need of more research or use minimization strategies.

OCECs are of primary concern to people if they are found in our drinking water while the major concern for aquatic life is in WWTF effluent. The following Vermont drinking water facilities get their raw source water from Lake Champlain:

ALBURGH VILLAGE WATER SYSTEM

ALLEN POINT WATER SYSTEM

BURLINGTON DEPT PUBLIC WORKS WATER DIV

CHAMPLAIN WATER DISTRICT (South Burlington, Jericho, Shelburne, etc.)

COOPERS MHP
GRAND ISLE CONSOLIDATED WATER DISTRICT
GRAND ISLE FIRE DISTRICT 4
NORTH HERO WATER SYSTEM
SOUTH HERO FIRE DISTRICT 4
ST ALBANS WATER DEPT
SWANTON VILLAGE WATER
TRI TOWN WATER DISTRICT
VERGENNES PANTON WATER DISTRICT
WEST WIND WATER SYSTEM

In New York the following communities get their water from Lake Champlain:

PORT KENT W.D.
ESSEX W.D.
WILLSBORO W.D.
CRATER CLUB WATER SUPPLY
ROUSES POINT VILLAGE W.D.

In Québec, the only community water supply using Lake Champlain as its water source is Bedford/Philipsburg on Missisquoi Bay.

Because these drinking water facilities get their source water from Lake Champlain, if there are OCECs in the source water, it is possible that they will end up being ingested by people. Wastewater Treatment Facilities which empty into the Lake Champlain Basin in Vermont are listed in the next section.

1.1 SOURCES of OCECs:

There are three major modes of entry of OCECs which end up in the surface waters of the Champlain Basin. These sources are: urban storm water runoff, WWTF effluent and sludge, and runoff from agricultural lands and other rural areas where pesticides or manure are applied. Each source has a different suite of characteristic contaminants, so it is often possible to predict, at least generally, what the source is from the pattern of detections in a given water body, as described below.

Urban runoff: Runoff from lawns, parking lots, roofs, and other surfaces to ditches, streams or storm drains is a major source of anthropogenic pollution to our lakes and rivers. Lawn care pesticides as well as gas, oil, antifreeze or other transportation related chemicals are examples of OCECs with an urban source. A recent example of concern with respect to urban runoff has been the use of pavement sealers on driveways and parking lots. In areas where coal tar based sealants are being used, concentrations of polycyclic aromatic hydrocarbons (PAHs) entering urban stream water and sediments are up to 1000 times higher than untreated pavement, and still ten times higher after five years (4). Urban runoff of this sort ends up in storm drains, ditches, and streams and eventually reaches the water and sediment of rivers and lakes. In some cities, a portion of the water from storm drains is channeled into WWTF where the OCECs are either degraded, removed with the sludge, or pass through to enter our surface waters. Characteristic urban runoff pollutants include: heavy metals and hydrocarbons from motor vehicle use, PAHs from pavement sealants and other sources, and pesticides and nutrients from lawn care pesticide and fertilizer use.

Wastewater Treatment Facilities (WWTFs): WWTFs in urban areas or from manufacturing facilities treat whatever goes down the drain. These facilities are designed to remove solids and nutrients from the waste stream and disinfect the treated water before it enters the environment. They are generally not designed or optimized for the removal of OCECs from the waste stream (42, 43). In some areas, these facilities also treat water from storm drains. Generally those pollutants which are not very water soluble will be either broken down by the bacteria in the WWTF or removed with the solids during the treatment process. If pollutants are water soluble and not easily broken down by the bacteria in the WWTF they will tend to pass through the WWTF and end up in our surface waters with the treated effluent. Pharmaceuticals are a class of OCEC of major concern because they are often not totally metabolized by the

person consuming them, leading to significant amounts of medicines being excreted and flushed. Soaps, detergents, fabric softeners, whiteners, antimicrobials and any other similar products used around the house/office/store/factory in an urban environment also go down the drain and end up at the WWTF. Again, some of these will be broken down or removed from the waste stream within the WWTF, but others will still be present in the water leaving the facility (effluent). Some urban areas have combined wastewater and storm water treatment facilities which treat storm water thru WWTFs before releasing it to surface waters. This helps to remove some of the pollutants from the above urban runoff category mentioned above. Unfortunately, these systems can periodically overflow if large rain events overwhelm capacity, allowing untreated storm water AND wastewater to be released into surface waters. These are termed Combined Sewer Overflows (CSOs). There are 96 WWTFs in the Champlain Basin: 60 in Vermont, 29 in New York, and 12 in Québec.

Non-Point Source Runoff: Water flowing off of agricultural fields, golf courses, rural lawns, and other areas where pesticides are intentionally applied over large areas can be a significant source of pesticides (as well as nutrients) into our surface waters after rain events. These are especially difficult to quantify or regulate because the source is not a specific stream, storm drain or WWTF, but dispersed runoff from large areas. Runoff from these sources can carry significant amounts of OCECs if a rain event occurs shortly after a pesticide, fertilizer or manure application. OCECs may enter streams, ditches, rivers, and lakes along with eroded soil, dissolved in water flowing over the ground, from shallow ground water, or as aerosol drift during pesticide applications.

In general, small streams receiving runoff will be exposed to short term, relatively high concentration spikes of pollutants after rain events, while bigger rivers will contain prolonged waves of contaminants at lower concentrations. Therefore, small streams are more likely to see contaminants at acutely toxic levels while larger rivers will be subject to extended periods of chronic concentrations of toxins.

2. ORGANIC CONTAMINANTS OF EMERGING CONCERN IN THE AQUATIC ENVIRONMENT

Everything a modern person does, from eating and drinking to driving to work or reading the newspaper has impacts on the environment around us. Energy is used, and waste products are generated. Much of what we consume, whether it be food or water or medicines, passes through our bodies un-metabolized. Many of the home care products we use such as soaps, detergents, perfumes and deodorants, etc. end up washing down the drain. Clothing and other products that we buy may be treated with preservatives, anti-microbials, stain repellants and more. It is becoming clear that many of these chemicals do not disappear after performing their intended function, but remain in the environment for extended periods with unknown, unintended consequences. Once OCECs reach the environment, they may be broken down rapidly in sunlight or by bacteria, may not be water soluble and therefore sorb onto soils, sediments, or other solids, may be volatilized and end up in the air, or may be water soluble and persistent enough for them to be found in our surface waters. These last are the emphasis of this report.

Until recently, regulatory concern has dealt with those environmental pollutants which survive for long in the environment and are termed “persistent organic pollutants” (POPs) such as DDT, PCBs, and other chlorinated compounds. Many of the modern OCECs break down fairly quickly in the environment so they do not meet the traditional definition of “persistent”. But, if they are entering the environment at a relatively constant rate, as with WWTF effluent, then they may have similar effects on the biota as persistent pollutants. This chronic, low level exposure may lead to gradual ecosystem change at a rate which is undetectable.

In the last thirty years or so, as our ability to analyze for trace organic contaminants has improved, researchers are discovering many of these man-made compounds at low levels in our surface and ground water and in the air. This report will concentrate on those current use organic contaminants (OCECs) which tend to stay in the water column of our surface waters. In many cases our ability to detect these OCECs has far outstripped our ability to determine whether these compounds are having any effect on the biota at the detected concentrations. Traditional toxicity tests have been designed to find the concentration where a compound is acutely or chronically toxic to an individual species (LC50, LD50, EC50, etc.). Often the environmental concentration of these trace OCECs are orders of magnitude lower than the

laboratory determined acute or chronic toxicity, so it is extremely difficult to determine or predict possible effects. Pharmaceuticals and pesticides though, as well as some other OCECs, are designed to be biologically active, so they are likely to have effects on biota at far lower concentrations than toxic levels. In addition, toxicity tests are only performed on a fairly narrow range of species which it is hoped are representative, but they are not necessarily the most sensitive species in a given area. Also, food chain and other subtle ecological effects are often beyond our current ability to understand. Therefore, for the purposes of this paper, emphasis will be on what is being detected in our surface waters. This paper is not intended to be a review of ecotoxicology of OCECs, but simply a compilation of the current information on levels of OCECs in the Champlain Basin.

The following is a listing of several of the standards, guidelines, etc. that have been developed to guide decision makers as to whether pollutant concentrations are a concern. Unfortunately, for most pesticides and other OCECs, there are no regulatory limits or guidelines on allowable concentrations in surface waters, wastewater, or even drinking water.

The USEPA has developed enforceable standards for allowable levels of various contaminants in drinking water which can be found here: <https://www.epa.gov/ground-water-and-drinking-water/table-regulated-drinking-water-contaminants#Organic>

USEPA also has Human Health Benchmarks for Pesticides at: <https://iaspub.epa.gov/apex/pesticides/f?p=HHBP:HOME:1180984486989711> These are not enforceable standards but drinking water values below which there is not likely to be human harm.

In 2008, the USEPA produced a white paper explaining how to develop an Aquatic Life Criterion for emerging contaminants (B). USEPA Aquatic Life Criteria can be found at <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table> These numbers can be used by states to create enforceable concentration standards.

EPA has also developed Aquatic Life Benchmarks for pesticides, which are guidelines to be used to decide if a water body area needs more investigation:

<https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration>

The Canadian Council of Ministers of the Environment has created Canadian Environmental Quality Guidelines at: <http://st-ts.ccme.ca/en/index.html> which may be used by provinces to develop enforceable standards.

Summarizing what we know about the environmental chemistry and fate of OCECs is complicated by the fact that there is a large variety of sources and chemistries involved. A brief amount of background on sources and classes of contaminants follows with references for further information.

2.1. PESTICIDES:

Pesticides are used to kill plants, insects and other animals, fungi, and bacteria, and as such are used in the home, in industry as well as urban, rural, and agricultural settings. Agricultural uses of herbicides, fungicides, and insecticides are the major uses which are likely to lead to pesticides getting into our surface waters, although lawn and garden care products washing off into storm drains and urban streams can be a significant source in urban areas (10).

Pesticides in current use in North America are amongst the most well characterized of the OCECs. Pesticide use is highly regulated in the U.S. by the USEPA, and there is a large amount of information on commercial pesticide use in agricultural and urban environments (5). Commercial pesticide use in Vermont can be found at: http://agriculture.vermont.gov/pesticide_regulation/pesticide_usage_reported

Pesticide use data for New York can be found at:

<http://ai.psur.cornell.edu/> or: <http://pmep.cce.cornell.edu/psur/11report.shtml>

A report on pesticide sales in Canada as a whole for 2014 has been produced (6), and information for Québec can be found at: <http://www.mddelcc.gouv.qc.ca/pesticides/bilan/index.htm>.

Regulation of pesticide use generally presumes that if the pesticide is applied properly it will not lead to undue environmental consequences after use. Historically, if a pesticide is used properly, the user or producer is not held

responsible for any environmental effects. An example of the unintentional short-sightedness of this system is the insect repellent DEET. Because this product is used topically, there was no concern when it was registered as to its presence or toxicity in surface waters. Unfortunately, it has been found that DEET washes off of our bodies, survives WWTF treatment, and is ubiquitous in surface waters (38, 39).

In the late 1990's, significant changes occurred in both pesticide usage and our ability to detect trace quantities of organic pollutants in the environment. High Performance Liquid Chromatography paired with Mass Spectrometry as a commercially available analytical tool was introduced in the 1990's, enabling detection of many more organic compounds at very low levels compared to previous environmental analyses, often in the low parts-per-trillion range.

In 1996, the Food Quality Protection Act (FQPA) was signed into law in the U.S. which revamped the regulation of pesticides, requiring EPA to consider children when reviewing pesticide safety, requiring cumulative risk to be evaluated and other issues involved in reviewing and re-registering pesticides. This eventually led to the phase-out of many uses of organophosphate (OP) insecticides and other highly toxic pesticides. Also in the 1990's, crop plants were developed which were genetically modified to be resistant to the herbicide "Roundup" (glyphosate). This led to a gradual change in herbicide use, from atrazine being the most popular agricultural herbicide in the 1990's to glyphosate now being the dominant herbicide worldwide (5).

Major concern over the past 40 years has concentrated on insecticides because of their widespread toxicity and the secondary effects of organochlorine insecticides on birds. Insecticide chemistry has changed from organochlorine insecticides in the 1960's designed to be very potent and persistent, to organophosphate insecticides in the 1980's, with broad range toxicity but designed to break down relatively quickly. Organophosphate use declined in the 1990's because of the FQPA, replaced by pyrethroid insecticides which are less toxic to mammals. However, they were found to be persistent in sediment and highly toxic to aquatic insects. In the late 1990's, neonicotinoid insecticides were introduced which were thought to be very specifically toxic to insects and also to break down fairly quickly. Perhaps most importantly, they are systemic insecticides which are potent and persistent enough to be coated on corn and soy seeds at planting yet continue to protect the young plant from insects as it grows. This eliminates the need to spray whole fields with insecticides leading to less "collateral damage" from spray drift. These characteristics made them very popular and effective, so that currently most corn and soy seeds planted in the U.S. are treated with these chemicals. Neonicotinoids (neonics) are now the most widely used insecticides worldwide.

The U.S. Geological Survey (USGS) is one of the major sources of data on the occurrence of pesticides in the surface waters of the U.S. Stone et al. (7) reviewed trends in pesticide occurrences in U.S. rivers from 1992-2011. Corn herbicides such as atrazine and metolachlor, and their metabolites, dominated the detections across urban, agricultural and mixed use watersheds in both the 1990's and 2000's. In the 1990's, 17% of agricultural streams had at least one mean pesticide concentration exceeding a human health benchmark annually, while in the 2000's only atrazine exceeded a human health benchmark in one stream.

Battaglin et al (8) published results of a 2005-2006 USGS investigation into detections of fungicides in soybean growing areas of the U.S. in response to a large increase in fungicide use on soybeans. At least one fungicide was detected in 56% of samples, with azoxystrobin and metalaxyl found most frequently. They concluded that levels detected were at least one order of magnitude below toxicity estimates for aquatic organisms.

Battaglin et al (9) summarized USGS data from 2001 -2010 on the occurrence of glyphosate and its metabolite AMPA. Glyphosate is the active ingredient in the herbicide Roundup™ and its use has increased dramatically worldwide with the introduction of "Roundup Ready" type crops around 2000. Glyphosate was found in approximately 50% of all water samples from streams and rivers, while AMPA was found in excess of 70% of stream and river samples. Maximum concentrations of both glyphosate and AMPA were found in ditches and tile drains at about 400 µg/L, but still significantly below accepted human (700 µg/L) or aquatic life health criteria (1800 µg/L chronic fish benchmark).

In 1999, Lee & Lee (10) found the majority of toxicity in urban California streams was due to structural pest control (termites and ants) and lawn care uses of diazinon and chlorpyrifos (organophosphates). Also in 1999, USGS (11) found atrazine, simazine, and metolachlor to be the most commonly found herbicides across the country for all land uses. Diazinon, carbaryl, and chlorpyrifos were the dominant insecticide detections, primarily in urban areas. They concluded that atrazine and metolachlor are signature pesticides for corn based agriculture, while diazinon, carbaryl, chlorpyrifos and malathion act as signature group for urban pesticide use. Six pesticides, two herbicides and four

insecticides, were found to exceed chronic aquatic life criteria at ten or more sites so these were of special concern. These were: atrazine, cyanazine, azinphos methyl, chlorpyrifos, diazinon, and malathion.

In 2009, the USGS surveyed pyrethroid insecticide concentrations across the U.S. and found bifenthrin and permethrin to be the dominant detections in both urban and agricultural areas. Cyfluthrin and cypermethrin were detected only in urban areas. Pyrethroid insecticides are essentially not water soluble so they adhere to soil/sediment particles where they may cause toxicity to aquatic invertebrates. Most of the (theoretical) toxicity in this study was associated with urban samples containing cypermethrin and or bifenthrin (12).

By the early 2000's, researchers started to look for and find neonicotinoid insecticides, the new class of systemic insecticides. It was found that these compounds are highly water soluble, somewhat persistent in aquatic environments and highly toxic to aquatic insects. Already by 2000 concerns were being raised about neonic toxicity to honeybees and other pollinators (13). Because these pesticides are systemic, it has been found that they translocate to all tissue of treated plants, including pollen, nectar, and guttation fluid at potentially toxic levels. The European Union has had restrictions or bans on neonicotinoids starting in 2008 because of concerns to pollinators. In Holland, widespread contamination of surface waters were found in the 2000's due to the high solubility and persistence of neonics in waters (14). Imidacloprid (the most commonly used neonic) was the pesticide which exceeded regulatory levels most in Holland in 2003-2004 (15).

Because of the persistence, water solubility, and toxicity of neonicotinoids, the USGS has been monitoring surface waters extensively for them since 2013 (16) when they surveyed streams in high corn and soybean growing areas of Iowa. Clothianidin, imidacloprid, and thiamethoxam were detected most frequently, with clothianidin being detected in 75% of samples at levels up to 257 ng/L (0.257 µg/L or ppb). These are the neonicotinoid insecticides primarily used to treat seed corn. Neonics were frequently detected at low levels prior to planting in 2013, indicating persistence from the previous year's uses. The USEPA has set chronic invertebrate aquatic life benchmarks for imidacloprid (1050 ng/L) and clothianidin (1100 ng/L). The EU suggests (17) a chronic level of concern at 200 ng/L for imidacloprid, and Canada has an interim level of 230 ng/L, both in the neighborhood of levels found in this USGS study (16). The authors were especially concerned because neonics all bind to the same target receptor in insects and therefore may act cumulatively and also bind irreversibly so toxicity may be cumulative over time.

As a follow-up, the USGS undertook a nationwide survey for neonics in 2012-2014 (18). Included in this study were the following targeted projects: agricultural streams during rain events, urban streams randomly over time, and a WWTF affected stream. In the nationwide survey, clothianidin and thiamethoxam were primarily associated with agriculture while imidacloprid was primarily urban. Total (combined) neonic levels reached a maximum of 450 ng/L. Maximum stream concentration during high flow storm events in agricultural areas were similar to (16), even though flow was much higher, so concentrations were similar but load was much higher in (18). When looking at urban streams, imidacloprid was the dominant neonic, found in 87% of samples with no relationship between concentration and flow. The WWTF portion of this study looked at neonic concentrations above and below a WWTF outflow and found only clothianidin and imidacloprid. Again, because clothianidin had an agricultural source, it was detected both above and below the WWTF while imidacloprid was primarily found in the WWTF effluent and below. There was no detectable degradation of neonics for 2.9 km below the plant. These studies indicate that neonics persist in the environment for extended times at levels close to those which are toxic to aquatic insects.

