Emerging Contaminants in Metropolitan Chicago Rivers

Paul M. Mack
Sierra Club – River Prairie Group
DuPage County, Illinois

September, 2008

cover photo:Sample site WB on the west branch of the DuPage River, with pedestrian bridge in background. August, 2008.

Contents

Abstract 1
Introduction 2
1.1. Motivation for Study 3
1.2. Goals of Study 3
1.3. Region of Study 4
Characterization of Study Region 5
2.1. Regional Characterization 5
2.2. Watershed Characterization 6
2.3. Stream Characterization 9
2.4. Site Characterization 9
2.5. Collection Parameters 13
Characterization of Analytes 15
3.1. PPCPs 15
3.2. Biogenic Compounds 18
Presentation of Data 21
4.1. PPCPs 23
4.2. Biogenic Compounds 27
4.3. Underreporting of Total Concentrations 30
Recontextualization of Data 33
5.1. Salt Creek: 2007 versus 1999 33
5.2. Metropolitan Areas: Chicago versus Kansas City 36
5.3. Adjacent Stages: Water Column versus Effluent 40
Conclusion 43
Acknowledgements 54
Appendices 55
Appendix A – Scope of the Term Emerging Contaminants 55
Appendix B – Primary EC Sources, Transports, and Fates: 56
Appendix C – Region of Study 59
Appendix D – Land Use in the Region 60
Appendix E – Land Use Detail 62
Appendix F – Population Density in the Region 63
Appendix G – The Three Watersheds of this Study 65
Appendix H – Upstream Dischargers of Significance 66
Appendix I – Sample Site Photographs 69
Appendix J – Streamflow Preceding Sample Collection 72
Appendix K – Biosolid and Sediment Comparison 75
Appendix L – Streamflow Preceding SC1999 76
Appendix M – Fifteen Year Prescribing Trend of Co-trimoxazole 77
Appendix N – Interregional Comparison 78
References Cited 80

Illustrations

Figure A.1 - Emerging contaminants in surface water 55
Figure B.1 - EC sources, transports, and fates; a closed system.....56
Figure C.1 - Regional map showing sample site locations.....59
Figure D.1 - Land use in the region, 2000 60
Figure D.2 - Land use in the watersheds, 2000 61
Figure E.1 - Land use detail in the watersheds, 2001 62
Figure F.1 - Population density in Cook County by census tract, 2000 63
Figure F.2 - Population density in DuPage County by census tract, 2000 64
Figure G.1 - Watersheds of Salt Creek and the East and West branches of the DuPage River, and their sampling sites.....65
Figure H.1 - Significant dischargers into Salt Creek, upstream of sample site SC 66
Figure H.2 - Significant dischargers into DuPage River - East Branch, upstream of sample site EB 67
Figure H.3 - Significant dischargers into DuPage River - West Branch, upstream of sample site WB.....68
Figure I.1 - Sample site SC, facing upstream 69
Figure I.2 - Sample site EB, facing downstream 70
Figure I.3 - Sample site WB, facing downstream.....71
Figure J.1 - Daily discharge data for Salt Creek at site SC, for three weeks preceding sample collection.....72
Figure J.2 - Daily discharge data for DuPage River - East Branch at site EB, for three weeks preceding sample collection; approximate.....73
Figure J.3 - Daily discharge data for DuPage River - West Branch, at site WB, for three weeks preceding sample collection.....74
Figure K.1 - Comparison of EC concentrations in biosolids and sediment; milligrams-per-kilogram dry weight 75
Figure L.1 - 1999 daily discharge data for Salt Creek at site SC, for three weeks preceding sample collection.....76
Figure M.1 - Fifteen-year prescribing trend of co-trimoxazole.....77
Figure N.1- Comparison of data from metropolitan areas of Chicago (CHG) and Kansas City (KC); PPCPs.....78
Figure N.2 - Comparison of data from metropolitan areas of Chicago (CHG) and Kansas City (KC); sterols 79

Tables

Table 1 – County characteristics 5
Table 2 – Watershed characteristics 6
Table 3 – Site locations 10
Table 4 – Site characteristics 12
Table 5 – Collection conditions 14
Table 6 – Analyte parameters – PPCPs by LC/MS/MS 17
Table 7 – Analyte parameters – biogenics by GC/MS 20
Table 8 – PPCP concentrations in ppt (ng/L) 23
Table 9 – Biogenic concentrations in ppt (ng/L) 28
Table 10– 2007 vs. 1999: PPCPs (ng/L) 35
Table 11– Chicago versus Kansas City: PPCPs (ng/L) 38
Table 12– Chicago versus Kansas City: biogenics (ng/L) 39
Table 13– Water column versus effluent: PPCPs (ng/L) 41
Table 14– Water column versus effluent: biogenics (ng/L) 42

Acronym and Abbreviation Definitions

BAF	Bioaccumulation factor
CAFO	Confined animal feeding operation
CAS	Chemical Abstracts Service registry number
CHG	Chicago metropolitan area study (this study)
CSO	Combined sewer overflow
DAF	Design average flow
DEET	N,n-diethyl-meta-toluamide
DWTP	Drinking water treatment plant
EB	East Branch (DuPage River) sample site
EC	Emerging contaminant
EDC	Endocrine disrupting compound
EFF	Effluent study (city of Ann Arbor)
GC/MS	Gas chromatography / mass spectrometry
GWA	Glenbard Wastewater Authority
HPLC	High performance liquid chromatography
HUC	Hydrologic unit code
IEPA	Illinois Environmental Protection Agency
KC	Kansas City metropolitan area study (USGS)
K_{OC}	Soil partition coefficient
K_{OW}	Octanol-water partition coefficient
LC/MS	Liquid chromatography / mass spectrometry
MDL	Method detection limit
MWRDGC	Metropolitan Water Reclamation District of Greater Chicago
NOAA	National Oceanic and Atmospheric Administration
OWC	Organic wastewater compound
POTW	Publicly owned treatment work
PPCP	Pharmaceutical and personal care product
RPG	River Prairie Group (Sierra Club)
SC	Salt Creek sample site
SC_{1999}	Salt Creek 1999 sample site (USGS)
SSO	Sanitary sewer overflow
STP	Sewage treatment plant
S_W	Water solubility
UHL	University of Iowa Hygienic Laboratory
USEPA	United States Environmental Protection Agency; also EPA
USGS	United States Geological Survey
WB	West Branch (DuPage River) sample site
WC	Water Column study (this study)
WRF	Water reclamation facility
WRP	Water reclamation plant
WWTF	Wastewater treatment facility
WWTP	Wastewater treatment plant

Units of Measure

area:

sq mi	square mile ($mile^2$)

mass:

g	gram
kg	kilogram (10^3 g)
mg	milligram (10^{-3} g)
µg	microgram (10^{-6} g)
ng	nanogram (10^{-9} g)

volume:

L	liter

flow velocity and volume:

fps	feet per second (ft/s; velocity)
cfs	cubic feet per second (ft^3/s; volume)
mgd	million gallons per day (10^6 gal/d; volume)

concentration:

ppm	parts-per-million (10^{-6})
ppb	parts-per-billion (10^{-9})
ppt	parts-per-trillion (10^{-12})

Unit Conversions

area:

acre	0.405	hectare
acre	0.004	sq kilometer
sq mile	258.999	hectare
sq mile	2.590	sq kilometer

length:

inch	2.54	centimeter
foot	0.305	meter
mile	1.609	kilometer

flow velocity and volume:

fps	0.305	meter per second (m/s; velocity)
cfs	0.028	cubic meter per second (m^3/s; volume)
mgd	3785.412	cubic meter per day (m^3/d; volume)

temperature:

Fahrenheit	(F – 32) ÷ 1.8 (degrees Celsius)

Abstract

Emerging contaminants research represents the newest chapter in the pollution narrative of the developed world, delving into the post-consumer fate of the manifold ingredients of contemporary life. Typical in many ways, suburban Chicago offers an ideal setting in which to survey such micropollutants in impacted waters, and this study is the first comprehensive investigation of its western watersheds.

The water columns of three freshwater, effluent-heavy streams were sampled at low flow for twenty five pharmaceutical, personal care, and biogenic compounds. Aside from three incidental antibiotics and an unseasonable insect repellent, all of the pharmaceutical and personal care analytes were detected in all of the samples. The biogenic analytes, conversely, were dichotomous, with the hormone panel going wholly undetected and most of the sterols being strikingly present.

Correlation among the three watersheds was good, with disparity attributed to the uneven efficacies of treatment facilities in the role of inadvertent mitigators, rather than the unlikely expression of abruptly incongruous consumption habits across a homogenous, localized area or remarkably selective amelioration in the receiving waters arising from minor hydrological differences among them.

To frame the region’s emerging contaminant profile in a larger context, the data was then juxtaposed with that of three studies from which it varied in time, space, and context. To the best extent possible, each study was chosen such that one parameter varied while the other two remained fixed. With time as a variable, this study’s data was examined beside that of an identical location first investigated nearly a decade ago, testifying to the viability of temporal analyses. With space as a variable, this study’s data was examined beside that of a similar metropolitan area, testifying to the plausibility of a region-independent, core contaminant profile. Finally, with mode as a variable, this study’s data was examined beside that of raw effluent, testifying to the feasibility of extrapolating contaminant levels in a given stage from those in an adjacent one.

1. Introduction

The past decade has seen greater attention paid to anthropogenic, ultra-trace contaminants in surface water. As detritus of modern life, such “micropollutants” were long suspected to be present in the environment, but, at concentrations that delve into the parts-per-trillion, confirmation eluded researchers until recent advances in technology made their detection more feasible and economical.

The corollary, of course, is that concentrations sufficiently low to hamper ready detection prove equally resistant to toxicity investigation. Such trace levels all but rule out acute effects, challenging researchers to tease out evidence of subtle responses to chronic, often multigenerational, low-level exposure in aquatic organisms that range from plants, algae, and bacteria to protozoa, micro- and macroinvertebrates, fish, amphibians, and to a lesser extent, birds and terrestrial animals (including humans) that utilize the water and its food sources; in short, a water body’s full food chain. It would be fair to say that modest advances in the detection of ultra-trace contaminants have outpaced the understanding of their effects.

Micropollutants go by many names, and this report makes use of the broadest term, *emerging contaminant (EC),* which, within this context, refers to any anthropogenic, ultra-trace, xenobiotic that has only recently begun to be detected in the environment, thanks to improvements in laboratory technology, and in particular, chromatographic mass spectrometry. The term, then, refers less to a compound’s recent emergence in the environment than to the research community’s nascent awareness of it there. A partial breakout of the term is illustrated in the flowchart of appendix A.

Given the breadth and inclusiveness of this term, it is often misinterpreted as a chemical classification in its own right or made synonymous with one of its constituent classes. While the former is a misunderstanding of the intent of the term, the latter results in an unnecessary narrowing of its scope. For example, one mistaken belief is that the term *emerging contaminants* is bound to the set of synthetic compounds, when, in fact, over one-third of the ECs in this study are produced naturally by plants and animals. Another is the belief that the term is synonymous with *endocrine disrupters*, a descriptive rather than categorical term, which identifies compounds with primary or ancillary hormonal (usually estrogenic) effects. These two examples also illustrate that the term is less a label for a static list of compounds than a general descriptor for a growing, multidimensional matrix of them, most of which remains unexplored and whose disparate members might share one or more properties, such as source, location, and effect. At the core are the ubiquitous ECs—“the usual suspects”—and surrounding them are constellations of regional-specific ECs, as well as those endemic to a particular watershed, lake, or river; a separate, intersecting dimension is reserved for their transformation products. It should be clear, then, that categories are less likely to be mutually exclusive than to overlap, their intersections a testament to the breadth of the field.

The breadth of the field, in turn, is a function of the diversity and complexity of the sources and fates of the contaminants themselves. Current conventional wisdom points to the wastewater

treatment plant (WWTP) as a primary point source,[1] with agriculture a primary nonpoint source. Secondary sources are thought to include industrial discharge, urban runoff, landfill leachate, and to a lesser extent, dispersion from wind and evaporation. In short, the production, consumption, and disposal of consumer foodstuffs and products. The primary sources and fates of ECs are illustrated in appendix B.

1.1. Motivation for Study

The three rivers in this study, Salt Creek and the east and west branches of the DuPage River, are freshwater streams located in the Chicago metropolitan area and are typical of effluent-heavy waterways in highly developed areas. As such, they have been the subject of ongoing nutrient testing by the Sierra Club's regional chapter, the River Prairie Group (RPG), for nearly a decade. Against that backdrop, this EC investigation represents a logical next-step in the evolution of interest in surface water contaminants within the research, environmental, and public realms, as well as the first such investigation of the DuPage River watersheds (and the first of the Salt Creek watershed in nearly a decade).

Units: ppt *versus* ppt

The rivers in this study have been well parameterized by RPG and state agencies for "macropollutants" such as chloride and nutrients. With some of those approaching concentrations in the parts-per-thousand range, an EC investigation represents an effort to bear down on the spyglass and descend the nine orders of magnitude that separate macropollutants from micropollutants. Therefore, all references to *ppt* herein refer to *parts-per-trillion* rather than *parts-per-thousand.* Note, too, that this definition implies the equivalency of *ppt* with *nanogram-per-liter* (ng/L).

1.2. Goals of Study

This study investigates twenty-five ECs in three effluent-laden rivers of a typical metropolitan area in an attempt to uncover the region's EC profile. In doing so, it also provides a snapshot of impacted surface water in the greater Chicago area, as well as metropolitan areas nationwide, given the ubiquity of consumables and their corresponding ECs. To this end, data is compared to a similar metropolitan area.

At the same time, the rivers discussed in this report owe a majority of their volume during low-flow conditions to WWTP discharge, during which time EC levels in the rivers are representative of those in effluent (minus dilution, uptake, transformation, degradation, and sorption). The water samples in this study were collected at just such a relative minimum, and a subsequent chapter compares their concentrations to those of raw effluent.

One of the rivers in this study was a participant in the landmark United States Geological Survey (USGS) study of ECs in 1999. Its recurrence here provides a unique opportunity to contrast two EC snapshots taken nearly a decade apart at the same sampling point.

1. *WWTP* is treated herein as a synonym for *POTW, STP, WRF, WRP, WWTF,* etc., except in proper nouns.

Finally, the study of ECs is a relatively new field still in its discovery mode, and this study adds to the growing body of awareness and empirical data. In the near future, ECs and their chronic toxicity profiles will become sufficiently well parameterized to inform policy and technological responses.

1.3. Region of Study

The geographical region of this study is Chicago's west metropolitan area, illustrated in appendix C.[1]

1. Sample sites are marked on all appendix maps.

2. Characterization of Study Region

This chapter presents the study area with progressively smaller granularity.

2.1. Regional Characterization

This study investigates emerging contaminants in three freshwater rivers of the Chicago metropolitan area. The thoroughly suburbanized region is characterized by traditional housing stock, relatively high population, some industrial development, and little agriculture.[1] The area's land use is illustrated in figure D.1 of appendix D.