Numerous studies in the past several years have investigated neonic levels in various environments such as: soils, (19), wetlands (20), puddles (21), stream sediment (22), and honey, pollen, wax, and honeybees (23). Neonics have been found to be toxic to various vertebrate wildlife (24), honeybee (25, 26), and aquatic invertebrate (27) species. Recent papers have also reviewed environmental fate (28) and neonic effects on ecosystem health (29, 30, and 31). Kreutzweiser et al (32) described research which demonstrated that leaves from neonic treated trees may be degraded more slowly by both earthworms and aquatic insects. Morrissey et al. (30) reviewed aquatic invertebrate toxicity data and conclude that Ephemeroptera, Trichoptera and Diptera are the most sensitive groups of aquatic insects to neonics. They also conclude that long term chronic effect thresholds for aquatic environments should be in the range of 0.035 µg/L (35 ng/L) to protect aquatic communities, and that 74% of studies reviewed had average concentrations exceeding this value.

All of this demonstrates that the neonicotinoid pesticides as a group are being extensively studied and are of great concern from the perspective of toxicity to pollinators in the terrestrial environment and aquatic invertebrates/insects in the aquatic environment. Imidacloprid is used extensively for lawn care insect control so is

likely to be found in CSOs and urban streams, while thiamethoxam and clothianidin are currently used as seed treatment for corn and soy seeds so likely to be found in rural, agricultural runoff.

2.2. PHARMACEUTICALS, PERSONAL CARE PRODUCTS, NATURAL HORMONES, and INDUSTRIAL CHEMICALS:

Starting in the late 1990s, concern has been increasing about trace levels of pharmaceuticals, personal care products, and natural human hormones (estrogens and testosterone), entering our surface waters, primarily from WWTFs. The book “Our Stolen Future” (33), published in 1996, raised awareness about the endocrine disrupting potential of many common products. In 1999, the NRC was commissioned to summarize current knowledge on endocrine disrupters in “Hormonally Active Agents in the Environment” (34). This extensive report, which looked at evidence for environmental endocrine disrupting effects on biota, dealt primarily with older legacy compounds such as DDT, PCBs, and dioxin-like compounds. Much of the recent research effort has been concentrated on characterizing what is entering and leaving our WWTFs and what makes it into our drinking water. General categories of organic contaminants which researchers are concerned about include: prescription and non-prescription pharmaceuticals, detergents, sunscreens, fragrances, pesticides, human reproductive hormones, flame retardants, and plant and animal steroids. Within these categories, the chemistry of the compounds differs greatly, so it is not possible to generalize on the fate or toxicity at the category level. Also, many recent investigations have tried to target as many of these types of chemicals at once as possible, so analyte lists often contain 100-300 compounds with highly varied chemical characteristics, uses and sources.

Pharmaceuticals: chemicals/medicines (prescription and not) intended to be ingested, by people (or their pets/livestock) for health benefits. These PPCPs are of especial concern because they are designed, produced, and marketed to have biological activity. Natural human estrogens such as 17 β -estradiol (E2) and synthetic estrogens used for birth control such as 17 α -ethinylestradiol (EE2) and their degradation products are of the greatest concern because of their known endocrine activity, but many medicinals also have known or suspected endocrine disrupting potential. Fish with skewed sex ratios downstream of WWTF outfalls have been attributed to estrogens and estrogen-like compounds (35). Antidepressants are another class of pharmaceutical of serious concern because they can disrupt hormone transmission in aquatic organisms (36).

Personal Care Products: PCPs are chemicals intended for use on a body or in the household, but generally not ingested. General categories include: antimicrobials, detergents and surfactants, synthetic musks, plus miscellaneous compounds. Because of the wide range of chemistries involved, it is not possible to generalize on the fate of PCPs, but the major source to the aquatic environment is through WWTF effluent or CSOs.

Antimicrobials: Antimicrobials used in personal care products such as soaps, lotions, and even toothpastes, have been of increasing concern because of their possible contribution to antibiotic resistance in bacteria, as well as their questionable effectiveness. The major antimicrobials currently on the market are Triclosan and Triclocarban. The U.S. Food and Drug Administration (USFDA) has recently announced the phase-out of antimicrobial products for homeowner use by 2017 (37).

Detergents and Surfactants: Detergents and surfactants are of significant concern because they are ubiquitous, highly water soluble, and some can act as endocrine disrupters. Nonylphenolethoxylates are common detergents which break down into the endocrine disrupter nonylphenol. Polyethoxylated tallowamine is a surfactant used in some pesticide products and is toxic to some aquatic organisms, such as amphibians.

Synthetic Musks: Used as fragrances in many personal care products. The polycyclic musks Galaxolide (HHCb) and Tonalide (AHTN) are persistent, bioaccumulate, and possibly toxic. These compounds are hydrophobic and tend to sorb to biosolids in WWTFs and/or sediments downstream of WWTF outfall.

Miscellaneous: *N,N*-diethyltoluamide (DEET) is a widely used insect repellent which is applied topically and is often found in WWTF influent and effluent (38). Not well removed by WWTFs, DEET is found in surface waters worldwide, but toxicity to aquatic life does not seem to be a large concern at environmental concentrations (39). Caffeine, nicotine and their metabolites are also ubiquitous in WWTF influent and effluent and are often used as indicators of the presence of effluent-impacted waters. Other compounds which do not seem to be of toxicological

concern but can be used as indicators include artificial sweeteners such as sucralose (Splenda®) and whiteners added to laundry soaps.

Industrial Chemicals: These chemicals are used primarily in industrial applications, but are also incorporated into products used in the home such as plastics, waterproofed cookware and garments, and flame-resistant cloth. These compounds will most commonly enter the aquatic environment through WWTF effluent or unrecognized industrial sources.

Flame Retardants: Much concern has been raised about the various flame retardants used industrially and in home products. Polybrominated Diphenyl Ethers (PBDEs), as with the synthetic musks, are compounds which bioaccumulate, are persistent, and tend to sorb to biosolids and sediments. Also of concern are the phosphate flame retardants such as: tris(2-chloroethyl) phosphate (TCEP), and tris(1-chloro-2-propyl) phosphate (TCPP).

Perfluorinated Compounds (PFCs): PFCs are used industrially to waterproof products and are used in flame retardants. The most commonly found are: perfluorooctanoic acid (PFOA) which is highly water soluble, and perfluorooctanesulfonic acid (PFOS) which bioaccumulates. Both of these compounds are highly persistent.

Plasticizers: Plastics are ubiquitous in the home, and some of the plastic precursors (plasticizers) enter our waste stream by leaching from plastics or as plastics breakdown. Phthalates and Bisphenol A are the most commonly detected plasticizers and they exhibit endocrine disrupting characteristics.

Pavement sealants, PAHs and other hydrocarbons: A major source of semi-volatile and volatile hydrocarbons in urban storm water runoff is pavement sealants made from coal tar or coal tar pitch. According to the USGS (4), coal tar based sealants predominate in the eastern and southern U.S., while asphalt based sealants dominate use in the western U.S. Polycyclic aromatic hydrocarbons (PAHs) from coal tar sealants end up in the air, soil, sediment, and water as these sealants age. PAHs and other hydrocarbons can also come from automobile tire wear, fossil fuels, and combustion by-products. PAHs in runoff from urban environments end up in settling ponds, streams, storm drains and WWTFs when storm drains enter WWTFs. PAHs are only slightly water soluble, but runoff from freshly sealed pavement is acutely toxic to aquatic organisms. Because PAHs are not very water soluble, much of the PAH load from treated areas ends up in stream and storm water retention pond sediment, as well as WWTF solids.

Plant and Animal Steroids: These include reproductive and other hormones excreted by people and animals, as well as phytoestrogens in foodstuffs. Natural steroids such as phytoestrogens produced by plants are of concern because of their possible estrogenic characteristics in animals. Concentrations of cholesterol, coprostanol, and other fecal sterols from animals have been used primarily to differentiate human from other animal fecal contamination of surface waters. As mentioned above, natural (and synthetic) estrogens are one of the most worrisome PPCPs because they are so biologically active.

In 1999, Daughton and Ternes (40) published an article summarizing work over the previous decade on the various categories of PPCPs, primarily in WWTF effluent. They expressed concern not only for groups such as musk fragrances which are toxic and bioaccumulate, but also over the chronic low level amounts of PPCPs which were starting to be reported in WWTF outflows. Even though these PPCPs are often not persistent like the older legacy organochlorines, they will behave like persistent chemicals as far as effect on aquatic organisms because they are constantly being added to the ecosystem.

In 1999-2000, the USGS undertook the first large scale nationwide stream assessment of modern, current use trace organic pollutants associated with WWTFs and urban runoff (41). Ninety-five compounds including prescription and non-prescription drugs and antibiotics, plasticizers, detergents, and pesticides were analyzed at 139 sites across the U.S. Table 1 is from (41) and it lists the compounds analyzed and their uses, detections, and advisory levels or LC50 for those compounds with data. Most of these compounds did not have acute or chronic aquatic life criteria at the time, and many still don't, so LC50 was included when available.

TABLE 1. Information on WWTF Pollutant Detections in U.S. (41).

chemical (method)	CASRN	RL	freq	max	med	use	MCL or HAL (23) (µg/L)	lowest LC ₅₀ for the most sensitive indicator species (µg/L)/no. of aquatic studies identified (24)	
		N (µg/L)	(%)	(µg/L)	(µg/L)				
Veterinary and Human Antibiotics									
carbodox (1)	6804-07-5	104	0.10	0	ND	ND	antibiotic	-	-/1
chlortetracycline (1)	57-62-5	115	0.05	0	ND	ND	antibiotic	-	88000 ^a /3
chlortetracycline (2)	57-62-5	84	0.10	2.4	0.69	0.42	antibiotic	-	88000 ^a /3
ciprofloxacin (1)	85721-33-1	115	0.02	2.6	0.03	0.02	antibiotic	-	-/0
doxycycline (1)	564-25-0	115	0.1	0	ND	ND	antibiotic	-	-/0
enrofloxacin (1)	93106-60-6	115	0.02	0	ND	ND	antibiotic	-	40 ^b /29
erythromycin-H ₂ O (1)	114-07-8	104	0.05	21.5	1.7	0.1	erythromycin metabolite	-	665000 ^d /35
lincomycin (1)	154-21-2	104	0.05	19.2	0.73	0.06	antibiotic	-	-/0
norfloxacin (1)	70458-96-7	115	0.02	0.9	0.12	0.12	antibiotic	-	-/6
oxytetracycline (1)	79-57-2	115	0.1	0	ND	ND	antibiotic	-	102000 ^a /46
oxytetracycline (2)	79-57-2	84	0.10	1.2	0.34	0.34	antibiotic	-	102000 ^a /46
roxithromycin (1)	80214-83-1	104	0.03	4.8	0.18	0.05	antibiotic	-	-/0
sarafloxacin (1)	98105-99-8	115	0.02	0	ND	ND	antibiotic	-	-/0
sulfachloropyridazine (2)	80-32-0	84	0.05	0	ND	ND	antibiotic	-	-/0
sulfadimethoxine (1)	122-11-2	104	0.05	0	ND	ND	antibiotic	-	-/5
sulfadimethoxine (2)	122-11-2	84	0.05	1.2	0.06	0.06	antibiotic	-	-/5
sulfamerazine (1)	127-79-7	104	0.05	0	ND	ND	antibiotic	-	100000 ^c /17
sulfamerazine (2)	127-79-7	84	0.05	0	ND	ND	antibiotic	-	100000 ^c /17
sulfamethazine (1)	57-68-1	104	0.05	4.8	0.12	0.02	antibiotic	-	100000 ^c 17
sulfamethazine (2)	57-68-1	84	0.05	1.2	0.22	0.22	antibiotic	-	100000 ^c /17
sulfamethizole (1)	144-82-1	104	0.05	1.0	0.13	0.13	antibiotic	-	-/0
sulfamethoxazole (1)	723-46-6	104	0.05	12.5	1.9	0.15	antibiotic	-	-/0
sulfamethoxazole (3)	723-46-6	84	0.023	19.0	0.52	0.066	antibiotic	-	-/0
sulfathiazole (1)	72-14-0	104	0.10	0	ND	ND	antibiotic	-	-/0
sulfathiazole (2)	72-14-0	84	0.05	0	ND	ND	antibiotic	-	-/0
tetracycline (1)	60-54-8	115	0.05	0	ND	ND	antibiotic	-	550000 ^d /3
tetracycline (2)	60-54-8	84	0.10	1.2	0.11	0.11	antibiotic	-	550000 ^d /3
trimethoprim (1)	738-70-5	104	0.03	12.5	0.71	0.15	antibiotic	-	3000 ^c /4
trimethoprim (3)	738-70-5	84	0.014	27.4	0.30	0.013	antibiotic	-	3000 ^c /4
tylosin (1)	1401-69-0	104	0.05	13.5	0.28	0.04	antibiotic	-	-/0
virginiamycin (1)	21411-53-0	104	0.10	0	ND	ND	antibiotic	-	-/0
Prescription Drugs									
albuterol (salbutamol) (3)	18559-94-9	84	0.029	0	ND	ND	antiasthmatic	-	-/0
cimetidine (3)	51481-61-9	84	0.007	9.5	0.58 ^a	0.074 ^a	antacid	-	-/0
codeine (3)	76-57-3	46	0.24	6.5	0.019	0.012	analgesic	-	-/0
codeine (4)	76-57-3	85	0.1	10.6	1.0 ^a	0.2 ^a	analgesic	-	-/0
dehydronifedipine (3)	67035-22-7	84	0.01	14.3	0.03	0.012	antianginal	-	-/0
digoxin (3)	20830-75-5	46	0.26	0	ND ^a	ND ^a	cardiac stimulant	-	10000000 ^a /24
digoxigenin (3)	1672-46-4	84	0.008	0	ND	ND	digoxin metabolite	-	-/0
diltiazem (3)	42399-41-7	84	0.012	13.1	0.049	0.021	antihypertensive	-	-/0
enalaprilat (3)	76420-72-9	84	0.15	1.2	0.046 ^a	0.046 ^a	enalapril maleate (antihypertensive) metabolite	-	-/0
fluoxetine (3)	54910-89-3	84	0.018	1.2	0.012 ^a	0.012 ^a	antidepressant	-	-/0
gemfibrozil (3)	25812-30-0	84	0.015	3.6	0.79	0.048	antihyperlipidemic	-	-/0
metformin (3)	657-24-9	84	0.003	4.8	0.15 ^a	0.11 ^a	antidiabetic	-	-/0
paroxetine metabolite (3)	-	84	0.26	0	ND ^a	ND ^a	paroxetine (antidepressant) metabolite	-	-/0
ranitidine (3)	66357-35-5	84	0.01	1.2	0.01 ^a	0.01 ^a	antacid	-	-/0
warfarin (3)	81-81-2	84	0.001	0	ND	ND	anticoagulant	-	16000 ^c / 33
Nonprescription Drugs									
acetaminophen (3)	103-90-2	84	0.009	23.8	10	0.11	antipyretic	-	6000 ^a / 14
caffeine (3)	58-08-2	84	0.014	61.9	6.0	0.081	stimulant	-	40000 ^b / 77
caffeine (4)	58-08-2	85	0.08	70.6	5.7	0.1	stimulant	-	40000 ^b / 77
cotinine (3)	486-56-6	84	0.023	38.1	0.90	0.024	nicotine metabolite	-	-/0
cotinine (4)	486-56-6	54	0.04	31.5	0.57	0.05	nicotine metabolite	-	-/0
1,7-dimethylxanthine (3)	611-59-6	84	0.018	28.6	3.1 ^a	0.11 ^a	caffeine metabolite	-	-/0
ibuprofen (3)	15687-27-1	84	0.018	9.5	1.0	0.20	antiinflammatory	-	-/0
Other Wastewater-Related Compounds									
1,4-dichlorobenzene (4)	106-46-7	85	0.03	25.9	4.3	0.09	deodorizer	75	1100 ^c /190
2,6-di-tert-butylphenol (4)	128-39-2	85	0.08	3.5	0.11 ^a	0.06 ^a	antioxidant	-	-/2
2,6-di-tert-butyl-1,4-benzoquinone (4)	719-22-2	85	0.10	9.4	0.46	0.13	antioxidant	-	-/0
5-methyl-1H-benzotriazole (4)	136-85-6	54	0.10	31.5	2.4	0.39	anticorrosive	-	-/0
acetophenone (4)	98-86-2	85	0.15	9.4	0.41	0.15	fragrance	-	155000 ^a /21
anthracene (4)	120-12-7	85	0.05	4.7	0.11	0.07	PAH	-	5.4 ^e /188

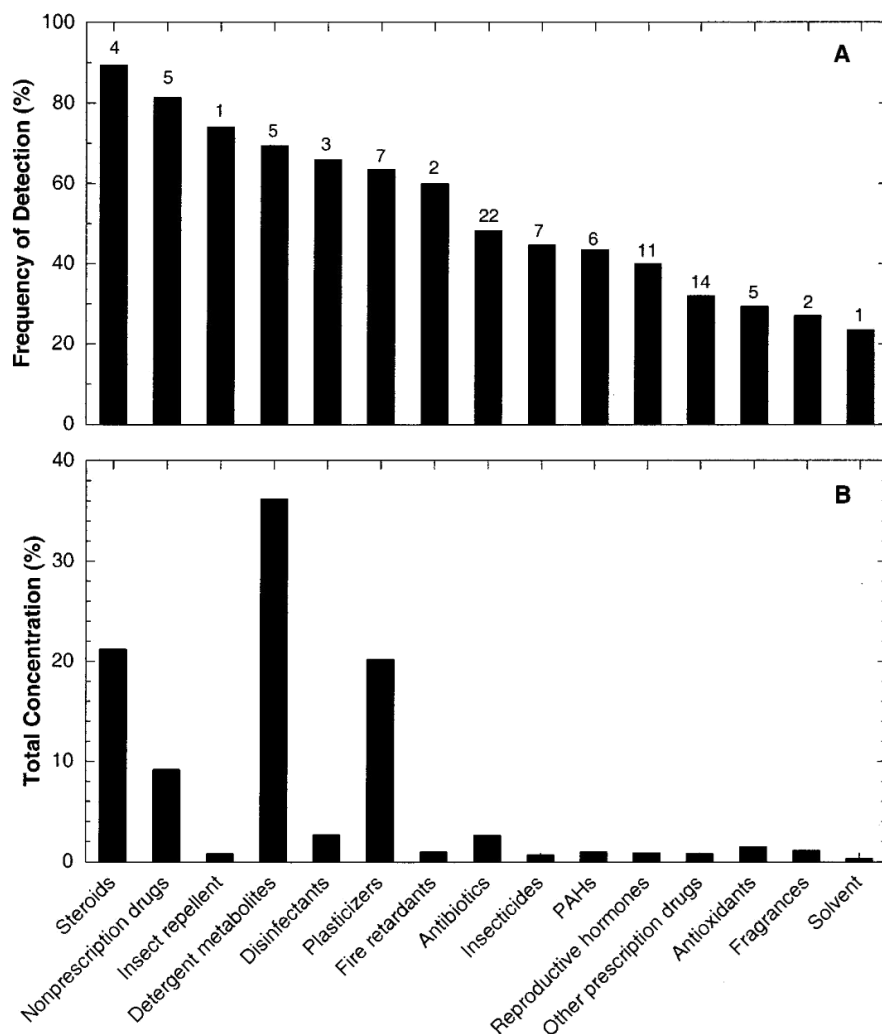
benzo[a]pyrene (4)	50-32-8	85	0.05	9.4	0.24	0.04	PAH	0.2	1.5 ^a /428
3-tert-butyl-4-hydroxy anisole (4)	25013-16-5	85	0.12	2.4	0.2 ^d	0.1 ^d	antioxidant	-	870 ^e /14
butylated hydroxy toluene (4)	128-37-0	85	0.08	2.4	0.1 ^d	0.1 ^d	antioxidant	-	1440 ^a /15
bis(2-ethylhexyl) adipate (4)	103-23-1	85	2.0	3.5	10 ^f	3 ^f	plasticizer	400	480 ^a /9
bis(2-ethylhexyl) phthalate (4)	117-81-7	85	2.5	10.6	20 ^f	7 ^f	plasticizer	6	7500 ^a /309

Other Wastewater-Related Compounds

bisphenol A (4)	80-05-7	85	0.09	41.2	12	0.14	plasticizer	-	3600 ^e /26
carbaryl (4)	63-25-2	85	0.06	16.5	0.1 ^a	0.04 ^a	insecticide	700	0.4 ^a /1541
cis-chlordane (4)	5103-71-9	85	0.04	4.7	0.1	0.02	insecticide	2	7.4 ^e /28
chlorpyrifos (4)	2921-88-2	85	0.02	15.3	0.31	0.06	insecticide	20	0.1 ^a /1794
diazinon (4)	333-41-5	85	0.03	25.9	0.35	0.07	insecticide	0.6	0.56 ^a /1040
dieldrin (4)	60-57-1	85	0.08	4.7	0.21	0.18	insecticide	0.2	2.6 ^c /1540
diethylphthalate (4)	84-66-2	54	0.25	11.1	0.42	0.2	plasticizer	-	12000 ^c /129
ethanol,2-butoxy-phosphate (4)	78-51-3	85	0.2	45.9	6.7	0.51	plasticizer	-	10400 ^e /7
fluoranthene (4)	206-44-0	85	0.03	29.4	1.2	0.04	PAH	-	74 ^e /216
lindane (4)	58-89-9	85	0.05	5.9	0.11	0.02	insecticide	0.2	30 ^c /1979
methyl parathion (4)	298-00-0	85	0.06	1.2	0.01	0.01	insecticide	2	12 ^a /888
4-methyl phenol (4)	106-44-5	85	0.04	24.7	0.54	0.05	disinfectant	-	1400 ^a /74
naphthalene (4)	91-20-3	85	0.02	16.5	0.08	0.02	PAH	20	910 ^c /519
<i>N,N</i> -diethyltoluamide (4)	134-62-3	54	0.04	74.1	1.1	0.06	insect repellent	-	71250 ^c /9
4-nonylphenol (4)	251-545-23	85	0.50	50.6	40 ^g	0.8 ^g	nonionic detergent	-	130 ^e /135
							metabolite		
4-nonylphenol monoethoxylate (4)	-	85	1.0	45.9	20 ^g	1 ^g	nonionic detergent		14450 ^a /4
							metabolite		
4-nonylphenol diethoxylate (4)	-	85	1.1	36.5	9 ^g	1 ^g	nonionic detergent	-	5500 ^a /6
							metabolite		
4-octylphenol monoethoxylate (4)	-	85	0.1	43.5	2 ^g	0.2 ^g	nonionic detergent	-	-/0
							metabolite		
4-octylphenol diethoxylate (4)	-	85	0.2	23.5	1 ^g	0.1 ^g	nonionic detergent	-	-/0
							metabolite		
phenanthrene (4)	85-01-8	85	0.06	11.8	0.53	0.04	PAH	-	590 ^a /192
phenol (4)	108-95-2	85	0.25	8.2	1.3 ^f	0.7 ^f	disinfectant	400	4000 ^c /2085
phthalic anhydride (4)	85-44-9	85	0.25	17.6	1 ^f	0.7 ^f	plastic manufacturing	-	40400 ^c /5
pyrene (4)	129-00-0	85	0.03	28.2	0.84	0.05	PAH	-	90.9 ^a /112
tetrachloroethylene (4)	127-18-4	85	0.03	23.5	0.70 ^a	0.07 ^a	solvent, degreaser	5	4680 ^c /147
triclosan (4)	3380-34-5	85	0.05	57.6	2.3	0.14	antimicrobial	-	180 ^e /3
							disinfectant		
tri(2-chloroethyl) phosphate (4)	115-96-8	85	0.04	57.6	0.54	0.1	fire retardant	-	66000 ^b /8
tri(dichlorisopropyl) phosphate (4)	13674-87-8	85	0.1	12.9	0.16	0.1	fire retardant	-	3600 ^e /9
triphenyl phosphate (4)	115-86-6	85	0.1	14.1	0.22	0.04	plasticizer	-	280 ^c /66
Steroids and Hormones									
cis-androsterone (5)	53-41-8	70	0.005	14.3	0.214	0.017	urinary steroid	-	-/0
cholesterol (4)	57-88-5	85	1.5	55.3	10 ^a	1 ^a	plant/animal steroid	-	-/0
cholesterol (5)	57-88-5	70	0.005	84.3	60 ⁿ	0.83	plant/animal steroid	-	-/0
coprostanol (4)	360-68-9	85	0.6	35.3	9.8 ^a	0.70 ^a	fecal steroid	-	-/0
coprostanol (5)	360-68-9	70	0.005	85.7	150 ⁿ	0.088	fecal steroid	-	-/0
equilenin (5)	517-09-9	70	0.005	2.8	0.278	0.14	estrogen replacement	-	-/0
equilin (5)	474-86-2	70	0.005	1.4	0.147	0.147	estrogen replacement	-	-/0
17α-ethynyl estradiol (5)	57-63-6	70	0.005	15.7	0.831	0.073	ovulation inhibitor	-	-/22
17α-estradiol (5)	57-91-0	70	0.005	5.7	0.074	0.03	reproductive hormone	-	-/0
17β-estradiol (4)	50-28-2	85	0.5	10.6	0.2 ^a	0.16 ^a	reproductive hormone	-	-/0
17β-estradiol (5)	50-28-2	70	0.005	10.0	0.093	0.009	reproductive hormone	-	-/0
estriol (5)	50-27-1	70	0.005	21.4	0.051	0.019	reproductive hormone	-	-/0
estrone (5)	53-16-7	70	0.005	7.1	0.112	0.027	reproductive hormone	-	-/11
mestranol (5)	72-33-3	70	0.005	10.0	0.407	0.074	ovulation inhibitor	-	-/0
19-norethisterone (5)	68-22-4	70	0.005	12.8	0.872	0.048	ovulation inhibitor	-	-/0
progesterone (5)	57-83-0	70	0.005	4.3	0.199	0.11	reproductive hormone	-	-/0
stigmastanol (4)	19466-47-8	54	2.0	5.6	4 ^a	2 ^a	plant steroid	-	-/0
testosterone (5)	58-22-0	70	0.005	2.8	0.214	0.116	reproductive hormone	-	-/4

Some of the most commonly found and highest concentration compounds were plasticizers (bisphenol A, Tris (butoxyethyl) Phosphate, and others) detergent metabolites (alkylphenol ethoxylates), caffeine, acetaminophen, triclosan, and coprostanol. While many compounds were detected frequently (see A, below) five detergent metabolites, seven plasticizers, and four steroids contributed about 80% of the total concentration of detections (see B, below). Concern was raised about the detections of reproductive hormones even though they were not in high concentrations, because of their biological activity.

Figure 1. Detection Frequency and Percent of Total Concentration for 15 Categories of Pharmaceuticals Found Across the U.S. (41). Numbers at the top of each bar indicate number of compounds in the category.



The USGS published a paper in 2004 (42) looking at the persistence of PPCPs as they travel through a typical drinking water plant from raw water input to finished drinking water, looking for essentially the same list as from (41) above. Forty of the analytes were detected in the raw water, and eighteen were detected in finished drinking water, see Table 2, below. None of the chemicals detected in finished water were above drinking water standards, but many PPCPs do not have any regulatory standard. Concern was raised because these compounds survive WWTF processing and drinking water plant processing. Although prescription drugs were of concern because of their known biological activity, those with known endocrine disrupting ability, and those industrial chemicals such as solvents, plasticizers, and flame retardants are a worry because little is known about effects of trace amounts on humans and environmental biota.

Table 2. PPCPs detected in finished drinking water from Across the U.S. (42)

CHEMICAL NAME	CAS #	USE	DETECTION PERCENT	MAXIMUM CONCENTRATION µg/L
Caffeine	58-08-2	Stimulant	100	0.119
Carbamazepine	298-46-4	Anticonvulsant	100	0.258
Cotinine	486-56-6	Nicotine metabolite	100	0.025
Dehydronifedipine	67035-22-7	Nifedipine metabolite	50	0.004
7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (AHTN)	21145-77-7	Fragrance	100	0.49
Anthraquinone	84-65-1	Manufacturing	42	0.072
Benzophenone	119-61-9	Fixative	58	0.13
Bisphenol A	80-05-7	Plasticizer	100	0.42
Bromoform	75-25-2	Trihalomethane	50	21
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl Cyclopenta-g-2-benzopyran (HHCB)	1222-05-5	Fragrance	92	0.082
<i>N,N</i> -diethyl-meta-toluamide (DEET)	134-62-3	Insecticide	25	0.066
Prometon	1610-18-0	Herbicide	25	0.096
Tetrachloroethylene	127-18-4	Solvent	58	0.1
Tri(2-butoxyethyl) phosphate	78-51-3	Plasticizer	83	0.35
Tri(2-chloroethyl) phosphate	115-96-8	Flame retardant	100	0.099
Tri(dichlorisopropyl) phosphate	13674-87-8	Flame retardant	100	0.25
Tributyl phosphate	126-73-8	Flame retardant	83	0.1
Triethyl citrate (ethyl citrate)	77-93-0	Cosmetics	50	0.062

In 2007, the Water Environment Research Foundation (WERF) published results of a study investigating removal efficiencies of WWTFs with different waste retention times (43). Of the 20 compounds followed through typical WWTFs, 14 were detected in at least 25% of the incoming samples and were defined as intermediate to frequent occurrence. Of the same 20, 10 had moderate to poor removal efficiency during the treatment. Of those, 6 had intermediate to frequent occurrence AND moderate to poor removal, so have a good chance of being in WWTF effluent. Those 6 are: BHA, DEET, Musk Ketone, triclosan, benzophenone, and Galaxolide. The synthetic musk galaxolide (HHCB) was observed to be especially resistant to removal during the treatment process. It was observed that longer retention times led to greater removal of most compounds studied. As can be seen from Tables 2 and 3, DEET and benzophenone appear to be two compounds which are likely to survive treatment in both a WWTF and a drinking water facility.

Table 3. Occurrence and Removal Efficiency of 20 Representative Wastewater Contaminants. (43).

<u>OCCURRENCE</u>	<u>REMOVAL</u>	<u>COMPOUNDS</u>	<u>CLASSIFICATION</u>
INFREQUENT	GOOD REMOVAL	METHYL-3-PHENYLPROPIONATE	FRAGRANCE
	MODERATE REMOVAL	OCTYLPHENOL	SURFACTANT (DETERGENT)
	POOR REMOVAL	TRI(CHLOROETHYL)PHOSPHATE (TCEP)	FIRE RETARDANT
	POOR REMOVAL	TRIPHENYLPHOSPHATE	FIRE RETARDANT
INTERMEDIATE	GOOD REMOVAL	N/A	N/A
	MODERATE REMOVAL	ETHYL-3-PHENYLPROPIONATE	FRAGRANCE
	POOR REMOVAL	BHA	ANTIOXIDENT
	POOR REMOVAL	DEET	INSECTICIDE
	POOR REMOVAL	MUSK KETONE	FRAGRANCE
FREQUENT	GOOD REMOVAL	CAFFEINE	PHARMACEUTICAL
	GOOD REMOVAL	IBUPROFIN	PHARMACEUTICAL
	GOOD REMOVAL	OXYBENZONE	SUNSCREEN
	GOOD REMOVAL	CHLOROXYLENOL	GERMICIDE
	GOOD REMOVAL	METHYLPARABEN	ANTIOXIDENT
	GOOD REMOVAL	BENZYL SALICYLATE	SUNSCREEN
	GOOD REMOVAL	3-PHENYLPROPIONATE	FRAGRANCE
	GOOD REMOVAL	BUTYLBENZYL PHTHALATE	PLASTICIZER
	GOOD REMOVAL	OCTYLMETHOXYCINNAMATE	SUNSCREEN
	MODERATE REMOVAL	TRICLOSAN	GERMICIDE
	MODERATE REMOVAL	BENZOPHENONE	SUNSCREEN
	POOR REMOVAL	GALAXOLIDE	FRAGRANCE

In 2008, USGS published results of a nationwide survey (44) of raw drinking water intakes. The most commonly detected contaminants in surface water sources were: cholesterol, metolachlor, cotinine, β -sitosterol, 1,7-dimethylxanthine. Groundwater contaminants commonly found were: tetrachloroethylene, carbamazine, bisphenol-A, 1,7-dimethylxanthine, and tri (2-chloroethyl) phosphate. The authors stressed that although prescription drug detections were not common, that may be because degradation products and metabolites were not analyzed for.

Pal et al (45) published a review in 2010 of OCECs occurrences and effects in freshwater worldwide, concentrating primarily on pharmaceuticals. They conclude that sex hormones (estrogens and androgens) are of the greatest toxicological concern, followed by cardiovascular drugs and antibiotics. Effluent and surface water concentrations greater than “predicted no effect concentration (PNEC) in particular were mentioned for the antibiotics trimethoprim and ciprofloxacin and the various estrogens.

King et al (46), looked at the birth control compound ethinyl estradiol (EE2) in WWTF effluent in Australia in 2014. They concluded that effluent entering receiving waters contained EE2 at levels greater than the PNEC of 0.1 ng/L and remained above that level up to 4km downstream.

In summary, there are a very large number of OCECs present in our WWTF effluent and to a lesser extent in our drinking water supplies. It is not possible to generalize on which classes of contaminant are likely to survive treatment

3.0 EXISTING DATA ON ORGANIC CONTAMINANTS OF EMERGING CONCERN FROM THE LAKE CHAMPLAIN BASIN.

3.1 PESTICIDES IN THE LAKE CHAMPLAIN BASIN:

Starting in 1996, reports of deformed leopard frogs began being reported from various wetlands around Lake Champlain. In 2000, the Vermont Dept. of Environmental Conservation (VTDEC) received funding from USEPA to do an in depth assessment of possible causes of these malformations (48). As part of this study, the Vermont Agency of Agriculture, Food, and Markets (VAAFM) measured levels of various pesticides in water and sediment in areas associated with deformed frogs. No pesticides were detected in sediment, and no relationship was found between deformities and pesticide levels, but pesticides were detected in water from several sites. As can be seen from Table 4, the only pesticides detected were atrazine and metolachlor, plus their metabolites. The significant finding was the detection of these corn herbicides and metabolites in wetlands under the influence of Lake Champlain in April, prior to corn herbicide applications for the year. This suggests that corn herbicides were entering Lake Champlain in sufficient quantities, and that these compounds are persistent enough that they survived the winter in trace quantities.

[illegible]

INSECTICIDES										
Diazinon	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
RIGHT OF WAY										
Imazapyr	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Flumetsulam	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nicosulfuron	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Metsulfuron methyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sulfometuron methyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diuron	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Primisulfuron	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
METABOLITES										
Desethyl atrazine	0.02 ppb	ND	ND	0.02 ppb	0.03 ppb	ND	0.02 ppb	ND	ND	ND
Desisopropyl atrazine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Alachlor ESA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Alachlor OA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Metolachlor ESA	0.05 ppb	ND	0.03 ppb	0.05 ppb	0.10 ppb	0.07 ppb	0.08 ppb	ND	0.05 ppb	ND
Metolachlor OA	0.02 ppb	ND	ND	0.02 ppb	0.04 ppb	0.02 ppb	0.03 ppb	ND	ND	ND
Acetochlor ESA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acetochlor OA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

In response to these findings, the VAAFM in 2001 initiated surface water monitoring efforts on Lake Champlain and its tributaries, primarily for corn herbicides and metabolites (49). As is true for all VAAFM pesticide studies since 2001, this was an informal, internal monitoring project undertaken as time permitted, with no external peer review, but data exists for the period 2002-2015. Most samples were collected by the VTDEC staff associated with the Lake Champlain Long Term Monitoring Program (LCLTMP), a collaborative effort of VTDEC, New York, DEC, the Province of Québec, the USEPA, and the LCBP. The full data set from this work is too extensive to include in the current report, but is summarized in Tables 5 and 6 and Figure 1 and 2 from (49). These data corroborate the earlier work which indicated chronic low level presence of corn herbicides in Lake Champlain, primarily atrazine and metolachlor and their metabolites. As can be seen from Table 5, atrazine, metolachlor, and their degradates desethyl atrazine, metolachlor ESA, and metolachlor OA have been by far the most common detections.