Because Chicago was founded on the western shoreline of a water body, urban expansion along its girth has proceeded west. Due to the relationship between urbanization and ECs, the sequence presented in each section of this report follows that east-to-west development gradient: Salt Creek, DuPage River East Branch, and DuPage River West Branch.

The region under study spans part of Cook County and most of DuPage County, summarized in table 1.

Table 1. County characteristics

County	Population	Land area (sq mi)	Population density (persons per sq mi)	Housing density (units per sq mi)
Cook County, IL	5,288,655	946	5592	2282
DuPage County, IL	932,670	334	2796	1068

Source: U.S. Bureau of the Census, *QuickFacts.* 2006 estimates. Actual 2000 population and housing densities are 5686 and 2217 for Cook, and, 2710 and 1006 for DuPage, respectively (ibid., *Fact Sheet).*

County population densities in the watersheds are illustrated with finer granularity in appendix F.

1. Although not a normative term, *suburban* is used herein to portray a landscape of relative low-density commonly associated with single-family residences, as well as to distinguish it from the term *urban,* which could connote Chicago proper or its high-density core. That said, the watersheds in this study lie within a larger region categorized by the U.S. Bureau of the Census as an *urbanized area,* with the exception of an approximately 15 square mile parcel on the western edge of the study area.

2.2. Watershed Characterization

Each of the three rivers in this study occupies a watershed bearing its name, and the three watersheds are adjacent to each other, forming a cohesive 355 square mile region, which spans twenty-three miles at its widest point and thirty-one at its longest, with an eastern edge twelve miles west of downtown Chicago and its Lake Michigan shoreline. The collective watersheds are illustrated in appendix G.

Growth in the Chicago area during the twentieth century progressed in the traditional manner, unfolding radially from its lake-constrained downtown. Not surprisingly, then, the easternmost watershed is the most urbanized of the three while the westernmost is the least; still, residential development predominates, accounting for approximately three-fourths of the developed land in the center watershed and two-thirds in the outer two. Land allocation in the watersheds is illustrated in figure D.2 of appendix D and detailed in appendix E.

The three contiguous watersheds are members of U.S. Environmental Protection Agency (EPA) Basin 2, and are catalogued under the USGS hydrologic unit code (HUC) hierarchy as constituents of the Des Plaines River Subbasin (HUC 07120004), which in turn, is within the Upper Illinois River Basin (HUC 0712), a subregion in the Upper Mississippi Region (HUC 07).

The watersheds are summarized in table 2.

Table 2. Watershed characteristics

Watershed	County	Drainage area (sq mi)	Urbanization[a] (%)	Residential (%)
Salt Creek	Cook, IL; DuPage, IL	149	78	50
DuPage River - East Branch	DuPage, IL	79	73	53
DuPage River - West Branch	DuPage, IL	127	64	44

Sources: Drainage by IEPA (2004a, 2004b, 2004c); 2001 urbanization and residential by Clarke (2008).

a. In contrast, it is worth noting that 1990 urbanization rates were 75%, 58%, 49%, and residential rates were 50%, 40%, 33%, respectively (IEPA 2004a, 2004b, 2004c). The nearly-unchanged state of Salt Creek watershed and double-digit growth in the more western two prevailed against the aforementioned development gradient. As the West Branch is the most rural of the three, it has likely absorbed the brunt of subsequent growth, losing the most tillage to the housing boom.

Point and Nonpoint Sources in the Watersheds

A watershed boundary is a hydrologist's construct, across which urban development proceeds unaware. Given the homogeneity of suburban landscapes, land use is sufficiently similar across the three watersheds that nonpoint and point sources can be generalized.

Nonpoint sources

The watersheds embodied by this study contain large impervious areas typical of suburban development. Urban runoff, a credible EC gateway in mild seasons, was of minimal influence here, as samples were collected during a cold, dry period, absent of precipitation and snowmelt.

Additionally, significant lengths of the rivers are flanked by public green space, which serve as a buffer to nonpoint impervious surfaces. A nonpoint source it its own right, green space may contribute biogenic ECs that are identical to (and indistinguishable from) those of humans, although its influence in this study is negligible due to ambient conditions. So, too, are microorganisms in the water column and sediment of a water body itself such sources; but, so too is their influence here negligible, as microbiological activity can be assumed minimal in winter months marked by frigid temperatures and attenuated sunlight.

Farms are not a significant source of ECs in this study: what little agriculture exists in the watersheds is primarily row crop, hay, and nursery, rather than livestock, production.[1] None of this study's analytes are field agrichemicals, and while several are veterinary medicines, the paucity of livestock precludes their significance here.

The veterinary medicines in this study are also administered to companion animals, which, too, are unlikely to have contributed to the aquatic EC load sampled by this study. Pet waste in runoff was likely minimal due to the aforementioned ambient conditions, in which the freezing temperature and snow cover would have tended to detain any liquid or solid waste deposited on the ground.

Thus, while nonpoint sources might represent a credible gateway of ECs in these watersheds during wet or mild weather, their influence at the time of sampling was negligible.

Finally, all three watersheds contain small lakes through which their rivers pass, which provide both hydrologic and contaminant buffering for upstream dischargers. Lakes likely result in downstream attenuation of those ECs with an affinity for sediment as well as those amenable to natural degradation; at the same time, however, they may serve as a source of some biogenic ECs.

Point sources

Commercial and light industry outfalls in the watersheds are primarily permitted for non-contact cooling water, which is not a source of ECs. Due to the aforementioned ambient conditions, storm sewer, combined sewer overflow (CSO), and sanitary sewer overflow (SSO) outfalls can be assumed to have been idle.[2] While some fraction of the inputs to the twenty-two WWTPs encompassed by this study are light industrial, land use data in the appendices suggests that its influence is limited. WWTPs, then, processing a primarily non-industrial feedstock, are the

1. The watersheds contain no confined animal feeding operations (CAFOs), which can be potent nonpoint sources of ECs.
2. While sanitary sewer service in the region is nearly universal, the prevalence of residential septic tanks in the riparian corridor is unknown. Straight-piping is prohibited by building code.

principal source of contaminants surveyed by this study, and are mapped in appendix H.[1]

2.2.1. Salt Creek Watershed

The Salt Creek Watershed is the easternmost of the three, as well as the demographically and geographically largest, straddling Cook and DuPage counties. This watershed is categorized under USGS HUC 0712000406.

Land use in the watershed is typical of an established metropolitan area, with 78% categorized as developed. Of the three watersheds in this study, Salt Creek contains the most dischargers (as much as the other two combined) and shoulders the greatest effluent burden.

Additionally, the most prolific point source in the three watersheds is found here. The Egan water reclamation plant (WRP), the most upstream discharger on Salt Creek, discharges more than all of this river's other dischargers combined, averaging 26.1 million gallons per day (mgd) in 2007 (MWRDGC 2007a) from an approximate population of 160,000 (MWRDGC 2008).[2] Egan WRP and its ten brethren are mapped in figure H.1 of appendix H.

2.2.2. East Branch DuPage River Watershed

The East Branch DuPage River Watershed is perched between the other two, and is geographically smallest. This watershed is categorized under USGS HUC 0712000410.

Approximately 73% of the watershed's acreage is developed, the median of its neighbors. An insignificant portion of this watershed lies in Will County.

The largest discharger in the watershed is the Glenbard Wastewater Authority WWTP, which averaged 10.9 mgd in 2007 (GWA 2008). The Glenbard facility and its three brethren are mapped in figure H.2 of appendix H.

2.2.3. West Branch DuPage River Watershed

Furthest west in the development gradient, the West Branch DuPage River Watershed is the least urbanized (with 64% of its acreage developed) and the most heavily agricultural (8.3%).[3] This watershed is categorized under USGS HUC 0712000410.

Insignificant portions of this watershed lie in Cook, Kane, and Will Counties.

The largest discharger in the watershed is the Hanover Park sewage treatment plant (STP), which averaged 8.4 mgd in 2007 (MWRDGC 2007b). Hanover Park STP and its six brethren are mapped in figure H.3 of appendix H.

---

1. The designation of WWTPs as primary *point sources* by EC studies reflects an adherence to the formal definition of the term rather than an indictment of the facilities. WWTPs are more accurately described as EC gateways rather than EC point sources.
2. 1990 data. Facility is the river's sole WWTP in Cook County.
3. 2001 data. Current figure has likely declined significantly per footnote in table 2.

2.3. Stream Characterization

The three freshwater rivers analyzed in this study present themselves cartographically as three vertical and nearly equidistant ribbons in the central-west Chicago metropolitan area. They are oriented along a north-south axis and are north-to-south flowing streams, which owe the bulk of their volume during low-flow conditions to WWTP discharge. As such, the term *discharge body* is used herein to refer to the receiving water body for one or more point and/or nonpoint sources. In an urban context, this would often be a river, lake, or reservoir which hosts at least one active outfall. The term encompasses the water column and sediment bed.

All three rivers eventually terminate in the Des Plaines River, which joins with the Kankakee River near the city of Joliet to form the Illinois River, which itself goes on to terminate in the Mississippi River.

While none of this study's rivers are tapped directly for drinking water use, they are sub-tributaries to the Illinois and Mississippi rivers, which serve as public water sources for downstream communities in several counties and states.

2.3.1. Salt Creek

At 45.9 miles, Salt Creek is the longest of the three rivers and shoulders the largest effluent load. Not particularly salty nor a creek, it terminates in the Des Plaines River shortly after its confluence with Addison Creek.

2.3.2. DuPage River – East Branch

As its name implies, the East Branch of the DuPage River is the easternmost of two tributaries to the mainstem DuPage River. It is 25.0 miles long and lies between and nearly equidistant from its western counterpart and Salt Creek, approximately six miles from the former and four from latter.

2.3.3. DuPage River – West Branch

The West Branch of the DuPage River is 35.4 miles long and lies approximately six miles west of and parallel to its eastern twin. The two converge as the mainstem DuPage River, which continues flowing south to the Des Plaines River.

2.4. Site Characterization

One sample site was chosen on each river, and is identified by an abbreviation of the river name: *SC* is the Salt Creek sample site, while *EB* and *WB* are those of the east and west branches of the DuPage River, respectively.

2.4.1. Location

Each sample site was chosen to coincide with an established test site downstream of the majority of significant point sources, as was illustrated in appendix H. This resulted in sites positioned in the lower one-half (EB), one-third (WB), and one-fifth (SC) of the rivers' spans. Site locations are parameterized in table 3.

Table 3. Site locations

Site	River	City	Latitude Longitude	Mile marker[a]	USGS gage	IEPA gage
SC	Salt Creek	Western Springs, IL	N41° 49' 33" W87° 54' 01"	37.1	05531500	GL-09
EB	DuPage River - East Branch	Lisle, IL	N41º 47' 42" W88º 4' 47"	13.4	05540210[b]	GBL-10
WB	DuPage River - West Branch	Warrenville, IL	N41º 49' 30" W88º 10' 44"	24.2	05540095[c]	GBK-05

Sources: SC coordinates by USGS (2007a), EB and WB by author; mileage by LaTour (2008a).

a. From riverhead (most northerly point). River lengths are 45.9, 25.0, and 35.4 miles, respectively (LaTour 2008a).
b. EB is situated between 05540210 and 05540230, approximately 0.5 mile from each.
c. 0.3 mile downstream of WB.

A downstream site contributes two benefits to a data set. As an aggregation node, all upstream point and non-point inputs are summed, providing a snapshot of the EC profile being bequeathed to the subsequent water body. The summing, in turn, exerts an averaging influence on the moderately differing inputs, diminishing the weight with which outliers might skew the data.

However, the simple notion of a snapshot belies the complexity of the underlying contaminant portrait by implying that a river is nothing more than a passive, inert vehicle.

In the context of a surface water analysis such as this, an outfall and downstream sample site form the endpoints of a *dilution gradient*, along which an EC's concentration diminishes in response to an array of forces, whose exact characteristics are unique to that EC and microenvironment. Three forces underlie a dilution gradient:

- *Transformation agent* is a biotic or abiotic mechanism which exerts a transformative force on an EC. The result is a *transformation product,* which may be another complex, potentially harmful molecule, or, a degradate. Eco-pharmacologically, the latter is benign and thus the preferred metamorphosis. The transformation modes are biotransformation, phytolysis, photolysis, and hydrolysis.

- *Sequestration agent* is a biotic or abiotic mechanism which sequesters an EC. These agents are eco-pharmacologically neutral, merely displacing an EC from one medium to another, rather than mitigating it. The sequestration modes are adsorption, bioconcentration, and volatilization.

- *Dilution agent* is any mechanism which reduces the concentration of an EC in the water column. As such, it encompasses the universe of transformation and sequestration agents, and depending on context, outright dilution via excess water.[1] Each EC has a unique susceptibility to the various dilution agents, with the exception of outright dilution, a nonselective force which uniformly reduces the water column concentrations of all ECs.

For a given EC, then, each point source engenders a dilution gradient, such that the analyte concentration at a downstream sampling point will reflect the superposition of all upstream dilution gradients, which, in turn, are contoured by the EC's response to the dilution agents therein over an exposure time determined by stream velocity.[2] In slow flowing rivers, such as those in this study, the half-life of a labile EC may be on the order of the transit time between gradient endpoints.

Of course, even along a relatively short length, a dilution gradient may be nonuniform. More than a function of distance, it accounts for the influence of intervening physical features such as lakes, wetlands, and waterfalls, which introduce additional transformation agents, manifested as discontinuities in the gradient. That said, dilution gradients of hydrologically similar rivers, especially within the same region, will bear resemblances to one other.

The gradient model illustrates that an EC from a given discharger may be subjected to a different spectrum of dilutive forces than that from a more downstream source, which cannot simply be modeled by extrapolation of an intermediate point.[3] In doing so, it highlights the complexity of EC analysis, in which a cocktail of contaminants from multiple sources traverse different dilution paths prior to arriving at the sampling site. To this end, subsequent chapters will present the primary WWTP and discharge body dilution agents, and, where known, their efficacy on specific ECs.

Finally, it is worth the reminder that all transformation and sequestration modes are incidental forces, to which an EC may be susceptible to some degree. The dilution agents in a WWTP or discharge body were not inserted there to specifically mitigate ECs; ECs are alien compounds and any encounter with (and response to) a native agent is purely accidental.

2.4.2. Characteristics

Site characteristics are presented in table 4. In the absence of precipitation, baseflow is a virtual trickle throughout the watersheds, attesting to the prominence of effluent in the waterways.

1. Incidentally, uptake by both flora and fauna is the gateway for biotic transformation and sequestration modes.
2. The gradient is two-dimensional to reflect slowly varying temporal components of natural dilution agents in a discharge body that exhibit periodic variation (diurnal, seasonal); the natural and man-made dilution agents in a WWTP can be similarly modeled. Nonpoint sources, including the river itself, might be modeled by a three-dimensional gradient.
3. The three agent classes also underlie WWTP dilution gradients, which are piecewise linear across processes.

Table 4. Site characteristics

Site	Drainage area (sq mi)	Baseflow[a] (cfs)	Velocity[b] (fps)	Mean discharge[c] (cfs)	Source discharge[d] (cfs)	Point sources[e]
SC	115.0	0.5	1.25	137	42.3	11[f]
EB	54.6[g]	0.5[h]	1.50[h]	79[h]	30.8	4
WB	90.4	0.0	1.30	108	29.1	7[i]

Sources: Drainage area from USGS, *National Water Information System: Stream/River Site Description*; baseflow from ISWS (2003); velocity from LaTour (2008b); streamflow (mean discharge) from USGS (2007a, 2007b, 2007c); source discharge and point sources from IEPA (2004a, 2004b, 2004c).

a. Estimated, by discounting point source contributions at low flow; as actual baseflow data is unattainable, these figures are provided for reference only. Annual-7-day-minimums are 2.1, 15, and 10 cfs, respectively; "90% exceeds" are 17, 29, and 28 cfs over 62, 18, and 39 years, respectively; EB averaged per note in appendix J (USGS 2007a, 2007b, 2007c).
b. Averaged over the period June 1999 to November 2007. Range of actual values were 0.26–2.60, 0.87–2.88, and 0.25–2.46, respectively.
c. Annual mean over 62, 18, and 39 years, respectively. See appendix J for context.
d. Average aggregate discharge of upstream point sources.
e. Significant upstream dischargers. See point source discussion in section 2.2. Illustrated in appendix H.
f. Does not include Arlington Race Track, a potential source of veterinary pharmaceuticals during the racing months of May–September.
g. Average of flanking USGS gages 05540210 and 05540230.
h. Average, per note in appendix J.
i. Does not include small WWTP in Pleasant Ridge mobile home park permitted for a design average flow (DAF) of 0.027 mgd into tributary Klein Creek.

2.4.2.1. SC

SC is located on Salt Creek in the center of Bemis Woods, a 300-plus acre forest preserve in Western Springs, Illinois. It is coincident with USGS gage 05531500, upstream (west) of the Wolf Road overpass. This site participated in the landmark EC reconnaissance performed by USGS in 1999 (Kolpin et al. 2002a), in which it was designated *IL03.* This site also bears the aliases *GL-09* by the Illinois Environmental Protection Agency (IEPA) and *WW_24* by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). The site is approximately seven miles south of RPG nutrient test site *SC2*, and is photographed in figure I.1 of appendix I.

2.4.2.2. EB

EB is located on the east branch of the DuPage River in Community Park, a 110 acre common in Lisle, Illinois. The site is situated on the river's north-south midpoint, approximately 900 feet north of Short Street. EB is coincident with RPG nutrient test site *EB3*, and is photographed in figure I.2 of appendix I.

2.4.2.3. WB

WB is located on the west branch of the DuPage River in the northwest corner of Warrenville Grove, a 128 acre forest preserve in Warrenville, Illinois. It is coincident with RPG nutrient test site *WB2*, approximately 100 feet downstream (south) of the Butterfield Road overpass, and is photographed in figure I.3 of appendix I.

2.5. Collection Parameters

Samples were collected on Monday, December 10, 2007. This day was the last in a dry spell, a period of low flow in which WWTP effluent signature would be prominent. While such low velocity affords contaminants with modest half-lives an opportunity to respond to dilution forces in transit to the sample site, the effect would be offset to some extent by the season's diminished sunlight and frigid temperatures.

One grab sample was collected from each test site, within the river centroid and at a depth of approximately six inches[1].

Ambient conditions were typical of a mild winter day, overcast and windless. Across the abutting three days (December 8–10), the average maximum temperature was 28° F and the precipitation was 0.06 inch (NOAA 2007). There was no evidence of snowmelt throughout the region, suggesting that runoff was not a significant contributor to streamflow. USGS data confirms that the sample date represented a relative low-flow condition; see appendix J, and, note in table 5 that the historical December 10 average is approximately 50% higher than the sample date at SC and WB, and 175% higher at EB.

In addition to an abundance of cold air and a lack of precipitation, diminished sunlight, due to short days and overcast skies, is also characteristic of Chicago's winter climate. The efficacy of dilution agents which consist of or utilize sunlight-mediated warmth, photosynthesis, and photolysis can be expected to be a minimum at such times.

Collection conditions are presented in table 5.

1. Due to treacherous ice conditions at WB, grab sample was retrieved approximately 8 feet from shore.

Table 5. Collection conditions

Site	Time	Water temperature (°F)	River depth[a] (ft)	Discharge[b] (cfs)	Median discharge[c] (cfs)
SC	1:45 p.m.	45	2.50	50	75
EB	12:30 p.m.	46	1.25	30[d]	82[d]
WB	11:15 a.m.	43	2.50	46	65

Sources: Streamflow (discharge and median discharge) by USGS, *National Water Information System: Real Time Data;* else by author.

a. Observed, approximate.
b. USGS flow data at sample time from nearest station. Compare with flow rates in table 4. As an observational side note, streams were virtually still, most likely on the low end of the ranges in footnote b of table 4.
c. Median value is December 10 average over 61, 17, and 38 years, respectively. See appendix J for context.
d. Average, per note in appendix J.

Short of an exhaustive discharge analysis of all watershed WWTPs, the largest discharger in each watershed can be treated as a barometer of aggregate discharge. The largest discharger upstream of SC, the Egan WRP, averaged 22.2 mgd (MWRDGC 2007a) in the abutting three days (December 8–10); upstream of EB, the Glenbard WWTP averaged 8.1 mgd in the same period (GWA 2008), and upstream of WB, the Hanover Park STP averaged 6.7 mgd (MWRDGC 2007b). Using baseflow data from table 4, the effluent burden of all three rivers can be estimated as greater than 98%.

2.5.1. Quality Assurance

All precautions against ultra-trace contamination were exercised. Aside from the foodborne sterols, sample collector (author) does not consume any of the analytes in this study. Samples were collected in preservative-spiked, one-liter amber glass bottles and immediately shipped in a refrigerated parcel by overnight courier to the University of Iowa Hygienic Laboratory (UHL).

3. Characterization of Analytes

Given the innumerable micropollutant candidates within urban surface water as well as the high cost of testing them, EC studies restrict themselves to some subset, focusing on a particular category of analytes, or, broadly surveying "the usual suspects." As the first EC investigation of the region, this study pursues the latter, and presents them within the context of appendix A.

As outlined in section 2.2, the region of study is a typical metropolitan one, highly residential with some industry and little agriculture, suggesting that the domestic sphere is the primary vector of waterborne ECs, via WWTP effluent.[1] For this reason, water samples were tested for pharmaceuticals and personal care products (PPCPs) and biogenic compounds. The distinction between these two panels will be maintained throughout this report.

Generally, waterborne ECs do not appear in concentrations sufficient for acute poisoning of aquatic organisms; therefore, toxicity data (LC_{50}) is not provided here.[2] It is believed that the threat posed by chronic exposure to micropollutants, singly and synergistically, is both multifaceted and largely unknown, rather than merely an extrapolation of those modes of toxicity known to traditional (human) pharmacodynamics.

3.1. PPCPs

Fifteen common PPCPs were investigated and are summarized in table 6. The diverse members of this group could be categorized into a variety of intersecting sets; that chosen in this report reflects the flowchart in appendix A, arranged by category, and therein, alphabetically.

3.1.1. Pharmaceuticals

Pharmaceutical analytes are categorized here as prescription and nonprescription. Their primary pathway to the environment is human and animal consumption and subsequent excretion (including metabolite[s]) via urine and feces.

A pharmaceutical is merely a compound that has been tailored to effect a specific physiological response in a target organism (the exceptions being cosmetic and diagnostic drugs).[3] The eco-pharmacology of a given pharmaceutical and its metabolite(s) is more difficult to predict; in a non-target organism, they may trigger the nominal response or unexpected ones.

---

1. Such an EC is given the moniker *organic wastewater contaminant* (OWC).
2. In their survey of the literature, Derksen et al. (2004) found that most human pharmaceuticals are acutely toxic to aquatic organisms at concentrations in the parts-per-million (ppm) range, three to six orders of magnitude greater than typical micropollutants.
3. In the context of ECs, the term *pharmaceutical* refers to the active ingredient(s) in a prescription or over-the-counter product; the respective metabolites may or may not be implied. The term *metabolite* herein includes all metabolic derivatives (such as conjugates), while *transformation products* encompasses the universe of exogenous (biotic and abiotic) by-products and degradates that arise in the post-consumer channel.

3.1.1.1. Prescription

This category spans seven antibiotics, and, an antiepileptic also prescribed as a mood stabilizer. The antibiotics are approved for human and/or veterinary use and include four sulfonamides, one macrolide (tylosin), one lincosamide, and one folic acid inhibitor (trimethoprim);[1] their metabolites and aquatic transformation products were not investigated. Nor, too, were illicit drugs considered.

3.1.1.2. Nonprescription

Nonprescription pharmaceuticals manifest themselves as over-the-counter medicines and as ingredients in foodstuffs.

Medicines

This group contains two common nonprescription pain relievers.

Foodstuffs

This group contains caffeine and its primary metabolite as well as a nicotine metabolite.

3.1.2. Personal Care Products

This group contains the active ingredient found in topical insect repellents as well as the disinfectant utilized in antibacterial soaps and sanitizers. The latter analyte is believed to be the only endocrine disrupter in this panel.

Unlike pharmaceuticals, personal care products are generally intended for external use. Neglecting the fractional portion absorbed and excreted, they primarily find their way to a WWTP after being washed off.

3.1.3. PPCP Analyte Parameterization

The PPCP analytes are parameterized in table 6.

1. The term *veterinary* herein can include livestock, fish (aquaculture), zoo animals, and companion animals. In an agricultural context, antibiotics are approved at therapeutic doses for treating disease and at subtherapeutic doses for prophylaxis and growth promotion.

Table 6. Analyte parameters – PPCPs by LC/MS/MS

	Analyte	CAS	MDL (ng/L)	Description[a]
Pharmaceuticals	Lincomycin	154-21-2	1.0	human & veterinary antibiotic[b]
	Sulfadimethoxine[c]	122-11-2	1.0	veterinary antibiotic
	Sulfamethazine	57-68-1	1.0	veterinary antibiotic[d]
	Sulfamethoxazole[e]	723-46-6	5.0	human antibiotic
	Sulfathiazole	72-14-0	1.0	human & veterinary antibiotic[f]
	Trimethoprim[e,g]	738-70-5	5.0	human antibiotic
	Tylosin	1401-69-0	1.0	veterinary antibiotic
	Carbamazepine	298-46-4	5.0	antiepileptic, mood stabilizer
	Acetaminophen[h]	103-90-2	1.0[i]	analgesic
	Ibuprofen[j]	15687-27-1	1.0[k]	NSAID analgesic
	Cotinine	486-56-6	1.0	nicotine metabolite
	Caffeine	58-08-2	5.0	stimulant
	Paraxanthine[l]	611-59-6	1.0	caffeine metabolite
Personal Care	DEET[m]	134-62-3	120	insect repellent
	Triclosan[n]	3380-34-5	1.0	broad-spectrum antimicrobial

Sources: Veterinary data from *Plumb's Veterinary Drug Handbook; Veterinary pharmaceuticals and biologicals: The veterinarian's PDR; Veterinary values.* Chemical Abstracts Service (CAS) registry numbers from National Institutes of Health Medical Subject Headings, http://www.nlm.nih.gov/mesh/MBrowser.html. MDL is *method detection limit.*

a. The distinction between human and veterinary drugs is obscured by the ability of veterinarians to prescribe a broad spectrum of human pharmaceuticals to animals in an off-label manner. This table reflects the distinctions maintained by the sources.
b. Both human and veterinary use is increasingly rare, the latter being displaced by clindamycin.
c. Sulfadimethoxine can also be paired with ormetoprim in a 5:1 ratio.
d. Formerly a human antibiotic.
e. Sulfamethoxazole is normally paired with trimethoprim, a synergistic 5:1 blend termed *co-trimoxazole;* trimethoprim, in contrast, sees solo prescribing (Arbini 2008). Both anecdotal evidence and the sources report co-trimoxazole's off-label use for livestock and companion animals.

f. Anecdotal evidence suggests its use is increasingly rare; human application currently relegated to topical use (Arbini 2008).
g. In veterinary contexts, sulfadiazine can be paired with trimethoprim in a 5:1 ratio termed co-trimazine.
h. Also known as paracetamol and as the brand names Excedrin and Tylenol.
i. SC = 5.0 (laboratory diluted sample to bring its concentration into instrument range).
j. Also known as the brand names Advil and Motrin. NSAID is *nonsteroidal anti-inflammatory drug.*
k. WB = 5.0 (laboratory diluted sample to bring its concentration into instrument range).
l. 1,7-dimethylxanthine. Caffeine and paraxanthine form the only parent-child pair here.
m. N,N-diethyl-meta-toluamide.
n. Often abbreviated as TCS. Triclocarban (TCC), another common disinfectant, is not investigated here, but is similar to triclosan in application, ubiquity, and hydrophobicity and thus is likely commonly colocated with it.

3.2. Biogenic Compounds

Ten prevalent steroids were investigated and are summarized in table 7, arranged by category, and therein, alphabetically.

The biogenic category is unique within ECs, as its compounds are produced by some combination of humans, animals, microorganisms, and plants.[1] That a biogenic compound might be both endogenous to a vertebrate and consumed by it—as well as biosynthesized by flora—precludes both the identification of the initial source and determination of the background (non-anthropogenic) concentration in a water body.

3.2.1. Hormones

This group includes one male hormone (an androgen), two female hormones (an estrogen and a progestogen), and a horse hormone utilized in human menopausal hormone replacement therapy (HRT). As intrinsic hormones, each is an inherent endocrine disrupting compound (EDC),[2] as distinguished from phytohormones (plants), mycoestrogens (fungi), and pseudohormones (synthetic chemicals), EDCs whose hormonal proclivity is ancillary and are not investigated in this study.

Progesterone and the estrogen estriol are produced by vertebrates, including women and men. In surface water, a hormone's progenitor cannot be identified using standard chromatographic mass spectrometry.

Like all steroid hormones, the four studied here are derivatives of cholesterol, as are two of the sterols. Unlike pharmaceuticals, parent-child relationships among biogenic compounds can be intertwined, and additionally complicated by bacteriological action, and thus, are not identified in table 7.

1. Humans are a sufficiently significant source of biogenic compounds in a discharge body to merit their classification as ECs. Conversely, while some antibiotics are biogenic, they are categorized by this study as PPCPs because the classification reflects principal sources in surface water.
2. *EDC* is treated herein as a synonym for *hormonally active agent* (HAA), *pseudo-hormone*, etc.