Table 5. Pesticide Detections in Lake Champlain and Tributaries 2002-2015. (49).*

ANALYTE	NUMBER OF SAMPLES	NUMBER DETECTS	MEDIAN OF DETECTS	MAXIMUM
			(PPB)	(PPB)
ACETOCHLOR	1309	31	0.08	5.6
ALACHLOR	1309	1	0.05	0.05
ATRAZINE	1333	697	0.076	33.8
CYANAZINE	566	4	0.031	0.149
DIMETHENAMID	1309	39	0.042	0.775
METOLACHLOR	1333	529	0.078	19.4
PENDIMETHALIN	827	8	0.026	0.057
SIMAZINE	1309	71	0.038	1.55
ACETOCHLOR ESA	1351	234	0.125	9.45
ACETOCHLOR OA	826	26	0.031	0.614
ALACHLOR ESA	1351	111	0.054	0.54
ALACHLOR OA	826	1	0.028	0.028
DESETHYL ATRAZINE	1374	331	0.051	5

DEISOPROPYL ATRAZINE	826	54	0.028	0.109
HYDROXYATRAZINE	826	140	0.035	0.264
DIMETHENAMID ESA	615	8	0.115	0.16
DIMETHENAMID OA	90	0	0	0
METOLACHLOR ESA	1374	1157	0.114	13.9
METOLACHLOR OA	826	528	0.050	2.65
DETECTION LIMIT 2002-2008 = 0.020 PPB				
DETECTION LIMIT 2009 - 2015 = 0.050 PPB				

* A portion of this data does not meet current VAAFM data reporting protocols.

Table 6 lists summary results by sampling site, for the more commonly found pesticides. As with the deformed frog study, the major compounds detected were atrazine, metolachlor and their metabolites.

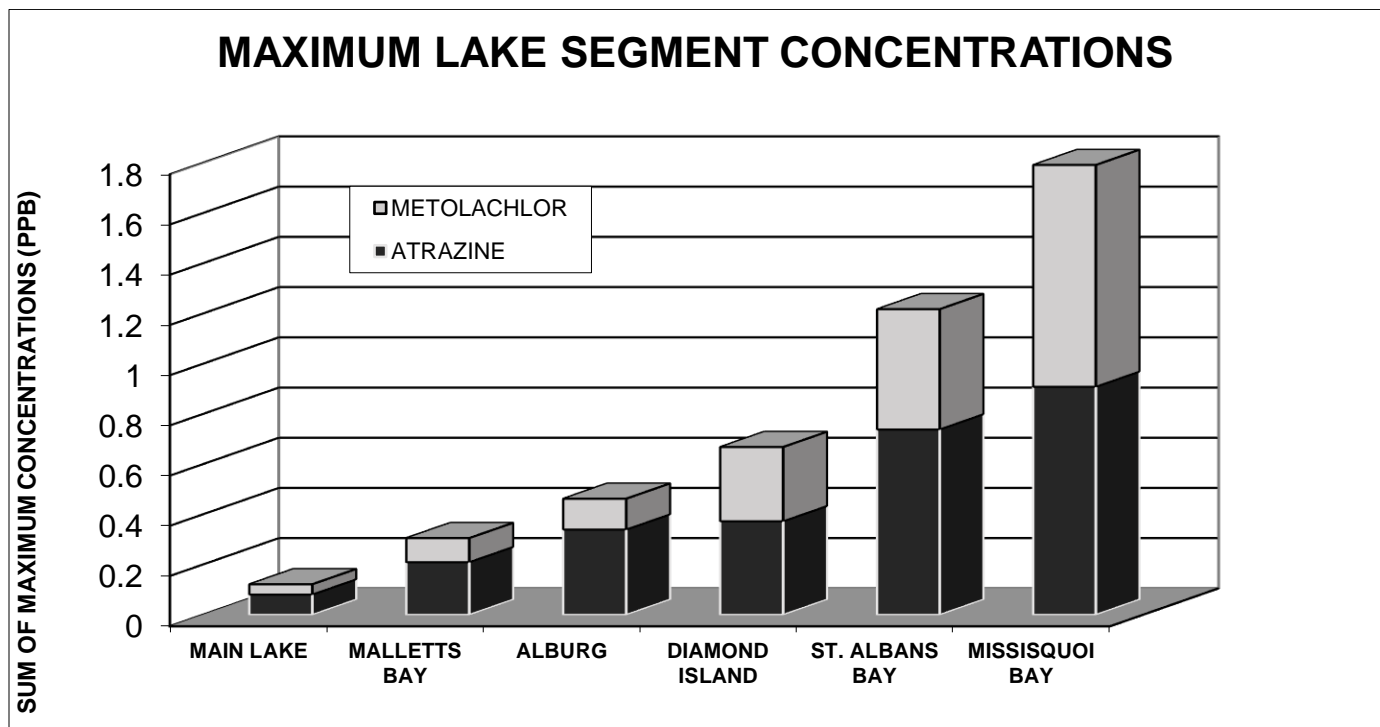
Table 6. Lake Champlain and Tributary Detections by Station (49).*

SITE	NUMBER OF SAMPLES	MAXIMUM	MAXIMUM	MAXIMUM	MAXIMUM
		ATRAZINE	DESETHYL ATRAZINE	METOLACHLOR	METOLACHLOR ESA
ALBURG CTR. (STA 46)	94	0.34	0.03	0.12	0.22
DIAMOND ISLAND (STA 9)	73	0.37	0.04	0.30	0.10
JEWETT BROOK (JEW02)	53	33.80	2.70	19.40	13.90
LAMOILLE RIVER	50	0.32	0.04	0.24	0.09
LITTLE OTTER CREEK	86	3.53	0.97	2.15	0.95
MAIN LAKE (STA 19)	90	0.10	0.02	0.11	0.12
MALLETTS BAY (STA 25)	55	0.21	0.02	0.10	0.08
MISSISSQUOI BAY (STA 50)	109	0.91	0.14	0.88	0.72
MISSISSQUOI RIVER	117	1.96	0.13	1.98	0.65
OTTER CREEK	53	1.88	0.12	1.58	0.24
PIKE RIVER	98	10.76	0.51	5.72	2.01
POULTNEY RIVER	32	0.64	0.05	0.43	0.14
ROCK RIVER	58	2.86	0.71	2.80	3.20
ST. ALBANS BAY (STA 40)	96	0.74	0.14	0.48	0.28
STEVENS BRANCH	38	0.28	0.72	0.33	2.60
WINOOSKI RIVER	56	0.20	0.07	0.19	0.07

* A portion of this data does not meet current VAAFM data reporting protocols.

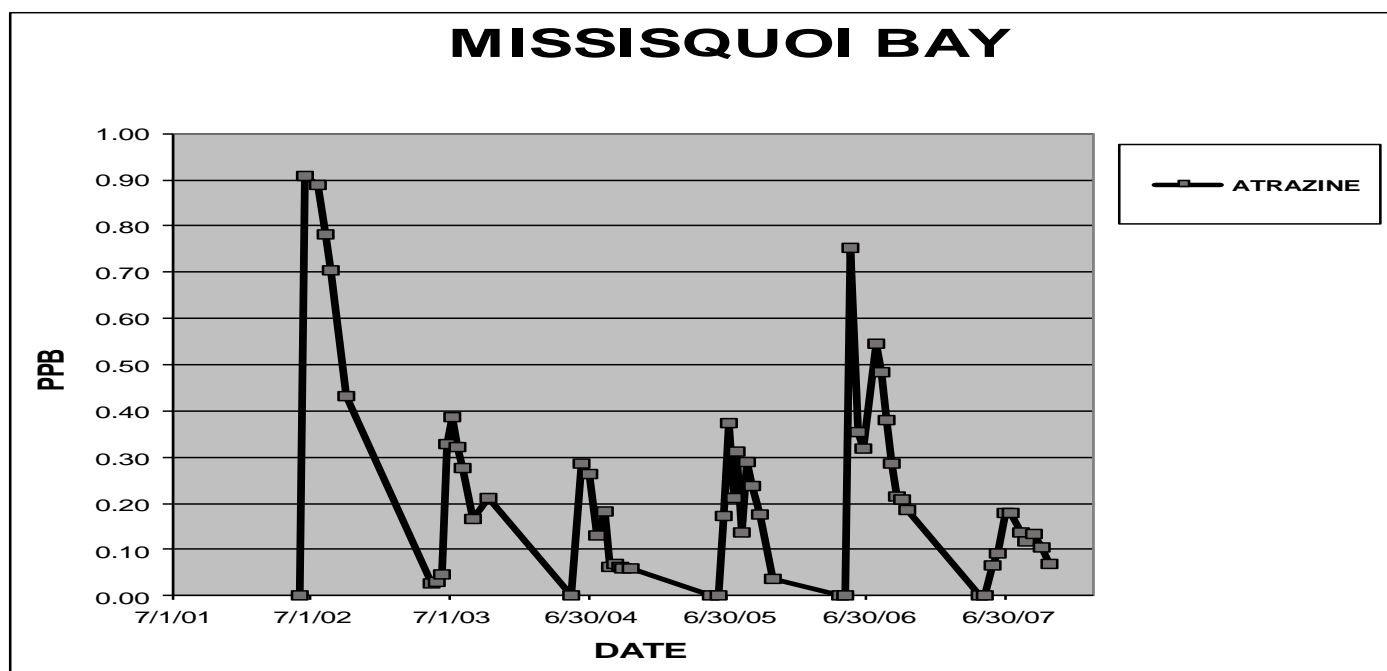
Missisquoi Bay and St. Albans Bay consistently show the highest concentrations of corn herbicides in Lake Champlain, reflecting the large amount of agriculture in the northern part of the watershed. Figure 2 shows atrazine and metolachlor concentrations in major lake segments.

FIGURE 2. Maximum Atrazine and Metolachlor concentrations in Major Segments of Lake Champlain, 2002-2007 (49).



A long term view of this data, as in Figure 3, shows the cyclic nature of pesticide runoff into Lake Champlain, and Missisquoi Bay in particular. A large surge in herbicide concentration occurs in early summer, shortly after corn is planted and pesticides are sprayed. The largest surge tends to occur when a large rainstorm occurs shortly after spraying. As the corn grows, large rainstorms are less likely to cause pesticide runoff. In Missisquoi Bay in particular, this large surge of pesticide runoff seems to have a residence time of several weeks to months before returning to background concentrations.

Figure 3. Trends in Atrazine Concentrations in Missisquoi Bay, 2002-2007 (49).



In 2001, the VAAFM collaborated with the VTDEC and UVM to do a small study looking at lawn care pesticides in urban runoff in Burlington, VT (50). This provides some of the only known data for OCECs in urban storm water runoff from the Champlain Basin. Significant findings in this study were that two herbicides were detected above Vermont acute water quality guidelines (2,4-D at 162 ppb, and pendimethalin at 2.9 ppb) as well as detecting MCPP at over 100 ppb, and detecting diazinon at 73% of water quality guideline in an urban stream (Englesby Brook). Toxicity tests with *Ceriodaphnia* found no acute toxicity from the samples tested.

TABLE 7. Summary Pesticide Results from Chittenden County, VT Urban Runoff (50).

Compound	Compound Type	Detection Limit (MDL)	Sample Detects	Site Detects	Max. ppb	Min. ppb	VT Acute Water	Detects greater than
		ppb					Quality Guideline	Water Quality Guideline
2,4-D	Herbicide	0.1	3 of 22	3 of 10	162	0.27	120	1
MCPP	Herbicide	0.1	4 of 22	3 of 10	115	0.19	1860	0
Dacthal 4	Herbicide	0.1	3 of 22	2 of 10	0.4	0.14	310	0
Diazinon	Insecticide	0.06	2 of 22	2 of 10	0.22	0.08	0.3	0
Pendimethalin	Herbicide	0.05	2 of 22	2 of 10	2.9	0.21	2.1	1
MCPA	Herbicide	0.1	0 of 22	ND	ND	ND	12	ND
Dicamba	Herbicide	0.1	0 of 22	ND	ND	ND	420	ND
Triclopyr	Herbicide	0.1	0 of 22	ND	ND	ND	1860	ND
Chlorpyrifos	Insecticide	0.05	0 of 22	ND	ND	ND	0.083	ND
Malathion	Insecticide	0.05	0 of 22	ND	ND	ND	1	ND

In addition to the above mentioned studies, the VAAFM has done periodic pesticide monitoring of surface water runoff from railroads and golf courses, both inside and outside of the Champlain Basin. Railroad herbicide monitoring has been ongoing intermittently since the early 2000's at the VAAFM at the request of the Vermont Pesticide Advisory Council (VPAC). The purpose was to monitor runoff from the ballast of treated tracks into neighboring streams, ponds, and ditches statewide. When the majority of this work was done, the main herbicides used were diuron, imazapyr, sulfometuron methyl, metsulfuron methyl, and glyphosate. Diuron was the compound of most concern, with levels up to 82 ppb in a ditch next to a switching yard with five tracks. The sulfonyl urea herbicides such as metsulfuron methyl and sulfometuron methyl have been of concern as well, because they are highly toxic to aquatic plants. It was concluded that areas with multiple tracks were most likely to exhibit significant runoff which might be of concern to aquatic plants. Detections in small streams and ditches often approached or exceeded Aquatic Life Benchmarks (plant) for diuron, metsulfuron methyl and sulfometuron methyl.

TABLE 8. Railroad Right of Way Herbicide Runoff Summary Table (49).

ANALYTE	Number of Samples	Number of Detects	Maximum (ppb)	EPA Aquatic Life Benchmark (ppb)
DIURON	333	65	82.800	2.4
FLUMETSULAM	333	0	ND	3.1
IMAZAPYR	333	77	3.630	24
METSULFURON METHYL	333	43	2.580	0.36
NICOSULFURON	333	0	ND	none
PRIMISULFURON	333	0	ND	none
SULFOMETURON METHYL	333	78	2.180	0.45

Golf course pesticide use is one of the most intensive uses of pesticides in Vermont per acre, in order to keep the turf in optimum condition. Again, the VAAFM has done some investigations of runoff from Vermont golf courses, mostly in the 2000's at the request of VPAC. Herbicides to kill weeds and fungicides to kill snow mold and other fungi are the main pesticide uses on Vermont golf courses. The fungicide chlorothalonil was the most serious concern, with four of sixteen detections greater than the chronic Aquatic Life Benchmark for invertebrates. Fungicides are applied on golf courses in late fall, to protect the turf from snow mold during the winter. Unfortunately, if a large rainstorm occurs after fungicide application and before snow cover, a surge of fungicide can enter waterbodies with runoff.

Table 9. GOLF COURSE RUNOFF SUMMARY TABLE (49).

ANALYTE	Number of Samples	Number of Detects	Maximum (ppb)	EPA Aquatic Life Benchmark (ppb)
Chloroneb	43	14	1.816	none
Vinclozolin	43	0	ND	60
Chlorothalonil	134	16	6.640	0.6
Chlorpyrifos	93	1	0.120	0.04
Iprodione	134	8	4.212	120
PCNB	134	54	4.281	18
Triadimefon	134	9	1.257	41
2,4-D	79	6	7.450	13.1
Dacthal Metabolites	52	0	ND	13500
Dicamba	79	2	0.100	61
MCPA	79	3	0.106	170
MCP	79	3	0.070	45500
Triclopyr	60	3	0.660	5900

In 2008, the VAAFM collaborated with the U.S. Forest Service to investigate whether pesticide use in the Batten kill watershed of Vermont might be contributing to the decline of the trout fishery there (51). In particular, the question was: are the hydrophobic insecticides bifenthrin, permethrin, pendimethalin, and PCNB being used in the watershed in sufficient quantity that they are accumulating in the sediments and causing toxicity to aquatic insects or fish. Although not in the Lake Champlain watershed, this study is significant because bifenthrin, a synthetic pyrethroid insecticide, was detected in one sediment sample at quantifiable levels with a trace also detected just downstream. Bifenthrin was detected at approximately 3 ng/g, approaching levels toxic to aquatic insects. This bifenthrin was thought to be the result of routine lawncare/landscaping activities in the small city of Manchester, VT. This and the study from Burlington, VT (50) demonstrate that typical urban/suburban pesticide use can lead to pesticide concentrations in our streams approaching toxic levels.

In 2006, the USGS investigated pesticide and other contaminants in select Lake Champlain and tributary sites as well as WWTFs (52). The aim of this study was to document "organic wastewater contaminants" in WWTF effluent, urban streams, and surface waters of the basin. Pesticides were not the main focus. The only pesticides detected were metolachlor and DEET. As one would expect, the majority of metolachlor detections were in lake and river samples not urban samples, since this is an agricultural herbicide. The maximum metolachlor detected was 0.11 ppb. DEET is an insecticide used primarily on people as mosquito repellent so it was detected primarily in WWTF and CSO effluent, with

a maximum detection of 1.24 ppb. In 2009, the USGS followed up on the above study to investigate the Burlington, VT CSO output of CECs during storm events (53); pesticides were not included. These USGS studies will be discussed in more detail below in section 3.2.

Although not directly relevant to this review of pesticides in surface waters, the VAAFM undertook to test pollen samples from two honeybee hives for neonicotinoids in 2012 and 2013 in response to interest by the Vermont Legislature (54). This work led to an investigation of neonicotinoids in surface waters and tile drain effluent, described below. Pollen was collected weekly from two honeybee hives in the Champlain valley, one in an area dominated by hay and pasture, while the other was dominated by corn fields. Tables 10 (2012) and 11 (2013) below show results only for those pesticides which were detected.

TABLE 10. Pesticide Detections in Honeybee Pollen in Vermont 2012 (54).

2012 PASTURE HIVE

<u>DATE</u>	<u>ATRAZINE</u>	<u>METOLACHLOR</u>	<u>IMIDACLOPRID</u>	<u>TRIFLOXYSTROBIN</u>
5/6/12 – 5/12/12				
5/13/12 – 5/19/12	2.6 PPB			
5/20/12 – 5/26/12	1.0 PPB			
5/27/12 – 6/2/12	6.1 PPB			
6/3/12 – 6/9/12	1.2 PPB			1.3 PPB
6/10/12 – 6/16/12	1.8 PPB			
6/17/12 – 6/23/12	3.8 PPB			
7/15/12 – 7/21/12				
7/22/12 – 7/28/12				
7/29/12 – 8/4/12				
8/5/12 – 8/11/12				
8/12/12 – 8/18/12				
8/19/12 – 8/25/12				
8/26/12 – 9/1/12				
9/2/12 – 9/7/12				

2012 CORN HIVE

<u>DATE</u>	<u>ATRAZINE</u>	<u>METOLACHLOR</u>	<u>IMIDACLOPRID</u>	<u>TRIFLOXYSTROBIN</u>
6/11/12 – 6/15/12	68 PPB	25 PPB	0.7 PPB	5.5 PPB
6/18/12 – 6/22/12	75 PPB	4.4 PPB		0.64 PPB
6/25/12 – 7/2/12	18 PPB	4.2 PPB		
7/9/12 – 7/13/12	19 PPB	1.1 PPB		
7/16/12 – 7/20/12	24 PPB	1.1 PPB		
7/25/12 – 8/1/12*	2.2 PPB			
8/2/12 – 8/9/12*	0.50 PPB			

TABLE 11. Pesticide Detections in Honeybee Pollen in Vermont 2013 (54).