A Word On Endocrine Disrupters

An EDC is any compound whose chemistry enables it to interfere with an animal's endocrine system, often as an agonist or antagonist. This can include, plainly enough, an authentic hormone (natural or synthetic, which is branded an EDC when encountered out of context), as well as a natural or synthetic compound which chemically mimics a hormone;[1] these latter compounds are generally less potent than the hormones they mimic. Estrogenic EDCs predominate and are not limited to altering the sex ratios, and, reproductive systems and behaviors, of vertebrates and invertebrates; for example, they may also aggravate estrogen-responsive tumors in those organisms.

Hormonal proclivity does not preclude other modes of toxicity for a compound.

Estrogen is an umbrella term for a group of metabolically intertwined and nominally female hormones, of which the primary three are estrone, 17β-estradiol, and estriol, frequently abbreviated *E1, E2,* and *E3,* respectively. That endogenous estrogens are neither scant, exclusively human, nor restricted to the female of the species is well known; in fact, Kumar et al. (2006) found total concentrations (E1+E2+E3; free and conjugated) in a pregnant swine of 7.5 ppm in feces and 2.3 ppm in urine (approximately 40% of which in each was estriol); in a boar (male), total concentrations were 2.5 ppm and 0.5 ppm, respectively.[2,3]

Estriol is less potent than its precursors, estrone and 17β-estradiol, but it is a major estrogen component in urine. That phtyoestrogens are less potent than endogenous ones may be partially offset by their high concentrations in the body due to diet.

Other EDC subclasses, such as thyroidal compounds, are less widely studied.

3.2.2. Sterols

This group includes three animal sterols and three phytosterols.

Some phytosterols are EDCs while others can be made so via bacterial action. The non-phytosterols here have no apparent ecotoxicity and serve merely as fecal indicators; cholesterol, coprostanol, and cholestanol are companions in the body and thus can be expected to be colocated in the environment. While coprostanol is synthesized in small amounts by animals, the most prolific source is believed to be the human gut and thus it is widely used as a human fecal indicator.

There is also a spectrum of less obvious sterol sources, the extent of whose contribution is both seasonal and unknown. Cholestanol and coprostanol, for example, can be produced in a WWTP or discharge body via anaerobic bacterial conversion of cholesterol (albeit to a likely insignificant extent), and plankton are yet another a source of cholesterol and cholestanol. So, too, with the

1. Seelig (2005) proposes ten categories of EDCs, some of which are neither ECs nor estrogenic: organochlorine pesticides, polychlorinated biphenyls, dioxins, alkylphenols, polycarbonate-derived products, phthalates, vinclozolin, organotin compounds, synthetic estrogens, and natural estrogens.
2. Values include metabolites to reflect their susceptibility to reconstitution via hydrolysis to E1/E2/E3.
3. Where practical, cited data is presented in its original units.

phytosterols: stigmasterol can arise from bacterial conversion of sitosterol, whose non-terrestrial sources include plankton such as algae. In fact, each of the three phytosterols in this study is produced in chemically identical form by both terrestrial plants and aquatic microorganisms, such that the progenitor might be identifiable by isotopic analysis but not standard chromatographic mass spectrometry (Harvey 2008).

3.2.3. Biogenic Analyte Parameterization

The biogenic analytes are parameterized in table 7.

Table 7. Analyte parameters – biogenics by GC/MS

Analyte		CAS	MDL (ng/L)	Description
Hormones	Equilenin[a]	517-09-9	100	equine estrogen for HRT
	Estriol[a]	50-27-1	250	reproductive hormone
	Progesterone[a]	57-83-0	100	reproductive hormone
	Testosterone[a]	58-22-0	100	reproductive hormone
Sterols	Cholestanol[b]	80-97-7	100	animal sterol[c]
	Cholesterol	57-88-5	100	animal sterol[c]
	Coprostan-3-ol[d]	360-68-9	100	animal sterol
	Sitosterol[a]	5779-62-4[e]	100	plant sterol[c]
	Stigmastanol	83-45-4	100	plant sterol[c]
	Stigmasterol	83-48-7	100	plant sterol[c]

Source: Chemical Abstracts Service (CAS) registry numbers from National Institutes of Health Medical Subject Headings, http://www.nlm.nih.gov/mesh/MBrowser.html. MDL is *method detection limit.*

a. Known endocrine disrupter. Progesterone, estradiol (estriol precursor), and testosterone are approved for use in livestock.
b. Also known as dihydrocholesterol, the body produces it in the same manner as cholesterol and coprostanol; i.e., in tissue and via bacterial conversion (biohydrogenation) in the gut, respectively.
c. Other sources include plankton. Plants produce trace amounts of cholesterol.
d. Converted from cholesterol by intestinal bacteria, via biohydrogenation, in birds and most mammals, it is the primary cholesterol metabolite in humans; the bacterial dependency assures that the ratio of the two compounds varies not only among species but also among individuals within a species.
e. The isomer β-sitosterol has a CAS number of 83-46-5 and is predominant in research literature. The two are used interchangeably herein.

4. Presentation of Data

The analytes detected here are frequently found in effluent-laden waters, and in similar concentrations.

For each analyte, consistency among the samples was very good (often within the same order of magnitude, and sometimes within 20%), due largely to the rivers' similar hydrology and effluent burden. Given the relatively small size of the study area and its homogeneity, consumption patterns in the three watersheds can be assumed uniform, suggesting that significant variation in a given analyte among the samples is due to the compound's susceptibility to unique dilution agent(s) in a wastewater treatment process and/or the discharge body (or conversely, the absence of such),[1] rather than, say, an order-of-magnitude difference in the consumption of that compound across a region that spans less than 400 square miles.[2] Comprehensive influent tests would prove or disprove this hypothesis.

That said, the three watersheds' WWTPs are of the same range of magnitudes (with the exception of the Egan WRP), based on permitted flows. Thus, differences in design and operation are likely to average out at a sample site downstream of numerous facilities, which, in turn, will minimize analytical disparity among the three watersheds.

The samples were collected from the water column and then filtered at the laboratory, implying that, with respect to the discharge body as a whole, the reported concentrations are inherently biased toward soluble, hydrophilic compounds, and correspondingly, analytes in suspension and those with an affinity for sediment are underreported.

The primary vehicle for most of this study's analytes is human waste (feces and urine).[3] The human waste, in turn, hosts ECs in some combination of product absorbed and product not absorbed, plus the fraction of the former metabolized into child compounds. Investigating their behavior in the post-consumer channel is complicated by the ability of a parent or child to undergo additional transformation outside of the body (including reversion of a child to the parent): exogenous transformation, biotic and abiotic, occurs in a WWTP and discharge body.

The universe of EC dilution agents, then, is as complex as it is expansive. Practical limits restrict the extent to which one EC study can pursue the myriad of child compounds; this study restricts itself to two metabolites.

---

1. Including a facility's hold time, which will be shorter than many EC half-lives. Thus, even if a compound is malleable by one or more of a facility's subprocesses, it may be discharged before fully degrading.
2. Within a watershed, influent concentrations of an EC among WWTPs may not be uniform, as a given facility might be weighted to a particular consumption/discharge demographic, such as a hospital or retirement community. Given the similar development character of the three watersheds, however, it is plausible that comparisons among them might inherently account for outliers, as each river's downstream sample site has visibility to a similar aggregate demographic.
3. For completeness, any bodily excretion or washing off of a topical product. Direct, human deposition of ECs into the rivers of this study is insignificant, as they see no recreational use beyond the occasional nonpowered personal watercraft or bank fisherman.

The limits of interpreting EC data: A reminder about conclusions drawn from laboratory analyses

Just as a detection-limited analyte in surface water is not implied absent therein, nor, too, in EC analysis does it suggest the analyte is absent in a prior stage. In the first case, water represents a dilution force that may depress concentrations below laboratory detection limits, and in the second, surface water's role as a matrix of biotic and abiotic dilution agents (as well as biogenic sources), rather than merely as an inert transporter of ECs, assures that concentrations in effluent will fall (or rise) post-outfall.

Using the same laboratory as the present study, Skadsen et al. (2004) performed an input-output analysis of a conventional WWTP in Michigan, comparing levels of ECs in influent and effluent to determine reduction rates. They found that sulfadimethoxine, acetaminophen, ibuprofen, cotinine, caffeine, cholestanol, cholesterol, coprostanol, sitosterol, stigmastanol, and stigmasterol were mitigated by over 90%, while sulfamethoxazole, trimethoprim, and tylosin underwent reductions of 19%, 8%, and 56%, respectively; the fractions into which these compounds degraded, transformed, or sorbed to biosolids were not explored. While one WWTP is hardly representative of all, such studies are useful for highlighting relationships between ECs and their fate as spectres in treatment facilities, such as nonuniform susceptibility to a treatment process (and, as other studies have shown, to a sub-process), and the resulting resistance of concentrations at a given stage to be utilized as facile predictors of those in adjacent stages.

Per the discussion of gradients in section 2.4.1, each OWC has a dilution trajectory that is unique to its chemistry and environment—a unique response to the forces encountered in a particular WWTP and discharge body. Specifically, the response reflects a compound's susceptibility to the spectrum of dilution agents in a given wastewater treatment process and discharge body. The juxtaposition of ECs' unique chemistries with inadvertent dilution agents unique to both a WWTP and discharge body (and to segments within them) precludes the derivation of definitive lateral and longitudinal relationships. Even at a particular WWTP subprocess or point in the discharge body, no universal relationship exists with which to derive the concentration of one EC from that of another, nor to predict the concentration of a given EC at an adjoining stage, much less in a different facility or river. An implication is the lack of a general coefficient with which a surface water EC concentration can be extrapolated back to that in effluent, nor effluent back to influent (and further still, to consumption level). While trends and approximations can be inferred, exact values and general coefficients cannot; extrapolations, then, must be performed with care.

For example, it would be specious to conclude from a glance at table 8 that influent concentrations of trimethoprim at Salt Creek facilities are four times those of triclosan or one-half those of trimethoprim at facilities on the west branch of the DuPage River. Were there only one facility on each river, this would still hold true.

Perhaps the stage most amenable to extrapolation is the first. Given that the architecture of human bodies is somewhat more uniform than that of WWTPs, pharmacokinetic data is sufficiently well parameterized to suggest that pharmaceutical consumption estimates derived from influent investigations accounting for metabolites might be accurate to a higher degree than extrapolations among post-influent stages. Of course, that accuracy will still be circumscribed, by metabolic variability.

Nor, too, is EC data a facile barometer of absolute or relative ecotoxicity, as concentration alone does not determine the extent of adverse bioactivity in non-target species. Especially when they are within the same order of magnitude, a general statement cannot be made that the more abundant of two compounds poses the greater threat to aquatic organisms (some of whom, incidentally, are dilution agents). A current thrust in "eco-pharmacology" is the pursuit of chronic toxicity data for given compounds and species.

4.1. PPCPs

Fifteen common PPCPs were investigated, and are summarized in table 8 per the sequence of table 6. Samples were analyzed by University of Iowa Hygienic Laboratory using high performance liquid chromatography with tandem quadrupole mass spectrometric detection (LC/MS/MS).

Table 8. PPCP concentrations in ppt (ng/L)

Site	Lincomycin	Sulfadimethoxine	Sulfamethazine	Sulfamethoxazole	Sulfathiazole	Trimethoprim	Tylosin	Carbamazepine	Acetaminophen	Ibuprofen	Cotinine	Caffeine	Paraxanthine	DEET	Triclosan
SC	6.0	<1.0	<1.0	350	<1.0	66	7.8	120	65	9.7	210	290	14	<120	16
EB	1.8	<1.0	<1.0	220	<1.0	200	2.4	170	8.5	14	11	310	24	<120	7.6
WB	35	<1.0	<1.0	410	3.7	120	2.8	142	12	130	51	290	64	<120	6.7

4.1.1. Pharmaceuticals

Given the various agents which act upon it in a WWTP and discharge body, an EC has a complex dilution gradient unique to that microenvironment. Sunlight-mediated photolysis in the receiving waters is one such pathway, and a study by the University of Minnesota (Werner et al. 2005) found wide variability in antibiotic susceptibility to such degradation, with half-lives of 6.5 days, 2.5 days, 3.5 hours, 17.5 days, and 1.5 hours for sulfamethazine, sulfamethoxazole, sulfathiazole, trimethoprim, and tylosin, respectively; the identified modes of action were direct and indirect photolysis, the latter of which is degradation via a short-lived reactive chemical.[1] A simple dilution gradient can thus be envisioned for a given compound, by selecting a pair of gradient endpoints (point source and sample site in appendix H) and projecting onto them a stream velocity (table 4) and half-life.

To further complicate the analyses, however, microorganisms in WWTPs and discharge bodies can, through hydrolysis, restore metabolites to their parent form.

1. A compound's amenability to degradation in a discharge body is undermined by its constant replenishment by point and nonpoint sources. Thus, regardless of their individual half-lives, all ECs are effectively persistent in a discharge body.

4.1.1.1. Prescription Pharmaceuticals

Veterinary Antibiotics – sulfadimethoxine, sulfamethazine, tylosin

Given the paucity of agriculture in the watersheds, and the unlikelihood of companion animals as a source of ECs at the time of sampling, it is not surprising that sulfadimethoxine and sulfamethazine went undetected. The detection of tylosin, then, albeit in single-digit concentrations, is somewhat of an anomaly: not only is its source not obvious, but its half-life is very brief, and, anecdotal evidence points to its infrequent use (Borowiak 2008).

Human Antibiotics – lincomycin, sulfamethoxazole, sulfathiazole, trimethoprim

Lincomycin and sulfathiazole are approved for both veterinary and human use, although the aforementioned caveat suggests their vector here is human.

That sulfathiazole was detected only at WB (and there only barely so), and lincomycin was only somewhat more pervasive, is suggestive of both their decreasing human use and the rivers' lack of veterinary inputs.[1] Given the sluggish streamflow (table 4) and relatively large distances between point sources and sample sites (appendix H), the short half-life of sulfathiazole could create dramatic dilution gradients; however, they would be seasonally attenuated to an unknown degree here.

Sulfamethoxazole and trimethoprim were strongly present; the former, in fact, had the most vivid imprint of the PPCPs overall. The extent to which their concentrations, absolute and relative, can be attributed to consumption and lability (in the body, WWTP, and discharge body) will be briefly explored through four parameters.

- **Consumption** – The pairing of sulfamethoxazole and trimethoprim in the ratio of 5:1 as co-trimoxazole is perhaps the most common incarnation of the two drugs,[2] although the latter sees some solo prescribing. Some fraction of their prevalence might be attributable to seasonally varying antibiotic consumption. Other studies, such as Skadsen et al. (2004), have revealed greater influent concentrations of antibiotics during winter months, corresponding to seasonal increases of respiratory tract infections.

- **Excretion** – Sulfamethoxazole and trimethoprim are excreted primarily in the urine as metabolites: 24–30% of the former is excreted in unmetabolized form, as is approximately 40–50% of the latter (RxList 2008a, RxList 2008b). The tendency for sulfamethoxazole to be excreted at 60% of the level of trimethoprim leads to an excretion ratio of 3:1; assuming no intervening hydrolysis, that ratio will be reflected in influent as well.

- **Mitigation** – Batt et al. (2006) demonstrated trimethoprim's susceptibility to a particular WWTP process: nitrifying activated sludge degraded trimethoprim by 50% in a WWTP and by 70% in a laboratory setting. In their subsequent study of four disparate WWTPs in New York (2007), the authors showed that each stage in a given plant yielded reductions in sulfamethoxazole and trimethoprim concentrations; the final (disinfection) stage could

1. Data from the National Center for Health Statistics seems to confirm lincomycin's diminutive stature, but its scarcity creates a data set of insufficient size to quantify with certainty.
2. Co-trimoxazole ratios expressed herein are of the form sulfamethoxazole : trimethoprim.

induce a modest response (chemical degradation via chlorination) or virtually none at all (photolysis via ultraviolet light). Neither antibiotic exhibited significant adsorption to biomass (not unexpected, given their high and nearly identical hydrophilicity [appendix K]), and across the four facilities, effluent levels of sulfamethoxazole were 34%–76% less than those in influent and trimethoprim levels were 70%–97% less, in contrast to the aforementioned study by Skadsen et al. (2004). Their transformation products were not investigated.

- **Half-life** – As previously mentioned, Werner et al. (2005) found the surface water half-life of trimethoprim to be seven times greater than that of sulfamethoxazole.

Co-trimoxazole's fingerprint? Sulfamethoxazole and trimethoprim in a 5:1 ratio
As an academic exercise, the four parameters can be used to approximate a general relationship of sulfamethoxazole to trimethoprim in surface water. As the two compounds are most commonly consumed coupled in a 5:1 ratio, their metabolic incongruence suggests an influent ratio of 3:1. Given that a WWTP might remove trimethoprim at a rate that is similar to or up to three times higher than sulfamethoxazole suggests an effluent concentration of 3:1–6:1. Finally, while the discharge body half-lives of the two compounds differ by a factor of seven, the actual disparity would be less, to an extent dependent on stream velocity and the distance between the point sources and sample site. An approximate ratio of the two compounds in surface water, then, could be expected to be that of effluent for a sample site within a few hours transit of the point source to 0.9:1 or less for one a few days downstream. Extensive solo trimethoprim consumption would lower these ratios.

In fact, just such disparities were found in SC (5.3:1) and WB (3.4:1); this spread of ratios is apparent elsewhere (Loper et al. 2007). EB was the outlier, with a ratio of nearly unity; without influent data, it is difficult to postulate why co-trimoxazole embossed itself so plainly on sulfamethoxazole and trimethoprim data from one area and not on that from another.

Antiepileptic – carbamazepine
Values here show very good correlation.

The prevalence of carbamazepine in surface water is perhaps only surpassed by its prevalence in research literature. Carbamazepine is widely cited in EC investigations, as much an indicator of its ubiquitous consumption as its ability to withstand WWTP processes and go on to persist in the discharge body: various investigations have found its effluent concentration to be more than 90% of that in influent (among them, Xia et al. 2005), and it exhibits a half-life of 328 days in a water/sediment matrix and 47 days in water alone (Loffler et al. 2005).[1]

4.1.1.2. Nonprescription Pharmaceuticals
Analgesics – acetaminophen and ibuprofen
Acetaminophen and ibuprofen are widely consumed, and thus, widely detected. Concentrations here were on par with those seen elsewhere, but their diminutive stature belies the extent of their

1. The metabolite 10,11-dihydro-10,11-dihydroxycarbamazepine was considerably more labile, with half-lives of eight and seven days, respectively.

consumption. In fact, a study of two WWTPs in Michigan by Skadsen et al. (2006) revealed that, aside from caffeine, acetaminophen and ibuprofen were the most prevalent compounds in influent, exceeding 32 μg/L and 3 μg/L, respectively, the former being two orders of magnitude higher than all but one of the other PPCPs.

The concentrations observed here are a testament to the extent to which they are digested by both the body and a WWTP. Less than 9% of acetaminophen and 1% of ibuprofen are excreted in unmetabolized form in urine (RxList 2008c, RxList 2008d), which go on to drastic reduction in the facility: Xia et al. (2005) cite two studies in which WWTP processes eliminated 90% of the latter from effluent, while Skadsen et al. (2004) witnessed reductions in acetaminophen by four orders of magnitude and in ibuprofen by two orders. A higher concentration of the former in SC and the latter in WB may be more reflective of dilution agent disparities than regional differences in consumption.

For acetaminophen, Loffler et al. (2005) reported a half-life of 3.1 days for both a water/sediment matrix and water alone, with complete degradation within two weeks. Similarly, ibuprofen exhibited a half-life of ten days in water alone, and degraded by 90% in less than six days for a water/sediment matrix and approximately twice that for water alone.[1] Given the relatively short transit time between the point sources and sample points, the diminutive water column concentrations of ibuprofen, and to a lesser extent acetaminophen, were likely the result of dilutive forces in WWTPs rather than in the discharge bodies.

Foodstuffs – cotinine, caffeine, paraxanthine
The human body metabolizes nicotine into cotinine, and caffeine into paraxanthine (1,7-dimethylxanthine); in the human body, approximately 80% of caffeine is metabolized into this compound (Lelo et al. 1986).

Cotinine varied by a factor of four from one sample to the next, the widest disparity of any of the PPCP analytes. Huerta-Fontela et al. (2008) reported that influent concentrations of cotinine among eight WWTPs were similar, and their removal efficiency ranged from 76% to greater than 99%.

Caffeine, conversely, had the best agreement of the analytes, within 7%. In contrast, paraxanthine, its metabolite, varied to the same degree as most of the other analytes. Not only does paraxanthine fail to maintain the consistency of caffeine, it does so without regard to their 1:4 ratio.

Similar disparities were seen in a study of influent and effluent of eight WWTPs by Huerta-Fontela et al. (ibid.), in which the ratio between the two compounds in influent varied among the facilities, as did their susceptibility to degradation: the removal efficiency of caffeine ranged from 75% to 99%, while that of paraxanthine ranged from 70% to greater than 99%, comparable at some facilities while differing by as much as 25% at others. Given their considerable and nearly identical hydrophilicity (appendix K), high removal efficiencies are likely due to transformation rather than sorbtion.

1. The metabolite 2-hydroxyibuprofen degraded by 90% in both media within seven days.

While the discarding of unconsumed caffeinated drinks would contribute to the caffeine-paraxanthine disparities, the widespread lack of agreement between the two compounds, as well as that among paraxanthine samples, cannot be wholly attributed to nonuniform dilution forces, and suggests that there is much about their metabolism and exogenous lability that remains to be learned.

4.1.2. Personal Care Products

DEET (N,N-diethyl-meta-toluamide) is a widely used topical insect repellent. The sole seasonal analyte of this study, it is a warm weather product unused in Chicago's cold winter months. As such, it went undetected in all three samples.

Triclosan concentrations were in good agreement with effluent data. MWRDGC (2006) reported an effluent concentration of 70 ppt in the Egan WRP, placing it in the same order of magnitude of the value of 16 ppt found here. Interestingly, the report illustrates triclosan's hydrophobicity, noting an influent concentration of 4100 ppt and a subsequent biosolid concentration of 29.9 mg/kg, suggesting a sorption rate of 98%.

Similarly, the MWRDGC Hanover plant reported an effluent concentration of 90 ppt (ibid.) and a sorption rate of 97%, lending plausibility to the value of 6.7 ppt found here. Similar rates have been reported elsewhere (e.g., Xia et al. 2005), and as biosolids are frequently applied to land as fertilizer, a WWTP's removal efficiency merely serves to shift the toxic burden from water to land, and to do so in more concentrated form.

Triclosan is a good example of a polymorphous toxin. Like an antibiotic, it is capable of inducing pathogenic resistance (and conceivably, cross-resistance) and in sufficient concentration, exercises its bactericidal prowess. It has also been shown to be toxic to fish and algae, as well as to exhibit thyroidal endocrine disruption.[1]

4.2. Biogenic Compounds

Four hormones and six sterols were investigated, and are summarized in table 9 per the sequence of table 7. Samples were analyzed by University of Iowa Hygienic Laboratory using gas chromatography with mass selective detection (GC/MS).

As steroids are generally hydrophobic, they will tend towards biosolids in the facility and sediment in the discharge body. As this study analyzed filtered water, the values here underrepresent concentrations in biosolids and sediment.

1. Yang et al. (2008) found that triclosan concentrations as low as 0.53 µg/L (72 hour IC_{50}) were sufficient to inhibit growth of the green alga *Pseudokirchneriella subcapitata*. Of the twelve antibiotics they tested, it was the most potent; by comparison, tylosin-induced inhibition occurred at concentrations three orders of magnitude higher, and sulfamethoxazole, sulfamethazine, and trimethoprim at four-to-five orders of magnitude higher. When triclosan was paired with the other analytes, the resulting toxicity was additive.

Table 9. Biogenic concentrations in ppt (ng/L)

Site	Equilenin	Estriol	Progesterone	Testosterone	Cholestanol	Cholesterol	Coprostan-3-ol	Sitosterol	Stigmastanol	Stigmasterol
SC	<100	<250	<100	<100	200	2700	500	1100	<100	580
EB	<100	<250	<100	<100	440	4200	1400	1700	140	1800
WB	<100	<250	<100	<100	470	5000	3200	2200	200	1100

4.2.1. Hormones

Interestingly, none of the hormonal analytes were detected in the three rivers. That they may be present but at levels obscured by reporting limits two orders of magnitude higher than in the PPCP test is a possibility.[1] Further analysis is handicapped by the twin complications of metabolites: conjugates are the predominant urinary form of some hormones, and, can be microbially reconstituted, via hydrolysis, to an unknown extent in a WWTP and discharge body.

4.2.2. Sterols

Of all the analytes in this study, the sterol group had the greatest concentrations, with more than half of all samples penetrating the parts-per-billion range. The results are not unexpected; in contrast to PPCPs, these sterols are produced and/or consumed—and then excreted—by every person (and many of the animals) in a watershed, and produced by plants and microorganisms as well.[2]

Although exact amounts depend on diet and individual physiology, a study by Sekimoto et al. (1983) illustrates the relative magnitude of typical human sterol excretion, reporting that test subjects fecally excreted an average of 345 mg of coprostanol and 403 mg of cholesterol per day, with actual values going as high as 668 mg and 1024 mg, respectively. In their investigation of a conventional (activated sludge) WWTP in Canada, Spring et al. (2007) found that cholesterol, coprostanol, and stigmastanol levels in effluent were approximately 15%, 1%, and 8% of those in influent, respectively. Those two studies, together with the relatively large values found in the present study, suggest that influent levels of sterols are rather high, a suspicion confirmed by Skadsen et al. (2004) in their analysis of influent at a Michigan WWTP, which found concentrations as high as 130 μg/L, 1200 μg/L, 1500 μg/L, 480 μg/L, 33 μg/L, and 75 μg/L for the sterols in table 9, respectively.

1. This seems to be confirmed by a study of effluent from seven WWTPs by Desbrow et al. (1998), which failed to detect estriol, but did encounter its precursors estrone and 17β-estradiol at levels (1–76 ng/L, 1–48 ng/L, respectively) below the corresponding MDLs of table 9.
2. This amounts to little more than a recycling of sterols, as other aquatic microorganisms are consumers of them.

As an academic exercise, the preceding data can be used to estimate effluent sterol concentrations for a WWTP, and then be compared to the actual levels detected in the discharge body. For example, the Egan WRP was previously cited as servicing 160,000 people, resulting in a input cholesterol load of 64.48 kg/day. Using the 85% removal rate cited by Spring et al. (2007), 9.67 kg of cholesterol would be discharged in a volume of 22.5 mgd (MWRDGC 2007a), resulting in an effluent cholesterol level of 113.7 μg/L. In contrast, the aforementioned analysis by Skadsen et al. (2004), which utilized the same laboratory as the present study, reported a 98% removal rate, yielding an effluent cholesterol level of 15.2 μg/L, which correlates better with the actual measured value at SC of 2.7 μg/L in table 9.

Like the animal sterols, plant sterols are multiply sourced. Widely accepted as the most pervasive, sitosterol is found in vascular plants ranging from food sources to tree wood; stigmasterol is perhaps more relegated to the former and stigmastanol to the latter, although both can also be produced by microbial biohydrogenation of sitosterol (AET 1997). And, all three phytosterols can be sourced by freshwater algae (Harvey 2008).

These sources, in turn, have multiple pathways to surface water. The sterols may be indigenous and nonpoint (plants and trees in the riparian corridor, plankton in the water body itself) or arrive via point sources such as storm sewers or WWTP effluent (discarded food waste and vegetable oil, fecal matter after consumption, runoff). Because the composition of a given steroid does not differ by source, standard chromatographic mass spectrometry cannot identify its origin. Some researchers have proposed that sterol sources can be inferred from their ratios in the discharge body, but there appears to be little agreement on the exact ratios.

While the complex sourcing prevents exact identification of sterol sources in the watersheds, the preceding statements are reflected in the data. Sitosterol's prevalence in indigenous and anthropogenic sources is reflected in table 9 as the dominant analyte in its class. Less pervasive but still within sitosterol's range, stigmasterol may have seen its concentrations fortified by WWTP biotransformation. And, given the lack of timber industry in the watersheds (pulp mills or logging), stigmastanol's poor showing (by an order of magnitude) is reasonable.[1]

Many EC studies relegate waterborne sterols to biomarker status, and in particular, to the rank of fecal (usually human) indicator. However, directly and via biotransformation, the phytosterols can be hormonally active; for example, the estrogenicity of sitosterol is well known, and some studies have linked the masculinization of female fish to high levels of sitosterol and stigmastanol typical of paper mill effluent, which are microbially transformed to progesterone and then to androgens (Jenkins et al. 2003).[2]

Furthermore, given a vertebrate's reliance on cholesterol for steroid production, dismissing cholesterol as a biomarker discounts the possible harm to aquatic animals ingesting it extraneously. So, too, with phytosterols, whose ability to alter cholesterol absorption is well

1. While a watershed's indigenous sterol producers, such as plankton and terrestrial plants, might be a significant source of its aquatic sterols, they are unlikely to be so in this study's mid-winter rivers, for which runoff and planktonic biological activity would be seasonably attenuated.
2. The other major class of phytoestrogens, isoflavones, is not explored here.

known and introduces the possibility of a non-estrogenic mode of endocrine disruption. Finally, just as excess nutrients lead to algal blooms and the attendant eutrophication, so, too, might excess sterols lead to the overgrowth and overpopulation of microorganisms which consume them.

4.3. Underreporting of Total Concentrations

Due to the complexity and breadth of both ECs and the systems into which they are flushed—as well as the costs of analyzing them—most studies restrict their investigation to one matrix, at the expense of the others.