2013 PASTURE HIVE

<u>DATE (2013)</u>	<u>ATRAZINE</u>	<u>METOLACHLOR</u>	<u>THIAMETHOXAM</u>	<u>TRIFLOXYSTROBIN</u>	<u>CLOTHIANIDIN</u>
	ppb	ppb	ppb	ppb	ppb
5/5 - 5/11	ND	1.0	ND	ND	ND
5/12 - 5/18	13.3	9.4	ND	ND	ND
5/19 - 5/25	5.7	10.6	ND	ND	ND
5/26 - 6/1	0.7	2.1	ND	ND	ND
6/2 - 6/8	ND	ND	ND	ND	ND
6/9 - 6/15	ND	ND	ND	ND	
6/16 - 6/22	ND	ND	ND	ND	ND
6/23 - 6/29	ND	ND	ND	ND	ND
7/7 - 7/13	ND	ND	ND	ND	ND
7/14 - 7/20	ND	ND	ND	ND	ND
7/21 - 7/27	ND	ND	ND	ND	ND
7/28 - 8/3	ND	ND	ND	0.5	ND
8/4 - 8/10	ND	ND	ND	ND	ND
8/11 - 8/17	ND	ND	ND	ND	ND
8/18 - 8/24	ND	ND	ND	ND	ND

2013 CORN HIVE

<u>DATE (2013)</u>	<u>ATRAZINE</u>	<u>METOLACHLOR</u>	<u>THIAMETHOXAM</u>	<u>TRIFLOXYSTROBIN</u>	<u>CLOTHIANIDIN</u>
	ppb	ppb	ppb	ppb	ppb
5/11 - 5/15	5.3	7.7	0.8	ND	6.2
5/15 - 5/18	49.5	32.0	1.2	0.7	ND
5/19 - 5/23	12.3	18.6	ND	ND	ND
5/24 - 6/3	4.5	9.4	ND	ND	ND
6/4 - 6/5	2.9	6.6	ND	ND	ND
6/6 - 6/19	ND	1.9	ND	ND	ND
6/20 - 7/3	2.1	1.2	ND	ND	ND
7/4 - 7/8	ND	ND	ND	ND	ND
7/8 - 7/18	ND	ND	ND	ND	ND
7/24 - 7/31	ND	ND	ND	ND	ND
8/1 8/7	ND	ND	ND	ND	ND

As can be seen, atrazine and metolachlor were detected in pollen from both corn and pasture habitats, but the levels were 3-10 ten times higher in the corn field hive. Trifloxystrobin, a systemic fungicide used as a seed treatment, was the most commonly detected non-herbicide pesticide, being detected in 5 out of 48 samples. The neonicotinoid insecticides imidacloprid, clothianidin, and thiamethoxam were detected sporadically early in the summer. Essentially all pesticide detections were in May, June, and July, before corn would have been producing pollen, so these detections are not likely to be from corn pollen. Detections in mid-May to mid-June, corresponds to the time when corn is planted

and cornfields are sprayed with pesticides. It is not known what seed treatments were used on the seed corn for the neighboring fields, but most conventional corn is treated with neonics and strobilin fungicides (such as trifloxystrobin). Seed coatings have been shown to scrape off of seeds during planting, potentially exposing bees to lethal doses of neonics from wind blown dust (55). These data indicate that honeybees foraging near corn fields are being exposed to pollen contaminated with neonicotinoids at the time that corn is being planted. The source is unknown, but the 6.2 ppb clothianidin concentration is of concern, again because it is approaching toxic levels.

In addition to being of concern in itself, these data led the VAAFM in 2015 to focus their surface water monitoring efforts on a localized study looking at corn herbicide and neonicotinoid insecticide runoff from agricultural fields planted in corn and soy seeds treated with neonicotinoids. Samples were collected from tile drains in the St. Albans Bay watershed and the small streams they drained into, including Jewett Brook. Table 12 summarizes the results for 2015 from this study, which also included sampling on the Rock and Pike Rivers. Some preliminary data from 2016 is included. It can be seen that neonics, corn herbicides and metabolites were found routinely in the waters of Jewett Brook, the Pike River and the Rock River of the northern Champlain basin. Also of note is the observation that imidacloprid was observed only in Tile #8 and 9, which drain a soy field, while clothianidin and thiamethoxam were found in Tile #s 1-7, which drain corn fields. This tracks with the seed treatments used on the corn and soy planted on the fields (VAAFM, pers. comm. 2016), indicating that seed treatments may be leaching into groundwater and surface water quite quickly. In 2015, the highest levels of atrazine, metolachlor, and thiamethoxam were found in Jewett Brook, even higher than direct tile drain outflow. It is important to note that the neonicotinoids clothianidin and imidacloprid have both exceeded their Aquatic Life Benchmark in tile effluent, while clothianidin has approached one half of the benchmark in both Jewett and Stevens Brooks. Also note that atrazine routinely exceeds its benchmark of 0.001 ppb everywhere. On June 6, 2016, when Tile #8 effluent contained 4.17 µg/L clothianidin, it was flowing at approximately 294 L/min. Therefore, almost 2 g/day of clothianidin was being added to Saint Albans Bay during this period, from Tile #8 alone.

TABLE 12. Neonicotinoid and Corn Herbicide Runoff from Corn Fields in 2015 and 2016 (49).

SITE	IMIDACLOPRID	CLOTHIANIDIN	THIAMETHOXAM	ATRAZINE	METOLACHLOR	DESETHYL	METOLACHLOR
NAME						ATRAZINE	ESA
	Maximum ppb 2015(2016)	Maximum ppb 2015(2016)	Maximum ppb 2015(2016)	Maximum ppb 2015	Maximum ppb 2015	Maximum ppb 2015	Maximum ppb 2015
JEWETT BROOK (JEW01)	0.03(0.07)	0.33(0.49)	0.69(1.07)	26.00	39.00	2.00	11.00
PIKE RIVER	ND	0.05	0.24	3.30	4.00	0.12	1.40
ROCK RIVER	ND	0.14	0.21	1.10	3.40	0.32	4.30
STEVENS BROOK	ND	0.06(0.44)	0.10(0.23)	0.42	4.30	0.18	3.70
TILE #1	ND	1.20(0.31)	0.04(0.13)	0.90	4.10	0.70	23.00
TILE #2	ND	0.24(0.06)	0.11(0.06)	0.49	1.10	0.28	27.00
TILE #3	ND	0.43(0.31)	0.16(0.15)	1.00	1.30	0.77	32.00
TILE #4	ND	0.88(0.54)	0.26(0.18)	0.95	2.00	1.00	27.00
TILE #5	ND	0.55(0.59)	0.12(0.21)	1.00	1.80	0.78	25.00
TILE #6	ND	0.42(0.47)	0.08(0.23)	0.87	1.20	0.44	24.00
TILE #7	ND	0.03(ND)	ND	0.06	ND	0.06	2.08
TILE #8	0.84(0.10)	0.73(4.17)	0.10(1.31)	0.14	1.00	0.21	20.20
TILE #9	0.54(1.12)	0.64(0.60)	0.03(ND)	0.12	1.30	0.11	22.00
EPA Aquatic Life Benchmark (ppb)	1.05	1.1	17.5	0.001	8	1000	24000

The pesticide TFM (3-trifluoromethyl-4-nitrophenol) is used as a lampricide to control sea lamprey (*Petromyzon marinus*) larvae in the tributaries of Lake Champlain. Although toxic to many if not all aquatic animals, it is somewhat selective for primitive fish such as sea lamprey. When lampricide treatment is undertaken on one of the larger tributaries in Vermont, it becomes one of the largest pesticide applications for the year. In 2012, the Missisquoi River was treated with TFM, and both the US Fish & Wildlife Service (USFWS) who did the treatment, and the Québec Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques (MDDELCC) monitored TFM concentrations in Missisquoi Bay after treatment (56 & 57). Of particular concern was the Bedford Drinking water treatment plant in Bedford, Québec which draws its source water from Missisquoi Bay. The USFWS monitoring found that no TFM greater than the Vermont Department of Health health advisory level of 35 µg/L was detected in the Bedford raw source water (maximum of 33 µg/L on day four after treatment) and only trace amounts in the finished water. A maximum of 226 µg/L was detected on the eastern shore of the bay on day three. The MDDELCC also monitored TFM in the Bedford water supply and found similar results, but with more detections because their method was more sensitive, see Table 13 (from 56). TFM was detected at low levels 12 weeks after treatment, evidence of both the persistence of TFM in surface water and the relatively slow flushing of Missisquoi Bay during low flow.

TABLE 13. VERMONT and QUÉBEC TFM results for Bedford Québec raw and finished drinking water in µg/l (56).

Date	VERMONT RESULTS		QUÉBEC RESULTS	
	RAW	FINISHED	RAW	FINISHED
OCTOBER 2012				
26	ND	ND		
27	ND	ND	ND	ND
28	ND	ND		
29	ND	ND	ND	ND
30	33	ND		
31	ND	ND		
NOVEMBER 2012				
1	15,8	ND	14	0,5
2	32,7	ND		
3	26,1	T		
4	14,2	T		
5	T	T	4,4	0,84
6	ND	ND		
7	7,5	ND		
8	ND	ND	0,56	0,35
9	T	ND		
10	ND	ND		
11	T	ND		
12	T	ND	2,8	0,42
13	T	T		
14	T	ND		
15	ND	ND	0,95	0,04
16	ND	ND		
17	ND	ND		
18	ND	ND		
19	ND	ND		
22			0,78	0,33
26			1,5	0,17
29			1,4	0,23
DECEMBER 2012				

3		1,4	0,11
6		0,4	0,19
JANUARY 2013			
17		0,11	ND
Detection/Quantitation Limit µg/l	2,4 / 7,5	0,02 / 0,06	

3.2. PHARMACEUTICALS, PERSONAL CARE PRODUCTS, NATURAL HORMONES, and INDUSTRIAL CHEMICALS in the LAKE CHAMPLAIN BASIN

In response to passage in Vermont of Water Quality Standards in 1991, the Vermont DEC undertook testing of effluent grab samples from 37 WWTF in 1991 as a first step in assessing toxic discharges (58). Although detection limits mostly in the 2 ppb or greater range are inadequate by today's standards, this was an early effort to investigate unregulated organic contaminants in Vermont's surface waters. Detections of the volatile and semi-volatile industrial organics methylene chloride, toluene, chloroform, and acetone were most common, being found in greater than 5% of WWTF effluents. Chlorpyrifos, an organophosphate insecticide was detected in the Putney effluent at 0.5 ppb, and phthalates were detected in Brattleboro effluent. Analytes looked for but not found were not listed, but included organochlorine pesticides and PCBs.

Table 13. Detected Concentrations of OCECs in Vermont WWTF Final effluent, 1991 (58).

Publicly Owned Treatment Work-POTW	Methylene Chloride ppb	Toluene ppb	Chloroform ppb	Acetone ppb	4-Methyl Phenol ppb
Method Detection Limit	2	2	2	50	5
Barre City ¹					
Bellows Falls					
Bennington ²					
Brattleboro ³					
Burlington ⁴ Riverside	95		4	253	
Burlington Main	10	21	3	371	
Burlington North	3				
Castleton					
Chester	42	10			
Jacksonville					
Ludlow					
Lyndon					
Middlebury					
Montpelier	42				
Morrisville		6			
Newport		4			
North Troy					
Poultney					
Putney ⁵	10				

Publicly Owned Treatment Work-POTW	Methylene Chloride ppb	Toluene ppb	Chloroform ppb	Acetone ppb	4-Methyl Phenol ppb
Randolph					
Richmond	8				6
Rutland			4		
Saint Albans	2.5				
Saint Johnsbury					
Shelburne FD #1					
Shelburne FD #2					
South Burlington Airport Parkway			5		
South Burlington ⁶ Bartlett's Bay	79		5		
Springfield					
Stowe					
Swanton					
Vergennes		6			
Waterbury					
White River Junction					
Whitingham	9				
Williamstown					
Winooski		5			

1: also Tetrachloroethane 16 ppb
 2: also Tetrachloroethene 16 ppb
 3: also Diethylphthalate 12 ppb
 Dimethylphthalate 5 ppb
 4: also Ethylbenzene 24 ppb
 5: also 2-Methylnaphthalene 4 ppb
 C-4 Alkylbenzene Isomer 4 ppb
 Chlorpyrifos 0.5 ppb
 6: also Bromodichloromethane 4 ppb

A follow-up study by VTDEC in 1992 (59) investigated toxicity at ten of Vermont's final WWTF effluents, and did more chemical analyses. Acute or chronic whole effluent toxicity to the water flea *Ceriodaphnia dubia* and fathead minnow *Pimephales promelas* in up to 55% of the samples was observed and attributed to elevated ammonia. This report lists the first known mention of trace detections in Vermont surface waters of: the plasticizer/flame retardant Tris(2-butoxyethanol) phosphate, caffeine, and nonyl phenols. It must be noted that several of the CAS numbers in this table are not valid, so the identifications may be suspect. Again, analytes looked for but not found were not detailed.

Table 14. Organic Compounds Detected in Vermont Final WWTF effluent, 1992 (59).

POTW	DATE	COMPOUNDS DETECTED		Note
Burlington-Main (1)	4-3-92	Chloroform	2 ppb	E*
Riverside (2)	4-9-92	Chloroform	3 ppb	E
		Methylene Chloride	15 ppb	
		Toluene	2 ppb	
St. Albans	4-30-92	Chloroform	9 ppb	
	8-20-92	Acetone	1675 ppb	J**

South Burlington Bartlett Bay	7-30-92	Bromodichloromethane Dibromochloromethane	8 ppb 6 ppb	
Airport Pkway	4-9-92	Methylene Chloride Methyl butyl ether Chloroform	2 ppb <10 ppb 3 ppb	E E
Winooski	4-16-92	Methyl butyl ether	<10 ppb	E

*E = estimate

**J = value may be in error

- (1) Also detected: homologues of 1-(2-Methoxy-1-methylethoxyl)2-propanol. CAS # 20324-32-7
Tris (2-butoxyethanol) phosphate. CAS # 73-52-3 (**invalid CAS #**)
Trace of unknowns.
- (2) Also detected: N,N-Dimethyl-benzenemethanamine CAS # 103-83-3
2,5-Dimethyl-1-propylpyrrole CAS # 20282-39-7 (**invalid CAS #**)
Nonyl phenols
Caffeine
Tris (2-butoxy ethanol) CAS # 73-51-3 (**invalid CAS #**)
? Steroidal metabolite

In 1991 and 1992, UVM researchers analyzed sediment cores from throughout the basin for metals, PCBs, and chlorinated pesticides (60). Elevated levels of PAHs were found in sediment from the Burlington Inner Harbor. Levels increased with depth, indicating greater deposition in the recent past. The source was likely the nearby WWTF outfall and an oil barge offloading site.

The first Vermont study to target PPCPs specifically was initiated in 2002 with the collection of final effluent grab samples from 12 WWTFs to be analyzed for six PPCPs: Triclocarban, 17b-Estradiol, Estrone, 17a-Ethynylestradiol, Bisphenol-A, and 4-Nonylphenol (61). This study was also the first to have detection limits in the low ng/L (parts per trillion) range and to target hormones and other endocrine disrupters. The Bellows Falls facility seemed to have the highest concentrations of most compounds at the time.

Table 15. PPCPs in Vermont WWTF Final Effluent, 2002 (61).

Compound	Triclocarban	17b-Estradiol	Estrone	17a-Ethynylestradiol	Bisphenol-A	4-Nonylphenol	Wastewater Treatment Facility	Receiving Water
	15	<4	<4	5.2	22	420	Montpelier	Winooski River
	34	<4	<4	<4	<4	99	Hartford	Connecticut River
	170	11	12	28	60	3000	Bellows Falls	Connecticut River

	5.6J	6.3	4.5	<4	18	610	Stowe	Waterbury River
	51	12	21	11	110	1900	Northfield	Dog River
	66	59	5.5	<4	36	650	Burlington Main	Lake Champlain
	130J	<4	3.5J	<4	<4	290	Burlington Riverside	Winooski River
	37	<4	3.7J	<4	31	1000	Saint Albans	Steven's Brook
	15	<4	32	<4	40	310	Saxtons River	Saxtons River
	12J	<4	<4	8.6	16	430	Middlebury	Otter Creek
	13J	<4	<4	<4	23	170	Manchester	Batten Kill
	53	55	4.2	4.1	<4	370	Rutland	Otter Creek
concentrations in ng/L								
J = estimated								

In 2008, the VTDEC followed up with analysis of treated effluent from eight WWTFs releasing effluent to the Winooski River as well as two sites on the Winooski itself (62). This data set shows the variability in effluent PPCP concentrations in several WWTFs within a small geographic area. The Essex facility seems to dominate detections in this study, with significantly higher levels of: triclosan, 5-methyl-1H-benzotriazole, phenol, tributylphosphate, DEET, several phenolic surfactant metabolites, triethyl citrate, and bisphenol A.

Table 16. PPCPs in Winooski Basin of Vermont WWTF Final Effluent, 2008 (62).