This study restricts its scope to the water column, implying a bias toward soluble ECs residing there. In doing so, it underreports hydrophobic ECs, compounds which preferentially partition to organic material: biosolids (and to a lesser extent, filter media) in a WWTP and the riverbed sediment in a discharge body.[1] Depending on the extent to which a particular EC partitions, such underreporting may manifest itself as the underappraisal of concentration or the discounting of it altogether.

Not only does such underreporting handicap the ability to infer the magnitude of EC concentrations in biosolids and sediment from water column data, but in doing so, it threatens to understate the impact on the unwitting recipient; i.e., the response of terrestrial organisms to the land application of EC-laden biosolids and that of benthic creatures and bottom-feeders to sediment-bound ECs.

While no two WWTPs or discharge bodies exhibit identical transformation proclivities, a survey of EC concentrations in biosolids and sediment is useful in providing some notion of the magnitude of EC concentrations that are underaccounted for in the water column.

Before embarking on a comparative analysis, it is worth the reminder that biosolids, sediment, and the water column represent three physically and chemically distinct substrates offering unique affinities to hydrophobic and hydrophilic compounds, that may be further modulated by parameters of the immersion media, such as temperature and pH. Just as importantly, EC concentrations therein have a temporal component—the exposure time—which is a function of mobility. At the one extreme, sampling a river's water column is only capable of revealing instantaneous concentration, with virtually no accumulation history aside from aggregating upstream inputs. At the other extreme, sediment is somewhat stationary, and thus, is effectively a repository with a long and stratified history of water borne ECs. Biosolid represents an intermediate snapshot, a repository with history of a month or so.

Obviously, too, the three media have a spatial component: because a river is their vehicle, ECs in the water column and sediment at any given point in the discharge environment represent the sum of upstream point and nonpoint sources, whereas biosolid represents a single node.

1. As biosolids are commonly applied to land as fertilizer, hydrophobic compounds' affinity for organic matter suggests that they will go on to bind to soil.

EC research sometimes relies on a compound's octanol-water partition coefficient as a predictor of its affinity for non-aqueous and aqueous media; i.e., biosolids and sediment, and the water column, respectively. K_{OW} is a dimensionless, empirical ratio, often expressed logarithmically, of the equilibrium concentrations of an analyte dissolved in a mixture of two immiscible solvents, one of which is a hydrophobic organic (octanol; numerator), and the other of which is hydrophilic (water; denominator). As such, the coefficient indicates the degree to which a compound will partition between the two media, by which it will be deemed hydrophobic, or conversely, hydrophilic. Because octanol is analogous to natural organic matter and lipids in this regard, the coefficient is widely used as a dual predictor of environmental fate: K_{OW} predicts both the degree to which an EC will adsorb to organic substrates such as biosolids and sediment (hydrophobicity) and to which it will bioaccumulate in living organisms (lipophilicity).[1] As a general guideline, USEPA (1999) proposes that organic compounds with log $K_{OW} \geq 4$ are hydrophobic while those with log $K_{OW} \leq 1$ are hydrophilic; similarly, Mackay (1995) has indicated that significant bioaccumulation generally occurs for compounds with log $K_{OW} > 5$.[2]

In contrast, soluble compounds are preferential to water rather than organic matter, and are generally of lower molecular weight and more labile, biotically and abiotically, and thus, tend to be less persistent in water bodies and also less bioaccumulative (USEPA 2005).[3]

With the preceding remarks in mind, the results of two studies of non-aqueous media are presented and compared.

4.3.1. EC Concentrations in Non-Aqueous Media

Two USGS studies are useful for comparison. Kinney et al. (2006) analyzed biosolids from eight WWTPs in seven states, and Wilkison et al. (2005) analyzed sediment from three sites on a tributary to the Blue River in metropolitan Kansas City, Missouri. The subset of analytes that overlap with those in the present study are graphed in appendix K in units of parts-per-million (equivalently, milligrams-per-kilogram) not only to center the scalar values about unity, but also to lend tangibility to the concentrations.

The graph illustrates a number of interesting trends for the selected compounds. The most obvious is that non-aqueous concentrations of biogenics are generally two or more orders of magnitude greater than PPCPs, reflecting not only their greater hydrophobicity but also their greater concentration in influent.

---

1. In fact, K_{OW} is the determinant in soil partition coefficient (K_{OC}) calculations as well as those for bioaccumulation factors (BAF) of terrestrial plants and aquatic organisms, the latter of which imply that the concentration of an EC in an aquatic organism can be $10^{\log K_{OW}}$ higher than that in the surrounding water.
2. Bioaccumulation tapers off for log $K_{OW} > 7$, as affinity for organic matter surpasses lipophilicity.
3. The relationship of K_{OW} to water solubility (S_W) is not universally inversely proportional, so the two are sometimes considered together as a better predictor of EC fate. Of course, adsorption is also influenced by factors extrinsic to the compound, such as pH, receptor site characteristics, and exposure time.

The graph also illustrates that EC concentrations in sediment are on par with those in biosolids. While river sediment is a larger, more disperse volume onto which flowing, more dilute contaminants have less opportunity to deposit, it also represents an older repository than biosolids, as well as one which is accessible to indigenous biogenics.

A third aspect of the graph that merits attention is that each data point represents the concentration of one EC in one sample. The total EC concentration in a sample, of course, is quite higher; summing merely this small analyte subset reveals that concentrations in the biosolid samples approached 1 gram-per-kilogram (1 part-per-thousand).

4.3.1.1. Dimensional Analysis: *ppm* versus *ppt*

The most important aspect of the graph is the degree to which it contrasts with water column concentrations, evident in the divergent units.

When comparing the graph in appendix K to water column concentrations in tables 8 and 9, the critical difference to bear in mind is that the baseline unit in the graph is parts-per-million, while that in the tables is parts-per-trillion, a difference of six orders of magnitude. At such disparities, the exact scalars can be neglected, leaving only the exponents to highlight the inadequacy of water column analyses as gauges of hydrophobic ECs, biosolids, and sediment.

5. Recontextualization of Data

The previous chapter presented the EC data of three neighboring watersheds, and went on to compare them in the context of interlocked areas in a uniform region. This chapter extends that notion, moving the data from the isolated core of this study to the contexts of similar studies.

Any attempt to compare and reconcile two disparate data sets will harbor some degree of imprecision. However, the benefits of analyzing EC data in historical, regional, and sectional contexts outweigh the caveats: by revealing valuable information about such modal distributions, such analyses can provide context to prior EC investigations and help guide forthcoming ones. The caveats, of course, serve to illuminate the limits of such exercises. Rather than perfect correlation, then, the endeavor seeks to reveal relationships and trends.

5.1. Salt Creek: 2007 versus 1999

The present study's sample site, SC, was a participant in the landmark EC survey launched by USGS in 1999, *Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000.* Given a desire to investigate changes that might arise over the course of nearly a decade, SC was deliberately selected to coincide with that used by USGS (designated therein as *IL03* and herein as SC_{1999}).

The implied caveat in a comparison of two EC snapshots captured 8½ years apart is: the caveats are many. Such an analysis is likely to have as many variables as constants, such as:

- operational changes at WWTPs
- hydrological differences (season-, weather-, or WWTP-related; structural)
- transient events (CSO operation; aberrant weather, facility, or consumption event)
- seasonal variations in dilution agent efficacy (calendared WWTP disinfection; temperature, light, and, aquatic organism metabolism in the discharge body)
- seasonal and year-to-year variations in the consumption of a PPCP[1]
- divergences in laboratory equipment and methods (different laboratories, technologies, and their detection limits; technological advances)

That said, SC_{1999} and SC are snapshots—legitimate in their own right—and it would be remiss to ignore the unique opportunity to contrast EC data from identical sites nearly a decade apart.

5.1.1. SC_{1999} Collection Parameters

USGS collected sample SC_{1999} on Wednesday, May 19, 1999 at 2:00 p.m.[2] The date is approximately one month prior to summer solstice, in contrast to that of the present study, which is near the winter solstice; seasonal differences in data, then, are expected. To minimize diurnal effects, SC was sampled at the same time of day as SC_{1999}.

1. In fact, one proposed application of EC research is the tracking of consumption patterns.
2. USGS performed a second, different test of SC sixteen months later which is ignored here, as the intersection of its analyte set with that of the present study is too sparse to justify the inclusion of a tertiary set of variables.

The seasonal polarity of SC_{1999} and SC is not only a matter of warm versus cold weather, but also one of wet versus dry.[1] The average maximum temperature for SC_{1999} over the abutting three days (May 17–19) was 72° F, whereas for SC it was 28° F; in the same interval, precipitation for SC_{1999} was 0.67 inch (following 1.59 inches the previous week), whereas for SC it was 0.06 inch (NOAA 1999). Streamflow data for SC_{1999} is graphed in appendix L, and the flow disparity is apparent when viewed beside figure J.1 in appendix J: the volume of water flowing at SC_{1999} was over five times greater than at SC.

The watershed's largest facility accounts for more than half of all WWTP discharge into Salt Creek. Egan WRP's 1999 average discharge rate was 26.4 mgd, averaging 30.2 mgd in the three days (May 17–19) abutting sampling of SC_{1999} (MWRDGC 2000), 30% higher than that of SC.[2]

With the preceding statements in mind, it is evident that the large disparity in flow rates between SC_{1999} and SC cannot be attributed to WWTP discharge. Assuming the Egan facility is, to some degree, a barometer of all municipal dischargers in the watershed, the aggregate contribution of WWTPs could only have been a fraction of the overall flow disparity of 550%. Thus, the additional volume can be attributed primarily to precipitation, and its diluting effect on ECs will cause SC_{1999} concentrations to be many times less than SC's. Seasonal weather patterns, then, will be the overriding caveat in a comparison of these two data sets: dilution is perhaps most to blame for imperfect correlation between them, and is exacerbated in some cases by relatively high reporting levels, resulting in analytes with a weak baseline presence (single- or double-digit ppt) being visible in SC but not in SC_{1999}.

While the accompanying runoff, via both point and nonpoint gateways, might represent an EC source in SC_{1999} that was not present in SC, the only common analytes likely to be affected are the veterinary antibiotics, although to a likely insignificant extent.

5.1.2. Intersection of Analyte Sets

SC_{1999} shares all of SC's PPCP analytes, except carbamazepine, DEET, and triclosan.[3] As SC_{1999} did not include biogenics, the comparison will be limited to the PPCP panel.

5.1.3. Comparison of PPCP Data: 2007 versus 1999

Temporal PPCP data for the studies' Salt Creek site is detailed in table 10.

1. The seasonal polarity also extends to sunlight and its attendant dilution agents and indigenous biogenic sources: Chicago winter months are characterized by overcast skies and a short day.
2. Over the ensuing decade, the plant has undergone no upgrades or changes that would affect its EC emissions (MWRDGC 2008).
3. USGS's second test of SC (footnote 2 on page 33) included DEET and triclosan, which were detected at 0.240 ppb and 0.100 ppb, respectively.

Table 10. 2007 vs. 1999: PPCPs (ng/L)

Year	Lincomycin	Sulfadimethoxine	Sulfamethazine	Sulfamethoxazole	Sulfathiazole	Trimethoprim	Tylosin	Acetaminophen	Ibuprofen	Cotinine	Caffeine	Paraxanthine
2007[a]	6	r	r	350	r	66	8	65	10	210	290	14
1999[b]	270	r	r	r	r	13[c]	r	r	r	48	220	r

Source: 2007 data from table 8 of the present study. 1999 data from USGS, *Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000*, site IL03. *r* denotes value below reporting level.

a. Values rounded up for consistency.
b. Source denotes the first six analytes (sulfadimethoxine–tylosin) as method 1 (LC/MS) and the last six as method 3 (HPLC). Reporting levels for *r* entries are 50, 50, 100, 100, 50, 9, 18, 18, respectively. Values originally stated in units of µg/L.
c. Estimated value.

The aforementioned caveats notwithstanding, possible sources of the consistent and discrepant data pairs in table 10 will be explored.

5.1.3.1. Pharmaceuticals

5.1.3.1.1 Prescription Pharmaceuticals

Veterinary Antibiotics – sulfadimethoxine, sulfamethazine, tylosin

That two studies, nearly a decade apart and in diametric seasons, failed to detect sulfadimethoxine and sulfamethazine is a testament to their irrelevance in the watershed.

Given the dilution that accompanied SC_{1999}, it is plausible that tylosin was present in 1999 water in low single digit concentrations but obscured by a reporting level nearly one order of magnitude larger than the concentration detected in 2007.

Human Antibiotics – lincomycin, sulfamethoxazole, sulfathiazole, trimethoprim

Sulfathiazole and lincomycin are approved for human and veterinary applications, and given sulfathiazole's limited role in the former and the lack of obvious inputs for the latter, it is not surprising that it went undetected in both studies, although a high reporting level in SC_{1999} erodes the confidence of this conjecture.

The virtual absence of lincomycin at SC contrasted with its strong presence at SC_{1999}, especially in light of dilution, is more difficult to explain. The disparity could reflect long term and/or seasonal usage trends. As mentioned in previous chapters, various sources have noted lincomycin's declining use in recent years. At the same time, it may see seasonal veterinary use in a large horse racing facility with numerous stormwater outfalls into Salt Creek, which operates May–September under a discharge permit that accounts for animal waste.

Similar long- and short-term trends in the remaining two antibiotics may also be reflected in the respective data pairs. Data from the National Center for Health Statistics (appendix M) shows co-trimoxazole (sulfamethoxazole and trimethoprim) in a steep, multi-year descent which culminates in 2001 and then rapidly ascends again. Superimposed on that trend, however, might be their seasonally-weighted use (increased consumption in winter months). While the trimethoprim data pair plausibly correlate, due to dilution, trends, or some combination thereof, similar conjectures about sulfamethoxazole are precluded by a high reporting level.

5.1.3.1.2 Nonprescription Pharmaceuticals

Analgesics – acetaminophen and ibuprofen

Acetaminophen and ibuprofen were likely the victims of dilution and obscurant reporting levels in SC_{1999}, with that of ibuprofen exceeding the level found in SC.

Foodstuffs – cotinine, caffeine, paraxanthine

Assuming that dilution is the primary obstacle to parity throughout table 10, SC_{1999} shows excellent correlation with SC for cotinine and good correlation for caffeine. An obscurant reporting level hampers the extension of that correlation to paraxanthine, a metabolite of the latter.

5.1.3.2. Personal Care Products

Although it was not part of SC_{1999}, it is worth noting in the contrasting values of DEET the expression of a seasonally consumed product. As outdoor pest insects are active only during warm months in northern Illinois, it would be expected that insect repellent use would be limited to that time. Predictably, then, DEET was detected at 240 ppt in the warm month of SC_{1999} (see footnote 3 on page 34) and went undetected in the cold month of SC.

5.2. Metropolitan Areas: Chicago versus Kansas City

The landscape of American consumption is arguably less varied than that of its geography. As only the former is responsible for fomenting micropollutants, the general uniformity of consumer habits suggests that a uniform palette of ECs—a constellation of “the usual suspects”—is likely to be found in discharge bodies across the United States, in cities large and small.