Analyte (results in ug/L)	Waterbury	Richmond	IBM	Essex	Winooski	Burlington- Riverside	South Burlington	Burlington- North	Winooski River (at Riverside Marina)	Winooski River (at Route 127 bridge)
Antimicrobial disinfectant										
Triclosan	0.244	E0.143	< 0.2	0.519	< 0.2	E0.143	< 0.2	E0.127	< 0.2	NA
Anticorrosive										
5-Methyl-1H-benzotriazole	0.343	0.275	0.6	4.65	0.265	0.916	0.682	0.249	0.226	NA
Antioxidant										
3-tert-Butyl-4-hydroxyanisole (BHA)	<0.2	<0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	<0.2	< 0.2	NA
p-Cresol	<0.2	E0.141	< 0.2	E0.117	< 0.2	< 0.2	E0.0317	E0.0657	< 0.2	NA
Deodorizer										
1,4-Dichlorobenzene	< 0.2	E0.161	< 0.2	0.284	E0.0486	0.42	0.214	E0.125	<0.2	NA
Disinfectant										
Phenol	<0.2	< 0.2	< 0.2	0.249	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	NA
Fire Retardants										
BDE congener 47	<0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	NA
Tributyl phosphate	0.458	< 0.2	< 0.2	0.451	E0.0625	E0.184	E0.0844	E0.0745	< 0.2	NA
Tris(2-butoxyethyl) phosphate	<0.2	< 0.2	< 0.2	<0.2	<0.2	0.189	0.283	< 0.2	<0.2	NA
Tris(2-chloroethyl) phosphate	0.408	0.341	0.0334	0.634	0.319	0.244	0.35	0.295	<0.2	NA
Tris(dichloroisopropyl) phosphate	0.267	0.502	< 0.2	0.679	0.459	0.276	0.375	0.572	<0.2	NA
Fragrance/Flavorant										
3-Methyl-1H-indole	< 0.2	E0.0321	< 0.2	<0.2	E0.0197	E0.0217	< 0.2	E0.0324	< 0.2	NA
Acetophenone	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	NA
Acetyl hexamethyl tetrahydro naphthalene	E0.0486	E0.189	< 0.2	E0.191	E0.072	E0.137	E0.153	0.233	< 0.2	NA

Analyte (results in ug/L)	Waterbury	Richmond	IBM	Essex	Winooski	Burlington- Riverside	South Burlington	Burlington- North	Winooski River (at Riverside Marina)	Winooski River (at Route 127 bridge)
Hexahydrohexamethyl cyclopentabenzopyran	E0.152	1.89	<0.2	2.14	0.856	1.12	1.17	1.85	<0.2	NA
Isoborneol	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Isoquinoline	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Camphor	<0.2	E0.119	<0.2	E0.11	<0.2	E0.0286	E0.106	<0.2	<0.2	NA
Menthol	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Fungicide										
D-Limonene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Herbicide										
Atrazine, water	<0.2	<0.2	E0.038 4	<0.2	E0.0555	<0.2	<0.2	<0.2	<0.2	NA
Bromacil	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Metolachlor	<0.2	<0.2	<0.2	0.91	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Prometon	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Insecticide										
Carbaryl	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Chlorpyrifos	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Diazinon	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Dichlorvos	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Pesticides										
9,10-Anthraquinone	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Metalaxyl	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Pentachlorophenol	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	NA
Indole	<0.2	E0.0624	E0.010 3	<0.2	E0.0241	E0.0237	<0.2	E0.0187	<0.2	NA
Insect Repellent										
DEET	<0.2	<0.2	<0.2	0.91	<0.2	<0.2	<0.2	<0.2	<0.2	
Non-ionic Detergent Metabolites										
4-Cumylphenol	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
4-n-Octylphenol	<0.2	E0.181	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
4-Nonylphenol	<1.6	<1.6	<1.6	2.81	<1.6	E0.673	E0.811	E0.48	<1.6	NA
4-Nonylphenol diethoxylate	<3.2	<3.2	<3.2	5.83	<3.2	<3.2	<3.2	<3.2	<3.2	NA
4-Nonylphenol monoethoxylate	<0.2	<0.2	<0.2	2.71	<0.2	<0.2	<0.2	<0.2	<0.2	NA
4-tert-Octylphenol diethoxylate	<3.2	<3.2	<3.2	E0.515	<3.2	E0.222	E0.611	<3.2	<3.2	NA
4-tert-Octylphenol monoethoxylate	<1	<1	<1	<1	<1	<1	<1	<1	<1	NA
4-tert-Octylphenol	<0.2	<0.2	<0.2	0.318	<0.2	<0.2	<0.2	<0.2	<0.2	NA
PAHs										
1-Methylnaphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
2,6-Dimethylnaphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
2-Methylnaphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Anthracene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Benzo[a]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Carbazole	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Fluoranthene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Phenanthrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Naphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	NA
Plant / Animal Steroids										
3-beta-Coprostanol	0.943	<0.8	<0.8	1.84	1.09	1.55	2.35	0.822	<0.8	NA

Analyte (results in ug/L)	Waterbury	Richmond	IBM	Essex	Winooski	Burlington- Riverside	South Burlington	Burlington- North	Winooski River (at Riverside Marina)	Winooski River (at Route 127 bridge)
beta-Sitosterol	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	NA
beta-Stigmastanol	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	NA
Cholesterol	1.54	0.907	< 0.8	2.36	2.02	0.782	1.82	1.2	< 0.8	NA
Plasticizers										
Benzophenone	0.438	0.348	0.0484	0.738	0.227	0.321	0.482	0.424	< 0.2	NA
Bis(2-ethylhexyl) phthalate	<0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	NA
Bisphenol A	< 0.4	< 0.4	< 0.4	0.327	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	NA
Bisphenol A-d3 (percent recovery)	82.8688	90.0386	0	52.463 2	79.8972	31.2795	86.5523	74.4605	59.214	NA
Diethyl phthalate	<0.2	< 0.2	< 0.2	0.972	0.217	<0.2	< 0.2	< 0.2	0.27	NA
Triethyl citrate	0.199	E0.145	< 0.2	1.31	E0.123	0.49	0.431	0.601	E0.0378	NA
Triphenyl phosphate	<0.2	< 0.2	< 0.2	<0.2	E0.0422	E0.0405	E0.0502	E0.0662	< 0.2	NA
Other										
Tribromomethane	0.195	< 0.2	0.119	< 0.2	< 0.2	<0.2	0.543	< 0.2	< 0.2	NA
3,4-Dichlorophenyl isocyanate	0.917	0.411	< 0.2	1.42	E0.984	0.248	0.599	1.4	< 0.2	NA
Caffeine	<0.2	E0.094	<0.2	E0.149	<0.2	E0.0845	<0.2	<0.2	E0.0624	NA
Cotinine	< 0.8	< 0.8	< 0.8	0.516	< 0.8	< 0.8	0.217	< 0.8	0.108	NA
Isophorone	E0.0228	E0.0167	< 0.2	<0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	NA
Isopropylbenzene	<0.2	< 0.2	< 0.2	0.249	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	NA
Methyl salicylate	<0.2	< 0.2	< 0.2	0.0435	0.0352	<0.2	< 0.2	< 0.2	< 0.2	NA
Tetrachloroethene	<0.4	<0.4	E0.010 6	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	NA
Columbia Analytical Services (ng/l)										
Bisphenol A	<10	<10	<10	110	<10	<10	<10	<10	<10	<10
Diethylstilbestrol (DES)	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Estradiol	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Estriol	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Estrone	<1.0	1.5	<1.0	9	1.3	<1.0	<1.0	<1.0	<1.0	<1.0
alpha-Estradiol	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Fluoxetine (ng//l)	1.9	46	<1.0	110	620	78	64	71	1.1	1.5
Iopromide	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

In 2006, the USGS undertook to study OCECs in several WWTFs of the Champlain Basin, as well as several stream and lake sites (52). This widespread investigation of OCECs in the Champlain basin, looked for 62 primarily wastewater compounds, with particular emphasis on WWTF effluent and CSO inputs to surface waters. Table 17 summarizes results for those compounds detected in five or more samples. This major survey looked at water from 6 stream/river sites, 5 lake sites, and effluent from 6 WWTFs (Burlington, St. Albans, and Plattsburg) in order to give a broad overview of OCEC levels as of 2006. The data indicate that CSO flow and leaking sewer pipes are likely to be a significant source of OCECs into the urban streams studied. PAHs were found in urban streams, apparently not related to WWTF effluent. The likely source is runoff from paved surfaces related to asphalt, tire wear, sealcoat, and fossil fuels. Table 18, below, lists all data from this study.

TABLE 17. Range of Concentrations for Compounds Detected by Wastewater Method in Samples of CSO Effluent, and Median and Maximum Concentrations for Compounds Detected in WWTP Effluent and Urban-Stream Stormflow Samples, 2006 (52).

**Analyte	Range in CSO Concentration	Median /Maximum Concentration*	
		WTPP Effluents	Urban-Stream Stormflow
Detergent Degradates			
4-Nonylphenol diethoxylate	2.4-7.7	11 / 23	1.1 / 2.0
4-Octylphenol diethoxylates	nd	0.59 / 1.4	0.15 / 0.29
4-Octylphenol monoethoxylates	nd-0.35	0.28 / 1.6	nd / 0.073
4-tert-octylphenol	nd	0.12 / 0.91	nd / 0.046
p-Nonylphenol	1.1-2.4	2.5 / 14	nd / 0.77
Organophosphate Esters			
Tributyl phosphate	nd-0.056	0.15 / 0.65	nd / 0.038
Triphenyl phosphate	0.14-0.17	0.13 / 0.64	nd / 0.082
Tris(2-butoxyethyl)phosphate	1.0-9.2	0.87 / 19	0.43 / 0.68
Tris(2-chloroethyl)phosphate	0.082-0.085	0.18 / 0.58	nd / 0.057
Tris(dichloroisopropyl)phosphate	0.092-0.11	0.19 / 0.84	nd / 0.053
Fragrance / Flavorants			
3-Methyl-1(H)-indole	nd	0.037 / 1.3	0.030 / 0.053
Camphor	0.18-0.36	nd / 0.78	0.072 / 0.16
Galaxolide	0.37-0.43	1.25 / 3.7	nd / nd
Tonalide	nd-0.11	0.20 / 0.46	nd / nd
Pesticide			
Anthraquinone	0.19-0.30	nd / 0.53	0.23 / 0.71
Metolachlor	nd	nd / 0.034	nd / 0.11
N,N-Diethyl-meta-toluamide	nd-1.24	nd / 0.75	nd / 0.22
Polycyclic Aromatic Hydrocarbons (PAHs)			
1-Methylnaphthalene	0.024-0.026	nd / 0.017	nd / 0.45
2,6-Dimethylnaphthalene	0.006-0.025	nd / 0.010	nd / 0.11
2-Methylnaphthalene	0.035-0.040	nd / 0.016	nd / 0.21
Fluoranthene	0.067-0.082	0.0067 / 0.10	0.071 / 0.16
Phenanthrene	0.067-0.13	nd / nd	0.086 / 0.26
Pyrene	0.041-0.048	0.012 / 0.016	0.035 / 0.12
Sterols			
3-b-Coprostanol	1.58-1.68	0.20 / 0.49	nd / 0.54
b-Sitosterol	1.09-1.98	nd / 0.85	nd / 1.08
b-Stigmastanol	nd-1.38	nd / 0.94	nd / 1.44
Cholesterol	5.2-6.8	0.43 / 1.0	0.50 / 1.1

Other Compounds

1,4-Dichlorobenzene	0.078-0.15	0.15 / 0.52	nd / nd
Caffeine	11-12	nd / 2.4	0.28 / 2.2
Carbazole	0.045-0.13	nd / 0.63	0.061 / 0.18
Cotinine	0.25-0.33	0.34 / 1.8	nd / 0.21
Isophorone	0.039-0.057	nd / 0.040	nd / 0.025
p-cresol	0.36-1.2	0.69 / 1.3	0.18 / 2.1
Triclosan	nd	0.52 / 1.5	nd / nd
Triethyl citrate (ethyl citrate)	0.060-0.16	0.38 / 0.58	nd / nd

Notes: nd, not detected.

*Concentrations in micrograms per liter.

**Compounds include those that were detected in five or more instances from the 13 total samples collected from CSO (two samples), WWTP (six samples), and urban storm samples (five samples).

Table 18. Full Data Set From (52) showing collection sites, dates collected, and results. Site abbreviations at bottom of table.

[illegible]

Tris(dichloriso propyl)phosp hate	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	[0. 01 06]	nd	nd	nd		nd	[0. 05 31]	[0. 02 14]	nd	nd	nd	nd	[0. 02 85]		0. 18 4	0. 14 1	0. 31 4	0. 19 6	0. 83 9	0. 09 3		0. 09 18	0. 10 7
3-Methyl- 1(H)-indole (Skatol)	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	[0. 03]	nd	nd	[0. 03 12]	nd	nd	0. 05 35	nd			0. 04 19	[0. 00 66]	0. 06 13	[0. 03 22]	1. 33	[0. 01 57]		nd	nd	
Acetophenon e	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0. 21 1	nd			nd	nd	0. 10 3	nd	nd	nd		0. 20 8	0. 21 1	
Camphor	nd	nd	nd	nd	nd	nd	nd		nd	[0. 01 55]	[0. 02 15]	[0. 01 13]	[0. 01 14]	[0. 01 09]	nd		0. 16	0. 06 92	[0. 01 67]	0. 10 3	0. 05 1	[0. 01 65]	0. 07 17	0. 05 05		nd	nd	nd	nd	0. 77 8	0. 07 17		0. 17 8	0. 36 4
Galaxolide Hexahydrohex amethylcyclo pentabenzopy ran (HHCB)	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd		[0. 21 2]	[0. 24 2]	0. 45 6	[0. 19 4]	nd	[0. 17 8]		nd	[0. 10 6]	
Isoquinoline	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	0. 45 2	nd		nd	nd
Tonalide Acetylhexame thyletrahydro naphthalene (AHTN)	[0. 00 98]	nd	nd	nd	nd	nd	nd		nd	nd	[0. 01 78]	[0. 01 57]	[0. 01 34]	nd	nd		nd	nd	nd	nd	nd	nd	nd		1. 9	1. 41	3. 67	1. 08	nd	0. 78 3		0. 37 2	0. 43 2	
Anthraquinon e	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		0. 2	0. 23 4	[0. 03 02]	0. 33 2	0. 11 8	[0. 02 46]	0. 70 7	0. 40 4		nd	nd	nd	nd	0. 53 5	nd		0. 29 8	0. 18 6	
Bromacil	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	0. 40 7		nd	nd	
Carbaryl	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd	[0. 01 39]		nd	nd	nd	nd	0. 56 5	nd		nd	nd
Chlorpyrifos	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd
Diazinon	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd
d-Limonene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	[0. 01 57]	nd		nd	nd	nd	nd	nd	nd	[0. 04 33]	nd		nd	nd	nd	nd	0. 19 3	[0. 01 88]		nd	0. 15 8
Indole	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0. 02 8]	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	0. 48 6	[0. 05 95]		nd	nd	

Metalaxyl	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd		nd	nd	
Metolachlor	[0.0309]	[0.0578]	[0.0271]	[0.0286]	0.163	0.242	0.137		0.161	[0.0702]	nd	nd	nd	nd		nd	nd	nd	nd	[0.0193]	nd	0.114	0.171		nd	nd	nd	[0.034]	nd	[0.0333]		nd	nd
N,N-diethyl-meta-toluamide (DEET)	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	0.144	nd	nd	nd	nd	0.219	nd		0.327	nd	nd	nd	0.75	nd		1.24	nd
Prometon	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd
1-Methylnaphthalene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0.02]	nd	nd	nd	nd	nd	0.451	[0.0267]		nd	nd	nd	nd	nd	[0.0166]		[0.0264]	[0.0244]
2,6-Dimethylnaphthalene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0.0059]	nd	nd	nd	nd	nd	0.106	nd		nd	nd	nd	nd	nd	[0.01]		[0.0251]	[0.006]
2-Methylnaphthalene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0.026]	nd	nd	nd	nd	nd	0.212	[0.0105]		nd	nd	nd	nd	nd	[0.016]		0.0402	[0.0353]
Anthracene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0.0074]	nd	[0.0071]	nd	nd	nd	0.0778	[0.0073]		nd	nd	nd	nd	nd	[0.005]		nd	nd
Benzo[a]pyrene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd
Fluoranthene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		0.071	[0.0268]	[0.0225]	0.0721	[0.0265]	[0.0055]	0.163	0.064		[0.0077]	[0.0088]	[0.0057]	nd	nd	[0.0104]		0.0821	0.0668
Naphthalene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	0.851	0.0935		nd	nd	nd	nd	nd	nd		nd	nd
Phenanthrene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		0.1	nd	nd	0.0863	nd	nd	0.263	nd		nd	nd	nd	nd	nd	nd		0.135	0.0674
Pyrene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0.035]	[0.0181]	[0.0115]	[0.037]	[0.0174]	[0.0033]	0.119	0.0465		[0.0125]	[0.0164]	[0.0108]	[0.01]	nd	[0.0128]		0.0478	0.041
3-beta-Coprostanol	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	[0.426]	nd	nd	[0.538]	nd		[0.208]	[0.486]	[0.199]	nd	nd	[0.405]		1.58	1.68
beta-Sitosterol	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	[0.842]	nd	nd	1.08	[0.286]		nd	[0.846]	nd	nd	nd	[0.712]		1.09	1.98

beta-Stigmasterol	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd	nd	nd	[0.94]	nd	nd	1.44	nd		nd	[0.93 9]	nd	nd	nd	[0.71 5]		nd	1.38	
Cholesterol	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	[0.48 4]	nd	1.1	[0.50 4]	nd	1.05	[0.45 6]		[0.42]	1.02	[0.44 1]	[0.31 1]	nd	0.78 6	5.15	6.8	
1,4-Dichlorobenze ne	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd		0.20 6	0.10 2	0.30 5	0.05 6	nd	0.51 7		0.14 8	0.07 76	
3-tert-Butyl-4-hydroxy anisole (BHA)	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd		nd	[0.02 28]	[0.05 58]	nd	nd	nd		nd	nd	
5-Methyl-1H-benzotriazole	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	[0.04 71]	nd	nd	nd	nd	nd		1.79	[0.30 2]	nd	1.21	nd	[0.21]		nd	nd
Benzophenon e	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd		nd	nd	0.34 5	nd	0.6	nd		nd	nd	
Bisphenol A	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	
Bromoform	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd		nd	[0.01 21]	nd	nd	nd	nd	[0.01 92]	91.7	30.1	
Caffeine	[0.01 99]	nd	nd	[0.01 9]	nd	nd	nd		nd	[0.02 7]	[0.03 52]	nd	nd	nd	nd		0.42	0.12 48	nd	0.27 7	0.11 3	nd	1.35 28	0.30 5		nd	nd	nd	nd	[0.00 49]	2.41	10.5	12.2
Carbazole	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		0.06 1	0.04 1	[0.00 65]	0.12 9	[0.02 72]	nd	0.17 6	0.09 5		nd	nd	nd	nd	0.63 4	nd	0.13 1	0.04 48	
Cotinine	nd	nd	nd	nd	nd	nd	nd		1.03	nd	nd	nd	nd	nd		[0.07 4]	nd	nd	nd	nd	nd	0.21	[0.04 14]		0.39 5	[0.10 8]	1.82	nd	1.03	0.28 2		0.24 6	0.32 5
Isoborneol	nd	nd	nd	nd	nd		nd		nd	nd	nd		nd	nd		nd	nd		nd	nd		nd			nd	nd	nd	nd	0.73 8	nd	0.08 76	nd	
Isophorone	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		[0.02 5]	nd	nd	0	nd	nd	0	[0.01 34]		nd	nd	[0.03 97]	[0.01 78]	nd	nd		[0.05 67]	[0.03 85]
Isopropylbenz ene	nd	nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd	[0.02 81]	nd		nd	nd	nd	nd	0.29 5	nd		nd	[0.00 87]
Menthol	nd	nd	nd	nd	nd		nd		nd	nd	nd		nd	nd		nd	nd		nd	nd		0.3			nd	nd	nd	nd	0.76	0.33	1.06	nd	

[illegible]

[illegible]

Table 19 shows unpublished results for sediment samples collected at several sites as part of (52). Note that the predominant detections in the urban streams and Burlington Bay are the PAHs; benzo[a]pyrene, fluoranthene, phenanthrene, and pyrene. In Missisquoi Bay, the only significant detections were p-cresol, usually an industrial compound, and skatole from mammalian feces. The source and significance of these is unknown.

Table 19. Wastewater contaminants in Sediments from the Lake Champlain Basin 2006. Site abbreviations are the same as in Table 18, above.

		Stream/River Sites						Lake Sites	
		SEB	SMR	SPB	SRB	SSB	SWR	LBB	LMB
Compound	Reporting Level (µg/kg)	7/12/06	7/31/06	7/12/06	7/18/06	7/18/06	7/31/06	8/17/06	8/17/06
1,4-di- chloro- benzene	<30	<35	<30	<35	<30	<35	<40	<265	<505
1-methyl - naphthalene	<30	<35	<30	<35	<30	56.58	<40	<265	<505
2,2',4,4'-tetra- bromo- diphenyl ether	<30	<35	<30	<35	<30	E11.04	<40	E168.9	--
2,6-dimethyl- naphthalene	<30	<35	E10.05	E5.971	<30	E48.7	E7.233	<265	<505
2-methyl - naphthalene	<30	<35	<30	<35	<30	83.09	<40	<265	<505
3- <i>beta</i> - Coprostanol	<500	E51.52	E71.88	E52.96	E34.49	E1401	E162.3	<2650	<5050
3-methyl-1(H)- indole (Skatol)	<50	E20.71	E14.11	E24.38	E9.243	E23.63	E13.46	E125.2	1261
3- <i>tert</i> -butyl-4- hydroxy anisole (BHA)	<90	<105	<90	<105	<90	<105	<120	<795	<1010
4-cumyl- phenol	<30	<35	<30	<35	<30	<35	<40	<265	<505
4-n-octylphenol	<30	<35	<30	<35	<30	<35	<40	<265	<505
4-nonylphenol diethoxylate	<600	<700	<600	E440.4	<600	<700	<800	<5300	<10100
4-nonylphenol monoethoxylate	<300	<350	<300	E264.8	<300	<350	<400	<2650	<505
4-octylphenol diethoxylate	<30	<35	<30	<35	<30	<35	<40	<265	<505
4-octylphenol mono- ethoxylates	<150	<175	<150	<175	<150	<175	<200	<1325	<2525
4- <i>tert</i> -octyl- phenol	<30	<35	<30	<35	<30	<35	<40	<265	<505
Aceto- phenone	<100	E44.6	E26.25	E32.32	E10.94	E61.27	E36.45	<795	<1010
AHTN (Tonalide)	<30	<35	<30	<35	<30	<35	<40	<265	<505

		Stream/River Sites						Lake Sites	
		SEB	SMR	SPB	SRB	SSB	SWR	LBB	LMB
Anthracene	<30	115.5	E12.6	E18.53	<30	159.9	E15.38	E111.2	<505
Anthraquinone	<30	136.3	E12.18	51.12	<30	252.7	E25.13	E229.4	<505
Atrazine	<60	<70	<60	<70	<60	<70	<80	<530	<1010
Benzo[a]pyrene	<50	318.3	E6.78	88.27	E1.52	471.7	E37.27	437	E51.11
Benzophenone	<30	<35	<30	<35	<30	<35	<40	E62.88	<505
Beta-Sitosterol	<500	E1572	E1018	E1400	E486.3	E3959	E2575	<2650	E6302
Beta-Stigmastanol	<500	E221.3	E363.5	E262.4	E88.55	E777.6	E596.7	<2650	E2527
Bis(2-ethylhexyl) phthalate	<150	E174.6	<150	E117.2	<150	289	<200	E469	<2525
Bisphenol A	<50	--	--	--	--	E100.3	E12.8	--	--
Bromacil	<300	<350	<300	<350	<300	<350	<400	<2650	<5050
Camphor	<30	<35	<30	<35	<30	<35	<40	<265	<505
Carbazole	<30	80.34	E7.367	E21.86	<30	114	E8.669	E83.86	<505
Chlorpyrifos	<30	<35	<30	<35	<30	<35	<40	<265	<505
Cholesterol	<250	E1240	E482.4	E898.3	E235.3	E3066	E873.5	<1325	E6127
Diazinon	<30	<35	<30	<35	<30	<35	<40	<265	<505
Diethylphthalate	<60	<70	<60	<70	<60	<70	<80	<530	<1010
D-Limonene	<30	<35	<30	<35	<30	<35	<40	<265	<505
Fluoranthene	<30	1317	E43.13	228.8	<30	1717	108.6	1109	E98.56
HHCb (Galaxolide)	<30	<35	<30	<35	<30	<35	<40	<265	<505
Indole	<60	E28.22	157.2	89.02	<60	E37.26	252.8	E501.8	E505.9
Isoborneol	<30	<35	<30	<35	<30	<35	<40	--	<505
Isophorone	<30	<35	<30	<35	<30	<35	<40	<265	<505
Isopropylbenzene	<60	<70	<60	<70	<60	<70	<80	<530	<1010
Isoquinoline	<60	<70	<60	<70	<60	<70	<80	<530	<1010
Menthol	<30	<35	<30	<35	<30	<35	<40	--	<505
Metolachlor	<30	<35	<30	<35	<30	<35	<40	<265	<505
N,N-di-ethyl-meta-toluamide (DEET)	<60	<70	<60	<70	<60	<70	<80	<530	<1010
Naphthalene	<30	<35	<30	<35	<30	97.46	<40	E67.12	<505
para-cresol	<50	202.5	E45.86	307.8	E15.59	E142.3	E63.44	<1325	6390
para-nonylphenol	<450	E160	<450	E236.6	<450	E192.3	<600	<3975	<7575
Phenanthrene	<30	530.1	E40.49	92.46	<30	951.7	50.18	436.5	<505
Phenol	<50	E215.8	E217.5	E103.9	E26.56	E243.8	E318.8	<265	<505
Prometon	<30	<35	<30	<35	<30	<35	<40	<265	<505
Pyrene	<30	1058	E33.51	175.7	<30	1368	89.22	922.4	E72.45

		Stream/River Sites							Lake Sites	
		SEB	SMR	SPB	SRB	SSB	SWR		LBB	LMB
Tributyl phosphate	<30	<35	<30	<35	<30	<35	<40		<265	<505
Triclosan	<30	<35	<30	<35	<30	<35	<40		<265	<505
Triphenyl phosphate	<30	<35	<30	<35	<30	<35	<40		<265	<505
Tris (2-butoxy-ethyl) phosphate	<90	<105	<90	<105	<90	<105	<120		<795	<1010
Tris (2-chloro-ethyl) phosphate	<60	<70	<60	<70	<60	<70	<80		<530	<1010
Tris (dichloro-propyl) phosphate	<60	<70	<60	<70	<60	<70	<80		<530	<1010

In 2007, the USGS built upon this work by investigating contributions of CSO flow to overall annual loadings to Lake Champlain from the Burlington Main WWTF and by adding hormones to the analyte list (53). Their results include load estimates into Lake Champlain for compounds both efficiently removed and poorly removed by WWTF (activated sludge) treatment. Loading from efficiently removed compounds was dominated by untreated (CSO) sewage, while poorly removed compound loadings were dominated by treated WWTF effluent. Therefore, cities with large (untreated) CSO discharges may be allowing significant OCECs into surface waters, even for compounds well removed by the WWTF. As can be seen from Table 20, some compounds are not well removed by the WWTF so they are seen almost as often in the treated waste as in the CSO.

Table 20. Detections of Trace Wastewater Contaminants, Burlington, VT (53).

COMPOUND	ABBREVIATION	REPORTING LIMIT (ng/L)	PERCENT DETECTION	
			PLANT EFFLUENT	CSO
Estrogens				
17-beta-estradiol	E2	0.8	25	93
Estriol	E3	0.8	55	100
Estrone	E1	0.8	90	100
Androgens				
11-Ketotestosterone	11-K	0.8	0	75
Androstenedione	ADSD	2	84	100
cis-Androsterone	CAN	0.8	74	100
Dihydrotestosterone	DHT	4	5	96

Epi-testosterone	EPI	4	0	76
Testosterone	TES	0.8	5	96
Wastewater Micropollutants				
3-beta-Coprostanol	COP	2000	95	100
Benzophenone	BEP	200	86	83
beta-Sitosterol	SIT	800	86	100
Bisphenol A	BPA	100	53	60
Caffeine	CAF	200	64	100
Cholesterol	CHO	2000	90	100
Galaxolide	GAL	200	100	100
Tri(2-butoxyethyl) phosphate (TBEP)	TBE	200	95	100
Triclosan	TCS	200	100	100

In 2008 and 2009, the USGS investigated the estrogenicity of WWTF effluent from several facilities in the Champlain Valley of New York, as part of a larger study of New York City WWTF effluents (63). Effluent from a pharmaceutical production facility in the Chazy, NY area was checked for estrogenicity and also analyzed for endocrine disrupters and hormones on four occasions. Samples were analyzed for 69 wastewater contaminants as well as 28 hormones and pharmaceuticals. Estrogenicity was estimated with a cell proliferation “e-screen” assay using human breast cancer cells. Results were generally below reporting levels for all compounds, with the exception of the spring 2009 sample. This sample contained significant amounts of: Estrone (11.075 ng/L), 4-androstene-3,17-dione (1.318 ng/L), 3-B-coprostanol (5131.167 ng/L), and cholesterol (20123.86 ng/L).

Vatovec et al. investigated daily changes in pharmaceutical levels in influent and effluent from the Burlington, VT Main WWTF in May 2014 (64). Effluent samples were collected daily for ten days and analyzed for a large suite of pharmaceuticals in order to assess changes in effluent during and after students from the University of Vermont were leaving at the end of the school year. The goal was to study the contribution of college students to the pharmaceutical loads in a city with a significant portion of college students, and to look for evidence of pharmaceuticals being flushed at the end of the school year. No evidence was found for significant flushing of unwanted drugs. Cardiovascular, diabetes, and antihistamine concentrations increased over the ten day period, likely due to less dilution of waste from older residents as students left. The following is a table with daily pharmaceutical concentrations in ng/L, as well as influent samples at the beginning and end of the study.

Table 21. Daily Burlington VT Main WWTF Influent and Effluent May 1-10, 2014 (64).

Site	Effluent										Day 1 Comparison		Day 10 Comparison	
											Influent	Effluent	Influent	Effluent
Date	May 1	May 2	May 3	May 4	May 5	May 6	May 7	May 8	May 9	May 10	May 1	May 2	May 10	May 10
10-Hydroxy-amitriptyline	19.6	17.6	27.5	16.4	15.0	32.9	24.3	21.3	30.3	31.0	14.2	15.8	10.3	20.4
Abacavir	16.0	13.7	17.2	12.9	10.8	18.2	9.59	13.4	14.2	13.8	26.2	9.89	20.6	8.87
Acetaminophen	59.6	29.6	82.7	65.4	22.3	43.2	43.1	30.7	71.5	68.4	30100	40.8	58900	46.8

Site	Effluent										Day 1 Comparison		Day 10 Comparison	
											Influent	Effluent	Influent	Effluent
Date	May 1	May 2	May 3	May 4	May 5	May 6	May 7	May 8	May 9	May 10	May 1	May 2	May 10	May 10
Acyclovir	1890	1150	1330	1400	995	1820	1260	1120	1440	1490	1800	997	2120	1160
Albuterol	9.48	9.95	15.2	11.1	8.53	18.9	13.6	11.8	15.9	16.7	11.0	8.25	11.5	12.1
Alprazolam	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	dnq	<4.3	<4.3	<4.3	<4.3
Amitriptyline	18.7	dnq	21.3	dnq	dnq	22.9	dnq	26.8	27.0	35.1	14.5	17.9	20.2	22.0
Amphetamine	30.21	22.64	30.89	23.55	14.69	35.86	29.43	24.19	33.80	31.02	319	20.23	293	22.95
Antipyrine	<58	<58	<58	<58	<58	<58	<58	<58	<58	<58	<58	<58	<58	<58
Atenolol	1160	905.0	1390	1020	874.0	1700	1070	1160	1570	1620	1030	678.0	1000	1100
Benztropine	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9	<7.9
Betamethasone	<57	<57	<57	<57	<57	<57	<57	<57	<57	<57	<57	<57	<57	<57
Bupropion	180	164	248	163	167	262	187	226	284	244	146	125	170	185
Carbamazepine	199	149	200	149	125	213	152	171	247	267	157	131	132	182
Carisoprodol	4.77	<2.5	6.71	<2.5	<2.5	<2.5	<2.5	<2.5	5.62	<2.5	<2.5	<2.5	<2.5	4.66
Chlorpheniramine	4.86	4.19	6.11	4.90	4.87	7.65	6.40	6.40	9.29	10.6	4.68	4.47	4.43	5.97
Cimetidine	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6	79.6	<5.6	102	<5.6
Citalopram	227	202	316	196	217	339	260	276	334	359	226	175	199	232
Clonidine	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Codeine	144	124	180	103	91.4	182	124	126	195	192	94.2	95.0	76.3	125
Dehydronifedipine	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	dnq	4.9	4.9	<4.9	<4.9
Desvenlafaxine	1240	1020	1500	966	918	1740	1220	1200	1660	1600	702	786	623	1140
Dextromethorphan	50.0	40.3	61.5	50.9	38.5	75.2	56.5	55.3	77.8	95.5	44.2	34.6	57.1	60.2
Diazepam (valium)	1.61	dnq	1.34	dnq	0.684	1.72	1.40	dnq	1.10	1.26	1.21	1.18	0.838	1.25
Diltiazem	53.7	46.4	62.8	42.9	41.6	65.9	58.8	57.3	71.5	90.5	87.6	43.1	96.8	64.7
Diphenhydramine	343	318	536	328	319	631	467	469	618	648	195	256	260	442
Duloxetine	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3
Erythromycin	dnq	dnq	28.8	<27	dnq	<27	<27	dnq	<27	<27	<27	<27	<27	<27
Ezetimibe	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13
Fadrozole	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
Famotidine	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	173	<2.1	260	<2.1
Fenofibrate	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Fexofenadine	1930	1560	2290	1440	1460	2620	1950	1970	2820	2910	1790	1250	1710	1870
Fluconazole	116	70.1	150	80.6	55.2	159	105	120	160	173	94.7	64.7	100	131
Fluoxetine	22.5	23.1	33.0	21.0	24.9	25.5	25.7	32.9	36.4	44.1	22.5	22.9	44.4	38.8
Fluticasone propionate	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92
Fluvoxamine	<27	<27	<27	<27	<27	<27	<27	<27	<27	<27	<27	<27	dnq	<27
Glipizide	<150	<150	<150	<150	<150	<150	<150	<150	<150	<150	<150	<150	<150	<150
Glyburide	<0.79	<0.79	<0.79	<0.79	<0.79	<0.79	<0.79	3.96	8.19	6.54	<0.79	<0.79	7.68	5.28
Hydrocodone	19.9	18.0	24.2	15.1	12.5	24.9	19.6	17.5	30.2	32.8	30.4	26.2	23.8	22.4

[illegible]

Site	Effluent										Day 1 Comparison		Day 10 Comparison	
											Influent	Effluent	Influent	Effluent
Date	May 1	May 2	May 3	May 4	May 5	May 6	May 7	May 8	May 9	May 10	May 1	May 2	May 10	May 10
Prednisone	<84	<84	<84	<84	<84	<84	<84	<84	<84	<84	<84	<84	<84	<84
Promethazine	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	14.4	<10
Propoxyphene	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4
Propranolol	57.1	47.2	67.8	43.5	34.2	67.7	54.5	51.5	67.5	77.1	65.1	46.7	32.0	53.2
Pseudoephedrine + Ephedrine	28.3	14.8	25.7	19.6	9.29	24.4	20.2	16.7	28.5	25.7	921	18.5	951	20.4
Quinine	92.2	72.4	164	112	81.8	128	88.2	74.1	111	171	84.6	60.6	127	132
Raloxifene	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9
Ranitidine	<38	dnq	dnq	<38	<38	<38	<38	<38	<38	<38	1470	<38	1140	<38
Sertraline	25.6	18.3	29.6	29.0	23.5	36.6	32.6	48.8	43.4	58.3	15.7	20.7	22.8	22.6
Sitagliptin	256	196	305	176	184	379	287	246	376	390	179	145	218	234
Sulfadimethoxine	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33
Sulfamethizole	<21	<21	<21	<21	<21	<21	<21	<21	<21	<21	<21	<21	<21	<21
Sulfamethoxazole	211	216	430	163	113	296	169	141	280	220	331	179	219	164
Tamoxifen	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80
Temazepam	41.1	35.2	46.9	33.1	36.3	63.0	55.1	46.1	61.3	66.3	21.1	26.0	<9.2	39.3
Theophylline	608	281	251	325	164	484	384	263	273	236	1800	367	1640	172
Thiabendazole	21.2	16.9	22.9	17.6	12.9	20.9	15.5	17.5	35.2	36.0	20.2	12.4	22.9	24.2
Tiotropium	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6	<8.6
Tramadol	493	404	590	472	414	740	501	482	666	669	358	264	403	464
Triamterene	46.5	120	100	45.6	36.8	48.5	43.3	39.8	50.1	58.8	26.0	27.6	34.9	39.3
Trimethoprim	325	268	507	274	202	434	277	277	370	390	359	237	226	252
Valacyclovir	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33
Venlafaxine	451	377	575	381	351	680	460	457	660	685	354	292	365	476
Verapamil	33.2	21.6	26.6	13.9	15.5	17.5	15.5	20.4	18.5	32.2	70.4	30.0	33.6	16.7
Warfarin	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	dnq	<3.0	<3.0	<3.0
1,7-Dimethylxanthine (p-Xanthine)	868	347	449	489	236	685	539	312	464	479	6960	472	13500	366
Atrazine	10.1	10.2	13.4	12.9	10.0	16.7	11.5	11.2	16.2	22.8	11.3	dnq	14.0	15.4
Caffeine	5470	2004	2210	3190	1140	3140	2510	1563	2100	1828	30000	3650	61200	1230
Cotinine	83.8	51.0	68.7	67.4	37.1	63.4	40.7	31.2	47.5	63.4	1006	54.8	1050	42.7
methyl-1H-benzotriazole	503	1070	1830	1920	1540	3210	2170	1230	1290	1490	480	374	703	1140
nicotine	dnq	<29	dnq	dnq	<29	<29	dnq	<29	dnq	43.0	4480	<29	3960	dnq
Piperonyl butoxide	16.8	22.1	72.2	39.0	33.7	34.9	44.0	50.2	60.3	140	60.0	23.3	262	64.5

^a dnq = detected not quantified; < = less than; non detect values reflect method detection limit.