This is not to say that the palette is rigid; regional consumption variations do exist, in both substance and degree. In comparing two regions, however, the former would simply add or subtract from, rather than rule out, a ubiquitous and relatively large palette core, while the latter may have less impact on relative surface water concentrations than does geographical variation (discharge body, as well as WWTPs). And, of course, any regional variations are themselves subject to seasonal and long term trends.

To these ends, the present study’s EC data area will be compared to that of a similar region, the Kansas City metropolitan area.[1] The degree to which their contaminant profiles correlate will attest to the veracity of the preceding statements.

1. The area straddles the states of Missouri and Kansas.

The Kansas City study, a USGS project titled *Water Quality in the Blue River Basin, Kansas City Metropolitan Area, Missouri and Kansas, July 1998 to October 2004,* was selected because of the regions' proximity and climatic similarity, as well as the thoroughness of the investigation and parallels to the Chicago study: like this one, the Kansas City study analyzed three effluent-heavy rivers in a large metropolitan area during low-flow conditions. Throughout this section, the Kansas City study will be referred to as *KC,* and the present study as *CHG.*

As conceded, a comparison of two disparate data sets is laden with caveats, and a regional one will inherit most of the variables listed in the previous section, plus the obvious differences in geography (including land use and hydrology), WWTPs, population and demographics, and, sample quantities,[1] to name a few. However, as extensions of comparisons among watersheds, comparisons among regions might embody some degree of the self-correction inherent to analyses of aggregated systems, in which variables that might otherwise contribute disparity to data pairs are common to both systems and offset each other. The elements within a given parameter in one region might, in the aggregate, be on par with those in the other, such that an element deemed unique or aberrant within one might, in fact, be common to both. For example, the total diversity of WWTP processes within a study region may be similar to that in another, diminishing the ability of either one to introduce gross disparities into the comparison.

Regardless, CHG bears sufficient parallels with KC's chief elements to merit a comparison. KC and CHG are legitimate EC profiles in their own right, and the homogeneity of the consumption landscape provides a stable foundation on which they can be tested for agreement. Beyond that, this comparison does not (and cannot) constitute an appraisal of the relative water quality or WWTP efficacy of the two areas, for any number of reasons.

5.2.1. KC Collection Parameters

USGS collected samples between May, 1999, and August, 2004, at which times the range of median streamflows for the three rivers was 0.70–50.0 cfs (Wilkison et al. 2006); compare to appendix J.

5.2.2. Intersection of Analyte Sets

KC shares approximately half of CHG's analytes, neglecting the antibiotics sulfadimethoxine, sulfamethazine, sulfathiazole, lincomycin, and tylosin in the PPCP panel and testosterone, equilenin, estriol, progesterone, cholestanol, and stigmasterol in the biogenic panel.

5.2.3. Regional Parameters

The distance between Kansas City and Chicago is approximately 400 miles. At 289 square miles, KC's region of study is 19% smaller than that of CHG, less of a factor perhaps than the disparity in size of the two studies' data sets: KC's is larger than that of CHG, its sites both more numerous and more frequently sampled, so its values can be expected to span a wider numerical range.

1. In the context of a comparison with the present study, the thoroughness of KC is also its Achilles' heel: data spans the years 1999–2004, introducing a temporal variable to the analysis.

At the same time, KC represents a less diverse treatment picture, encompassing three facilities with an average total discharge of 17.4 mgd (Wilkison et al. 2006). However, as this comparison is based on contaminant concentrations rather than overall volumes, the two data sets can attribute much of their correlation to the fact that their rivers are dominated to similar degrees by effluent during the low-flow conditions at which they were sampled.

Residential property accounts for 33% of the land use in the study area (compared with an average of 49% in CHG) and agricultural for 11% (compared with an average of 3% in CHG) (Wilkison et al. 2006). The 2000 population of the four county area was 1,345,940 (USBC 2000).

5.2.4. Comparison of Data: Chicago versus Kansas City

5.2.4.1. PPCPs

PPCP data ranges are detailed in table 11 and graphed in figure N.1 of appendix N.

Table 11. Chicago versus Kansas City: PPCPs (ng/L)

Site	Sulfamethoxazole	Trimethoprim	Carbamazepine	Acetaminophen	Ibuprofen	Cotinine	Caffeine	Paraxanthine	Triclosan
CHG[a]	220-410	66-200	120-170	9-65	10-130	11-210	290-310	14-64	7-16
KC[b]	49-118	15-42	8-62	31-639	120-351	22-156	24-1860	39-992	88-630

Source: CHG data from table 8 of the present study. KC data from USGS, *Water Quality in the Blue River Basin, Kansas City Metropolitan Area, Missouri and Kansas, July 1998 to October 2004*, table 8 median values (triclosan from table 7).

a. Values rounded up for consistency.
b. Reporting levels are 23, 14, 11, 9, 18, 23, 14, 19, and 50–1000, respectively. Values originally stated in units of µg/L.

The aforementioned caveats notwithstanding, the pairs of data ranges in table 11 will be explored.

5.2.4.1.1 Pharmaceuticals – Prescription

Human Antibiotics – sulfamethoxazole, trimethoprim

KC ranges of sulfamethoxazole and trimethoprim are uniformly lower than their CHG counterparts by a factor of approximately four. The disparity may be due to dilution and/or the multi-year consumption trends outlined in the prior discussion of SC_{1999}.

However, the more interesting aspect of these two data pairs is that their uniformity appears to extend laterally as well. While KC did not itemize data points for sulfamethoxazole and trimethoprim, the ratios of their median values averaged 3:1 (Wilkison et al. 2006), suggesting the fingerprint of co-trimoxazole.

Antiepileptic – carbamazepine
Carbamazepine is the only other PPCP whose KC value falls wholly below CHG, although they each maintain a spread of approximately 50 ppt.

5.2.4.1.2 Pharmaceuticals – Nonprescription
Analgesics – acetaminophen and ibuprofen
KC and CHG show a modest amount of overlap in the two analgesics, acetaminophen and ibuprofen, with CHG on the low end of each.

Foodstuffs – cotinine, caffeine, paraxanthine
As in the previous section's analysis of SC_{1999}, cotinine exhibits excellent correlation here. For caffeine and its metabolite, paraxanthine, CHG shows modest correlation with KC, whose variations are the greatest of the PPCPs. The parent-child relationships here reinforce the presumption that data disparity between regions is derived more from dilutive forces (WWTP and discharge body characteristics) than consumption ones: figure N.1 clearly illustrates that the relationship between caffeine and paraxanthine in KC is quite different than in CHG and reinforces its complexity. Were the disparity simply a matter of dilution, the two KC and CHG data pairs would be symmetrical but offset, in the manner of sulfamethoxazole and trimethoprim in the same figure.

5.2.4.1.3 Personal Care Products
Of the PPCPs, triclosan exhibits the poorest correlation, separated by nearly an order of magnitude.

5.2.4.2. Biogenic Compounds
Sterol data ranges are detailed in table 12 and graphed in figure N.2 of appendix N.

Table 12. Chicago versus Kansas City: biogenics (ng/L)

Site	Cholesterol	Coprostanol	Sitosterol	Stigmastanol
CHG	2700-5000	500-3200	1100-2200	140-200
KC[a]	875-6220	190-4150	960-3400	1180-1430[b]

Source: CHG data from table 9 of the present study. KC data from USGS, *Water Quality in the Blue River Basin, Kansas City Metropolitan Area, Missouri and Kansas, July 1998 to October 2004,* table 7 median values.

a. Reporting levels are 600–2000, 1000–2000, 2000, and 2000, respectively. Values originally stated in units of µg/L.
b. Sparse data set.

The aforementioned caveats notwithstanding, the pairs of data ranges in table 12 will be explored.

5.2.4.2.1 Sterols

Three of the four sterols show good correlation, with CHG ranges wholly within those of KC's larger data set. Correlation of the fourth, stigmastanol, is hampered by sparse data in KC.

The ratio of cholesterol to its metabolite coprostanol was larger in CHG than in KC, whose median values were chiefly in the ratio of 2:1.

5.3. Adjacent Stages: Water Column versus Effluent

Hydrologic data in table 4 attests to the extensive effluent burden of the three rivers in the present study. A comparison of their EC concentrations with those in raw effluent will confirm that, as well as illustrate the extent to which a heavily impacted discharge body's EC data is representative of that of effluent, and vice versa.

The city of Ann Arbor, Michigan, performed an EC analysis of the Huron River, including the municipal WWTP sited there. The investigation by Skadsen et al. (2004) is titled *The Occurrence and Fate of Pharmaceuticals, Personal Care Products and Endocrine Disrupting Compounds in a Municipal Water Use Cycle: A Case Study in the City of Ann Arbor.* Its effluent profile is the focus of this section and will be referred to as *EFF,* and the present study's data as *WC* (water column).

Given the lack of effluent EC data in the region of the present study, EFF is an ideal surrogate, and an important common denominator among the two studies is the use of the same laboratory and analytical methods to investigate a nearly identical set of analytes.

The degree to which the three rivers are dominated by effluent during low-flow conditions will be reflected by the likeness of the two data sets. Of course, EC concentrations in the water column of any highly impacted discharge body will be less than, but otherwise within reasonable range of, those in effluent, to an extent determined by dilutive forces, including outright dilution.

Considering the caveats of the previous two sections, imperfect correlation is expected here. In fact, unlike the data sets elsewhere in this report, EFF represents a single facility. Thus, a nonuniform parameter, such as a lopsided demographic, operational anomaly, or unique design element, will have a more pronounced impact on its data and contribute to disparity.

5.3.1. Effluent Collection Parameters

To minimize seasonal discrepancies in consumption and dilutive forces, data from the winter month (February) of EFF will be compared to averages of WC's three rivers.

Effluent samples were collected at the Ann Arbor WWTP on February 10, 2004 at 9:10 a.m. The facility's discharge rate averaged 17.1 mgd in the three days (February 8–10) abutting sampling (CoAA 2008).

5.3.2. Intersection of Analyte Sets

EFF shares all of WC's biogenic analytes and all of its PPCPs except paraxanthine, DEET, and triclosan.

5.3.3. Regional Parameters

The distance between Ann Arbor and Chicago is approximately 200 miles, between which sits Lake Michigan. The Ann Arbor WWTP serves a population of approximately 135,000 people.

5.3.4. Comparison of Data: Water Column versus Effluent

5.3.4.1. PPCPs

The aforementioned caveats notwithstanding, the PPCP data pairs in table 13 will be explored.

Table 13. Water column versus effluent: PPCPs (ng/L)

Site	Lincomycin	Sulfadimethoxine	Sulfamethazine	Sulfamethoxazole	Sulfathiazole	Trimethoprim	Tylosin	Carbamazepine	Acetaminophen	Ibuprofen	Cotinine	Caffeine
WC	14	r	r	327	r[a]	129	4	144	29	51	91	200
EFF[b]	9	1	r	860	r	610	r	350	5	20	r	310

Source: Chicago data averaged from table 8 of the present study. EFF data from Skadsen et al. (2004), table 5 effluent data for February. *r* denotes value below reporting level.

a. Below reporting limit in SC and EB, 3.7 ng/L in WB.
b. Reporting levels for *r* entries are 1, 1, 1, and 200, respectively. Values originally stated in units of μg/L.

5.3.4.1.1 Pharmaceuticals – Prescription

Veterinary Antibiotics – sulfadimethoxine, sulfamethazine, tylosin

The three veterinary antibiotic data pairs are near or below MDL, and their agreement reaffirms prior statements about the virtual absence of such pharmaceuticals in an urban watershed. In fact, in the corresponding influent data, Skadsen et al. (2004) reported that the two sulfonamides went undetected and tylosin was near the reporting level.

Human Antibiotics – lincomycin, sulfamethoxazole, sulfathiazole, trimethoprim

In EFF, lincomycin and sulfathiazole display the diminutive human and veterinary character observed in WC; the latter compound went undetected in influent as well (ibid.).

The sulfamethoxazole data pair and the trimethoprim data pair exhibit good correlation, with EFF values at low-order multiples of WC. The lateral correlation is less robust, but EFF displays some semblance of co-trimoxazole.

Antiepileptic – carbamazepine
The carbamazepine data pair exhibit good correlation, with EFF at a low-order multiple of WC.

5.3.4.1.2 Pharmaceuticals – Nonprescription
Analgesics – acetaminophen and ibuprofen
Acetaminophen and ibuprofen are present in EFF but less well correlated to their WC counterparts.

Foodstuffs – cotinine and caffeine
The caffeine data pair exhibit good correlation, with EFF at a low-order multiple of WC. Cotinine shows the poorest correlation, having gone undetected in influent as well (ibid.).

5.3.4.2. Biogenic Compounds
The aforementioned caveats notwithstanding, the biogenic data pairs in table 14 will be explored.

Table 14. Water column versus effluent: biogenics (ng/L)

Site	Equilenin	Estriol	Progesterone	Testosterone	Cholestanol	Cholesterol	Coprostanol	Sitosterol	Stigmastanol	Stigmasterol
WC	r	r	r	r	370	3967	1700	1667	113	1160
EFF[a]	r	r	r	r	1400	3200	3000	4700	270	1300

Source: Chicago data averaged from table 9 of the present study. EFF data from Skadsen et al. (2004), table 5 effluent data for February. *r* denotes value below reporting level.

a. Reporting levels for *r* entries are 50, 200, 200, and 200, respectively. Values originally stated in units of μg/L.

5.3.4.2.1 Hormones
As in WC, all hormone analytes went undetected in EFF. In fact, they also went undetected in Ann Arbor influent for all months of the same study.[1] However, like those of the present study, EFF reporting levels are sufficiently high to obscure low-ppm concentrations;[2] nor, too, are conjugates accounted for.

5.3.4.2.2 Sterols
The sterol data set is well correlated, and as in the PPCP comparison, EFF concentrations are at low-order multiples of their WC counterparts, cholesterol being the exception.

1. In a subsequent test of the Ann Arbor and Grand Rapids facilities, Skadsen et al. (2006) detected E1, E2, and E3 in influent at levels not exceeding 29 ng/L. WWTP mitigation ranged from 29% to 74%, with the exception of E2 in one sample which underwent no reduction.
2. Refer to footnote 1 on page 28.

6. Conclusion

This study investigated emerging contaminants in three watersheds of metropolitan Chicago. It was the first such examination of the DuPage River tributaries, and the first of Salt Creek in nearly a decade. Uniform throughout the relatively small region of study and typical in many ways, the three watersheds revealed a collective EC profile representative of developed areas.

A broad sample of PPCP and biogenic compounds were surveyed in the water columns of the watersheds' freshwater, effluent-heavy rivers at low flow. Land use in the area guided analyte selection, prompting the use of domestic panels.

Given the suburban setting of the study and the lack of runoff in the sampling interval, it is not surprising that veterinary antibiotics were largely absent in the data. Sulfadimethoxine and sulfamethazine went undetected in all samples, while tylosin appeared in single-digit concentrations. Lincomycin and sulfathiazole, approved for both veterinary and human use, were similarly exiguous.