3.4 MISCELLANEOUS CURRENT AND ON-GOING PROJECTS, 2016.

3.4.1 C. Vatovec from UVM is following up on her 2014 work on pharmaceuticals in Burlington, VT WWTF effluent. Projects include Burlington finished and raw drinking water testing, testing for illicit drugs in Burlington VT effluent, and testing the raw influent from the UVM Medical Center into the Burlington WWTF.

3.4.2 The VAAFM is continuing its investigations into neonicotinoid transport from corn fields by continuing tile drain sample analyses as well as soil cores in and near corn fields.

3.4.3 The Vermont DEC is doing on-going investigations into perfluorinated compounds in Vermont, primarily investigating groundwater contamination in the Bennington, VT area. Other areas of the state are being investigated as well, and both surface water and fish have been analyzed.

3.4.4 D. Garneau from SUNY Plattsburg has collected water samples from Lake Champlain Basin WWTFs and tested them for microplastics and microfibers. Although no OCEC testing was done, microparticles are known to absorb toxins.

4. RISK ASSESSMENT, PRIORITIZATION, GAPS AND FUTURE EFFORTS.

4.1 RISK ASSESSMENT and PRIORITIZATION.

Numerous reviews have been published in the last several years, trying to address ways to perform risk assessments and prioritize future work. Increases in the number of new chemicals (currently around 89 million registered chemicals) as well as improvements in analytical methods are leading to increasing numbers of detections of potentially toxic micropollutants. Without a prioritization scheme to determine which compounds are of most concern, the cost of this monitoring could spiral out of control. As far back as 1980, Richard Schoettger of the US Environmental Protection Agency stated, “the US scientific community does not have the time, research facilities, trained personnel, experimental animals, nor financial resources to provide the additional data needed for comfortable predictions of the possible environmental effects of a broad spectrum of chemical contaminants” (Schoettger RA. 1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. US Department of the Interior, Fish and Wildlife Service, Washington, DC.).

Busch et al. (65) collated data from seven major European studies looking at a total of 970 different chemicals with the goal of prioritizing them based on presence and toxicity. These authors proposed working toward a suite of bioassays which could determine effects on biota rather than simply measuring chemicals without knowing if they are affecting any organisms. 426 compounds were detected at least once in at least one study, but only 13 were detected in every study, seven more were detected in 6 of 7 studies, and another 27 were found in 5 studies. Those found during all 7 studies were: 1H-Benzotriazole, 5-Methyl-benzotriazole, atenolol, atrazine, caffeine, carbamazepine, ciclofenac, diuron, isoproturon, metoprolol, sucralose, sulfamethoxazole, and terbuthylazine. Compounds were grouped by mode of action with the goal of proposing bioassays which might capture groups of compounds exerting similar effects.

Gerbersdorf et al. 2015 (66) in their review of OCECs in aquatic environments, also emphasize that bioassays may be more useful than chemical analyses, because effects are at times identifiable at levels lower than chemical techniques are currently capable of. They mention that the European Commission has set Environmental Quality Standards for 17 α -ethinylestradiol (EE2), and 17 β -estradiol (E2) of 35 and 400 pg/L respectively, both of which are extremely difficult to quantify with current analytical techniques.

Murray et al. (67) reviewed OCECs as of 2010. Based on their assessment using occurrence data and human health “acceptable daily intake” information they determined that: EE2, carbamazepine, and bE2 are very high priority pollutants, and PFOA, PFOS, and DEHP, pesticides diazinon, methoxychlor, and dieldrin, and PPCPs DEET, triclosan, acetaminophen, and E1 are high priority pollutants. Also includes tables of “widely reported” industrials, pesticides, and PPCPs as well as brief summaries of each category.

Johnson and Sumpter (68) argue that current environmental monitoring and risk assessments are wasteful because there is little evidence of actual harm to the aquatic biota from any emerging contaminants. Instead, we should be concentrating our efforts on monitoring fish and wildlife populations. An example was made of the poisoning of Asian vultures by eating carcasses of cattle which had been treated with the anti-inflammatory drug diclofenac. No-one could have predicted without having done lab testing that vultures would be especially sensitive to diclofenac, so it makes more sense to be watching for problems with wildlife at an individual or population level rather than doing environmental chemical monitoring without evidence of a problem. They conclude: “Monitoring aquatic wildlife diversity and abundance over time is probably the single most important activity that we should be doing in freshwater environmental science today and vital to the risk assessment of chemicals.”

Baldigo et al. (63) compared chemical analyses of WWTF effluent with cellular “e-screen” bioassays for estrogenic effects. They found that there was often estrogenicity which was unexplainable using the results of analyses for 69 wastewater contaminants and 28 hormones and pharmaceuticals. Either synergism was occurring or estrogenicity was caused by compounds not analyzed for.

European risk assessments seem to be concentrating on pharmaceuticals, using Risk Quotient (RQ) type calculations. $RQ = MEC \text{ (max measured enviro conc)}/PNEC \text{ (predicted no effect conc, usually LC50/1000 or EC50/1000)}$. An $RQ < 1$ indicates no ecotoxicological risk. In 2015, a risk assessment was published (69) of PPCPs in Greek waters using existing data and Risk Quotients (RQs). Algae, *Daphnia* and fish RQs were calculated in treated wastewater effluent. Table 22 lists those contaminants with at least one RQ greater than 1.

Table 22. Estimation of Risk Quotients, RQ (MEC/PNEC) for the emerging organic contaminants contained in treated wastewater. (For all other micropollutants RQ values were below 1 in all target aquatic organisms) (69)

Emerging contaminants	RQ values		
	Fish	<i>Daphnia magna</i>	Algae
Pharmaceuticals			
Amoxicillin	<1	<1	44
Atorvastatin	NA*	2.4	NA
Azithromycin	<1	<1	15
Caffeine	<1	<1	927
Clarithromycin	<1	<1	31
Clofibric acid	<1	1.9	<1
Diclofenac	1.3	<1	1
Fluoxetine	<1	<1	1.2
Gemfibrozil	1.9	<1	<1
Ofloxacin	<1	<1	9.8
Pentobarbital	<1	<1	38
Phenobarbital	<1	<1	18
Sertraline	<1	<1	2.4
Sulfamethoxazole	<1	<1	3.5
Theophylline	<1	<1	38

Tramadol	7.5	13	1.0
Tylosin	NA	<1	1.2
Valsartan	<1	<1	2.4
Venlafaxine	<1	<1	1.1
Endocrine disrupters			
4-t-octylphenol	1.4	<1	<1
Bisphenol A	7.0	<1	1.1
Nonylphenol	835	67	30
Nonylphenol diethoxylate	54	24	31
Nonylphenol monoethoxylate	32	21	22
Triclosan	27	18	4914
Benzotriazoles			
Tolytriazole	<1	<1	1.5
Artificial sweeteners			
Sucralose	<1	<1	113
Siloxanes			
Octamethylcyclotetrasilane	20	NA	NA
Decamethylcyclopentasilane	NA	2076	NA
Dodecamethylcyclohexasilane	NA	NA	30

As can be seen, nonylphenol had by far the highest RQ in fish, while decamethylcyclopentasilane was of most concern for *Daphnia magna*, and triclosan was highest for algae, although many compounds had RQ> 1 for algae.

The USEPA has developed a process for investigating whether there are contaminants which are currently unregulated in drinking water which may need to be regulated. This process begins with EPA asking for input from experts and the public for possible candidates, then puts together a “Contaminant Candidate List” (CCL). As of 2016, the EPA is on version CCL4, which includes estrogens, perfluorinated compounds, as well degradates of the acetanilide herbicides acetochlor, alachlor, and metolachlor. Again, these are compounds which EPA is concerned may need regulating, but sufficient data do not exist to make that determination.

In conjunction with the CCL process, EPA periodically requests Public Drinking Water facilities to test their finished drinking water for a subset of the unregulated contaminants on the CC Lists. These requests are part of the “Unregulated Contaminant Monitoring Rule” (UCMR). EPA has just finished collecting data for UCMR3 and is preparing UCMR4. The purpose of the UCMR process is to help gather data on whether some of the contaminants of concern on the CC List are actually present in drinking water. Large (>10,000 person) facilities are required to do the testing, and a subset of smaller facilities will be paid by EPA to do the testing. A criticism of UCMR1 and UCMR2 has been that the reporting limit requirements were in the ppb range, not low enough to detect compounds at real world levels of possible concern. UCMR3 contains natural and synthetic human hormones and perfluorinated compounds with reporting limits in the low ppt range, however, none of the drinking water facilities in Vermont which take water from Lake Champlain were asked to test for the hormone contaminants. Perfluorinated compounds were tested for at the Burlington Water Treatment facility, but none were detected.

One area of ongoing discussion is the concept of avoiding the cost of testing for hundreds of compounds by selecting specific compounds to use as indicators of contamination from specific sources. Examples of this might be the ESA metabolite of metolachlor which is ubiquitous wherever corn is grown and metolachlor is used so it can be an indicator for corn/agricultural sources. Another example is the artificial sweetener sucralose (SPLENDA®). This

compound is made by selectively chlorinating sucrose to create a molecule which is essentially inert to biological degradation, does not bioaccumulate, is mostly non-toxic because it is so inert, and is highly water soluble so passes through WWTF intact. These chemical characteristics give it the potential to be an excellent indicator for WWTF effluent contamination of surface waters. It leaves open the question though of what is happening to all of the sucralose leaving our WWTFs. Is it accumulating in water or sediment to the point where it will be found to be toxic to something? Caffeine and nicotine (and their metabolites), DEET, cholesterol, and coprostanol, are all ubiquitous in WWTF effluent and can also be used as indicators. Indicators of untreated effluent include: caffeine, TBEP, and cholesterol because they are removed well by WWTF when functioning properly. Indicators of (untreated and/or treated) effluent include: TCP, galaxolide, NP2EO because they are not well removed during the WWTF process therefore are indicators of the presence of wastewater.

4.2 GAPS in CURRENT KNOWLEDGE of OCECs in the CHAMPLAIN BASIN. The following represent some of the significant gaps in what we currently know about OCECs in the Champlain Basin.

4.2-A: OCECs in biosolids and manure (70, 71, and 72). Although this report has concentrated on OCECs in the aquatic environment, it is clear that there is little or no data on OCECs in biosolids from Vermont WWTFs or in veterinary medicines in manure from dairy farms. Similarly, there is no information on these compounds in the soil or runoff from where these biosolids are spread on fields in the Champlain Basin, or tile drain effluent from fields where biosolids are spread. Also, data on OCECs in sediment below WWTF outfalls does not exist. The sediment samples analyzed by USGS (see Table 19) as part of their 2006 study are a first step in this process, and illustrate the need for more work (52).

4.2-B: Runoff from lawns, parking lots and other urban areas not going into WWTFs or CSOs. Some pesticides used on urban lawns are likely to wash off and by-pass the WWTF system, going directly into urban streams or storm drains draining into streams, rivers and eventually the lake. The neonicotinoid imidacloprid and other insecticides are of especial concern. PAHs, and other hydrocarbons from automobile use and paved areas will follow the same route. Are coal-tar based pavement sealants being used by homeowners in the basin? The only data found to date characterizing urban runoff not going into WWTFs is in (50,52).

4.2-C: Septic system contributions. Much of the Lake Champlain Basin is rural and therefore homes use septic systems. Any OCECs surviving a septic system could end up in shallow groundwater, which may feed surface waters (73).

4.2-D: WWTF effluent. The Burlington Main WWTF is the only facility which has been well characterized for its influent and treated effluent OCEC concentrations. As can be seen in section 1.1, there are many other WWTFs which release treated effluent into the surface waters of the basin. Each WWTF has waste with different characteristics and have different treatment capabilities so periodic surveys of all WWTFs in the Champlain Basin would provide useful information.

4.2-E: PFOA movement from Burlington Airport and other areas of high PFC use in the basin to urban surface waters may be a concern. PFOA is highly water soluble and persistent so it is likely to be in urban surface waters.

4.2-F: Raw and Finished drinking water testing. It would be useful to test the raw and finished drinking water from public surface water sources for the UCMR3 contaminants, especially the PFCs and hormones.

4.2-G: Risk prioritization. Similar to the Greek risk assessment mentioned above (69), existing WWTF data could be used to determine which if any effluent OCECs have $RQ > 1$ and therefore need to be investigated further.

4.2-H: A Long-term, formalized monitoring program for pesticides and other OCECs in the basin. The current VAAFM surface water pesticide monitoring program is an internal program serving the needs of the VAAFM. A formal, peer-reviewed sampling and analysis plan organized with the goal of collecting long-term comparable data would be useful. Incorporating it into the LCBP LCLTMP would ensure that this occurs. OCECs from urban runoff or WWTF effluent may not be amenable to incorporation into the current LCLTMP sampling scheme. Samples routinely collected

from urban streams, storm drains and WWTF effluent for a select group of OCECs over the long term would give valuable information on loading and variability. Automatic samplers might be a cost effective way to make this possible.

4.2-I: Bioassays of WWTF effluent similar to the “e-screen” technique used in (63) would highlight WWTFs of concern for endocrine disruption without expensive chemical analyses.

4.2-J: Incorporate OCEC (pesticides and veterinary medicines) testing into future “edge of field” type studies of agricultural runoff.

4.2-K: Testing of fish and other biota for OCECs which tend to bioaccumulate.

4.2-L: Likewise, toxins from cyanobacteria blooms in the lake are a potential source of toxins not addressed in this paper.

4.3: FUTURE EFFORTS:

The purpose of this paper is to collect any existing data on OCECs in the waters of the Lake Champlain Basin. Inevitably, some information has been missed, but nonetheless this will be a substantial base to build upon while discussing priorities for future work on OCECs in the basin. In order to move forward on this issue, a scoping process is necessary to decide what areas are of most concern, and where data gaps exist.

The next logical step is to summarize what is known about organic contaminants in other compartments of the Lake Champlain ecosystem, such as the sediments and biota. With this information in hand, the LCBP Toxics Workgroup should be convened along with select regulators and policymakers to review this existing knowledge, decide if there are urgent gaps which need to be filled, and develop a one day conference bringing together state, provincial, and federal regulators, researchers, and other interested parties to review current knowledge and discuss OCEC areas of concern in the basin within the water, sediment, and biological compartments. This could be held in conjunction with a Lake Champlain Research Consortium conference proposed for winter 2017-2018. The goal of this conference would be to develop prioritized lists of research/monitoring needs with a concomitant agreement by funding agencies to prioritize funding for these projects.

A one day conference might start with an overview of the issues, then presentations where several researchers, such as Pat Phillips, Christene Vatovec, or others, summarize their work in the basin. These would be followed by breakout sessions with the following groups discussing their concerns, needs, interests, or wishes:

WWTF operators

Drinking water facility operators

Regulatory program administrators

Researchers

Concerned citizens/NGOs

The products of these breakout sessions should be lists of compounds or groups of compounds of most concern to each group and the environmental compartment of concern. At the end of the day the conference as a whole could reconvene to compare lists, make comments, and attempt a grand prioritized list of areas of concern within the basin. Are there pieces of information that everyone agrees are missing and needed? Are there areas where we have sufficient information to agree that they are not a concern? Are there regulatory or legislative issues that can or should be addressed? The list(s) should then go back to the Toxics Workgroup to decide if there are areas where progress is feasible and funding should be sought. These would be forwarded to the TAC as part of the LCBP grant proposal process.

If OCEC testing is proposed, it is suggested that a two phase testing protocol be used. The first phase would emphasize screening of a large number of compounds, similar to what USGS has undertaken with WWTF effluent, in a small number of samples of water, sediment, and biota from those areas of most concern. This could be accompanied by “e-screen” estrogenicity testing. The Toxics Workgroup would be the logical group to select those contaminants of concern and sample locations, based on the outcome of the conference. Samples should be sent to national labs such as USGS or USEPA labs where tests for large numbers of OCECs have already been developed. Select indicators such as caffeine, DEET, sucralose, metolchlor ESA, and coprostanol should be included in phase one to determine if they might

be useful. Using the results of phase one testing, the Toxics Workgroup should propose, if appropriate, a long-term monitoring program for OCECs, similar to the existing Lake Champlain Long-Term Monitoring Program for inorganics and nutrients. The LCBP should use this monitoring program to build capacity for OCEC and “e-screen” testing within the basin by expanding the existing partnership with the Vermont Agriculture and Environmental Laboratory (VAEL) beyond the current nutrient and metals testing to include organics. In order to keep this program sustainable, the Toxics Workgroup should minimize the number of compounds and samples analyzed per year to a select few compounds of most concern and/or indicator compounds linked to specific sources. Phase one should be repeated approximately every five years to detect potential new compounds to add to the monitoring program. Presumably this would necessitate a long-term commitment between the LCBP and VAEL. No local, regional, or national funding organization is capable of sustaining a large-scale long-term monitoring program for OCECs in the Lake Champlain Basin, so if OCEC monitoring is to occur, strategic thinking must carefully target areas of most serious concern and limit the number of samples/analytes involved. Based on the current review, it appears that compounds of most concern are hormones, pharmaceuticals and other endocrine disruptors, in WWTF effluent, pesticides and PAHs in other urban runoff, and pesticides from agricultural runoff and tile drains.

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