That tylosin appeared in all three rivers, albeit in single-digit form, eludes facile explanation. The inability to identify the sources of such seemingly alien ECs is as frustrating as the possibility that they may merely be artifacts of the process. Increases in the sensitivity of analytical methods and in the diversity of the analyte palette will only increase the need to reconcile such idiosyncrasies in future studies, possibly challenging traditional assumptions about EC sources.

The human antibiotic analytes, sulfamethoxazole and trimethoprim, were strongly present—perhaps reflective of seasonally weighted consumption—and in ratios suggestive of co-trimoxazole. To that end, the text utilized the sources to estimate typical surface water ratios of the two compounds indicative of co-trimoxazole.

The antiepileptic carbamazepine appeared in concentrations on par with trimethoprim, but with better correlation. As a ubiquitous and persistent EC, its prevalence in surface water is perhaps exceeded only by its prevalence in research literature. The pharmaceutical most emblematic of impaired waters, carbamazepine is a nonseasonal, anthropogenic biomarker bar none, whose hydrophobic eschewal of the water column led the data to understate its overall levels in the environment.

As commonly observed, the nonprescription analgesic analytes, acetaminophen and ibuprofen, were detected in modest concentrations that belie their extensive use. The drugs are extensively metabolized by both the body and WWTP, and a study was referenced which reported influent concentrations up to three orders of magnitude higher than those detected in surface water here, attesting to the susceptibility of these labile compounds to dilution agents.

Across the three watersheds, cotinine exhibited the widest variation of the PPCPs, while caffeine—second only to sulfamethoxazole in overall concentration—exhibited the least, and paraxanthine, its metabolite, consented to a more intermediate posture. Despite the widely circulated pharmacokinetic data on caffeine and paraxanthine, their refusal to exogenously

maintain a 1:4 ratio (or any other identifiable one) deserves greater attention, as it may be indicative of a more fundamental misunderstanding in conventional EC wisdom.

Of the two PPCPs investigated, the insect repellent DEET went undetected. The sole seasonal analyte of this study, it would not see use during winter months.

Like carbamazepine, triclosan is a ubiquitous, hydrophobic EC whose modest water column concentrations obscure its overall prevalence. The text cited a study of triclosan's prevalence in biosolids and effluent at a WWTP in the watershed, whose concentrations were in good agreement with those detected here.

Man-made versus man made

The natural manner in which EC studies juxtapose PPCP and biogenic analytes is a testament to the breadth of the field. Unlike PPCP and industrial micropollutants, which are largely man-made in the synthetic sense, biogenic compounds are man made in the literal sense—endogenously created within man, and/or animals, plants, and microorganisms. As such, they are likely to be the most prevalent EC class in a WWTP and discharge body, and often, the most hydrophobic. Unfortunately, compounds so multiply sourced are onerous to investigate, as standard chromatographic mass spectrometry does not distinguish their myriad progenitors.

Despite their excretion by humans and other vertebrates in the watershed, the four hormones went undetected. Based on studies cited in the text, it is likely that they are present below the MDL, perhaps in the single-digit parts-per-trillion range.

While hormones were the only class to go wholly undetected, sterols, conversely, were the only class whose members encroached upon the parts-per-billion range. Cholesterol, both produced and consumed by humans and animals in the watersheds, had the strongest imprint of all analytes in this study, followed by coprostanol. Cholestanol is a minor companion of cholesterol in the body and appeared at levels approximately one-tenth of it in the discharge body. The text utilized the sources to calculate expected surface water concentrations of cholesterol, and in doing so, cited two divergent studies to highlight the lack of uniformity among WWTPs in their inadvertent mitigation of ECs.

Like the hormone analytes, phytosterols are multiply sourced and strongly present in the water column. Hydrophobically similar compounds, the concentrations of sitosterol, stigmastanol, and stigmasterol in surface water can be attributed to their prevalence in influent, the greater watershed, and the discharge body itself, the latter of which raises the interesting notion of an aquatic organism being at once an EC source, victim, and dilution agent. The likely source of phytosterols in this study was the domestic sphere.

Few of the analytes were bound to seasonal consumption, making the greater seasonal influence on this study environmental. Climate influences the concentration of aquatic ECs to an unquantifiable extent, and Chicago's winter weather is likely to throttle dilution agents in many ways: runoff and dilution would be forestalled by scant precipitation, dilution agents in the discharge bodies (and to a lesser extent, in the WWTPs, which may embody self-corrective mechanisms) would be constrained by cold temperatures, and sunlight-mediated processes would

be attenuated by a dearth of sunlight from shortened days, overcast skies, and a low solar altitude by which the sun fails to crest the tree canopy along these north-south oriented rivers. Similarly, as a discharge body can simultaneously be both a sink and source of ECs, the metabolism of biogenic EC sources would be at a minimum or even dormant.

As useful as it is to identify the environmental factors, quantifying their contributions is unfeasible. In winter months, the “elements” are simply the natural, inhibitive forces which throttle natural processes; the elements which comprise a season that much of the northern hemisphere experiences for a sizeable fraction of the calendar year. Thus, while dilution agent efficacy (and indigenous biogenics production) is likely at a maximum during warm months, framing the winter season as a subset of the summer runs the risk of implying that the summer season is the dilution agent baseline from which all others deviate. While a watershed might be more fully parameterized by EC tests performed in each of its distinct seasons, the seasonal disparity of EC concentrations in a discharge body is not so dramatic to disqualify a single test from representing the whole.

EC concentrations in the post-consumer channel were presented within the framework of a dilution gradient, a conceptual model which, in turn, was constructed with transformation and sequestration agents. Collectively termed dilution agents, these constructs represent inadvertent forces to which an EC may be labile, and as such, are the fundamental enigma underlying EC analysis: the study of a diverse set of micropollutants whose mitigation has been relegated to nonuniform, poorly identified, and sometimes little understood forces which were not intended for such a role. An EC’s relationship to a dilution agent in a WWTP or discharge body is less a deliberately paired mitigation scheme than a chance encounter between two strangers who will interact to some degree and for some time, if at all.

To illustrate the extent to which sequestration agents influence EC concentrations in non-aqueous media, the results of separate USGS biosolid and sediment studies were graphed in the appendix. Comparing that graph with the present study’s data dramatized the inadequacy of water column studies for revealing the magnitude of overall EC prevalence in a watershed, and also illustrated the use of hydrophobicity, via the parameter K_{OW}, in predicting the greater prevalence of biogenics over PPCPs in organic substrates.

The report also demonstrated the viability of comparing like studies. With perfect correlation explicitly not a goal, each study was selected based on common parameters, with the aim of uncovering relationships and trends therein. Otherwise dissimilar EC studies share a common set of underlying variables—namely consumption and WWTP objective—which are sufficiently uniform to facilitate comparison. Such comparisons allow this study’s data to be viewed in larger historical, geographical, and sectional contexts. At the same time, given the expense and complexity of EC analyses, the value of comparisons lies not only in uncovering trends and relationships, but also in providing context and guidance for forthcoming studies.

Intraregional Comparison

The main thrust of the present study was an exploration of micropollutants in three key watersheds of the Chicago metropolitan area, with the aim of uncovering the region’s EC profile. In doing so, it provided a natural platform on which to compare the data of three like areas within

a region sufficiently small and homogenous to assume uniformity in consumption, weather, hydrology, and WWTP objective, and thus, in aquatic EC profile. That recontextualization required the removal of the watersheds from a hydrological context and their redefinition as a homogenous, demographic entity. As that uniformity can be extended to the greater Chicago metropolitan area, so too can the EC profile revealed in this study.

The presentation of the watersheds' data in the main body of this report sought consistency in each analyte among them, to a largely successful degree. Good correlation was found, and where it was not, it highlighted the imperfect nature of such comparisons, where disparities—sometimes significant—will appear even as the primary variables are held constant. Disparities were attributed to variations in WWTP dilution agents rather than hydrological and consumptive influences. Overall, consistency was good, demonstrating the viability of a comparison of watersheds within a region and testifying to the veracity of the data collected from them.

Too, the disparities highlighted the fickle nature of grab samples. Unlike accumulative matrices, like biosolids and sediment, whose EC inventory varies slowly and continuously in the temporal and spatial realms, the water column is in perpetual flux. A grab sample of surface water, then, is a snapshot in time and space, with an inherent noise factor. As EC awareness gains inertia and research budgets begin receiving the attention they deserve, such sampling variability will be minimized by averaging multiple samples across time and space.

Interregional Comparison

The present study's investigation of three adjacent watersheds was readily extended to a comparison of them, on the premise of homogenous consumption patterns, climate, hydrology, WWTP objectives, and dilution agents. That intraregional comparison, in turn, was extended to an interregional one, in which the data was compared to that amassed by USGS for the Kansas City area, with the aim of demonstrating the existence of a shared EC profile—"the usual suspects" in the vernacular—which can serve as a guide to forthcoming EC studies.

The comparison, illustrated in the appendix, shows reasonable correlation of the PPCP and biogenic analytes, with most exhibiting overlapping concentrations and all ranges within two orders of magnitude.

All analytical comparisons, of course, embody imperfect parameter matching, and this one is no exception. The disparity in sample quantities was likely to blame for the disparity in a given analyte's ranges; too, the collection of Kansas City data over a period of time could have added short- and potentially long-term consumption trends and dilution agent variables to the comparison. The lack of broader overlap could be due to the studies' disparity in WWTP diversity.

That said, and the analyte set herein being a subset of "the usual suspects", correlation was sufficient to attest to the existence of common EC profile among the two regions. If, as the present study asserts, the American consumer landscape is a largely homogenous one, then the interregional parity could be extended still further, pointing to the existence of common, nationwide EC profiles, perhaps delineated by parameters such as medium (biosolids, sediment, water column) and watershed character (urban, rural).

A useful outcome of regional comparisons is the quantification of “the usual suspects”. EC research is sufficiently mature to merit codification of common EC profiles, depicting the ubiquitous ECs and their typical concentration ranges. Conversely, ECs which go widely undetected, such as the veterinary antibiotics in the present study, would be candidates for deletion. The profiles would depict the range of typical concentrations for each contaminant, perhaps normalized to streamflow, and would function as a priority list for a municipality interested in investigating its EC profile, providing “start here” guidance for the launching of a maiden investigation.

Temporal Comparison

The sample site SC first underwent micropollutant testing in 1999, as part of USGS’s landmark EC survey. The deliberate selection of that site for the present study created a unique opportunity to track EC trends over the course of nearly a decade.

The temporal comparison yielded a semblance of correlation in one-half of the analytes. Broader correlation was hampered by two variables, as dilution conspired with high reporting levels to obscure many values in the 1999 data set. While the comparison yielded some possible trends, its veracity may have been compromised by precipitation-induced dilution, which swamped underlying trends.

That better success was not realized does not point to a fallacy in the endeavor. Temporal testing holds promise, and the experience here underscores the importance of maximizing parameter alignment among the two investigations. Streamflow, a key parameter to the comparison, was diametric in the two studies, as the need to equalize flow rates deferred to the present study’s overriding goal of examining the region’s EC profile during low-flow conditions.

Temporal comparisons are valuable for a number of reasons, the most obvious of which is to track EC trends in various media. Too, they can be used to track consumption, and to gauge their utility in such a role, it would be a valuable exercise to analyze EC data across a given time interval against the backdrop of the corresponding consumption data.

Short term, temporal comparisons are already utilized by many researchers, in which samples collected hourly, daily, weekly, monthly, or seasonally are scrutinized for trends, such as consumption patterns and dilution agent efficacy.

Sectional Comparison

To confirm hydrological evidence of effluent loading in the watersheds, the present study’s EC data was contrasted to that of raw effluent from a study by the city of Ann Arbor, Michigan. In doing so, it also sought to demonstrate that EC concentrations in a given stage can be approximated from those in an adjacent one if done with care. The two studies utilized the same laboratory, test methods, and largely the same analyte sets, enhancing the veracity of the comparison.

Very good correlation was exhibited between the two data sets, with nearly identical deficiencies of antibiotics and hormones, and effluent concentrations of most other analytes at low-order multiples of those in the water column. Their likeness confirmed the degree to which the present

study's three rivers are dominated by effluent during low-flow conditions, while suggesting that a facility's effluent EC data might serve as a satisfactory surrogate for investigations of its highly impacted surface water in the absence of such, and vice versa. Too, the data sets' agreement attests to the existence of a common EC profile among the two areas arising from homogenous consumption patterns.

While the ability to extrapolate EC data to an adjacent stage does not obviate the need for tests thereof, it does provide guidance in the absence of such, an important aid in managing the cost and complexity of EC analysis.

◆ ◆ ◆

While the dangers posed by ECs are still largely unknown, a growing body of research has shown that their effects are multifarious, jeopardizing human and nonhuman health alike. Although the two are bridged by the latter's role in the food chain, they are usually discussed separately for clarity.

In the context of aquatic ECs, the primary subjects of exposure are organisms in the discharge body, and to a lesser extent, those in the riparian corridor. That waterborne EC concentrations are ultra-trace is offset by the nature of exposure: aquatic exposure is full body, continuous, and chronic—lifelong and often multigenerational—during which a full spectrum of waterborne ECs are respired. Exposure to the ingested subset is less frequent but is offset by biomagnification as prey ascend the trophic levels.

To consider just one class of ECs: a pharmaceutical is meticulously engineered to be both potent and pointed to a specific human receptor, and its metabolism and influence in a nonhuman species cannot merely be extrapolated from traditional (i.e., human) pharmacological data. In contrast to acute toxicity, the aquatic response to microdosed, chronic exposure may be nuanced and/or unconventional, and is being pursued within the context of eco-pharmacology: eco-pharmacokinetic research investigates the environmental metabolism of a compound, including aquatic transformation and sequestration agents, while eco-pharmacodynamic research investigates the effects of a compound on nontarget species. In an aquatic organism, and particularly an invertebrate, the former may reveal that a nontarget organism lacks the optimal ameliorative pathway (or equivalently, suffers from EC-mediated efflux pump impairment), increasing a compound's effective toxicity.

The latter, on the other hand, may reveal that the targeted receptor undergoes an undesignated response or is rooted in a different system. Of course, neither the response nor roots need be atypical for the reaction to be adverse, as the nominal (i.e., human) response might be sufficiently harmful in itself. And, while a growing body of EC research, both in-vivo and in-vitro, has demonstrated a myriad of deleterious effects on aquatic organisms, the studies are relatively short

term, a fleeting glimpse that passes before the effects of long term, low-level exposure have an opportunity to express themselves. Too, the response may manifest in a different location or manner than which experience or tradition has trained the researcher's gaze.

Unlike acute toxicity, chronic exposure to a micropollutant is unlikely to kill an organism outright nor impair a colony quickly, but may do so by inducing a subtle behavioral change, or an incremental, biological one, over successive generations that eventually put it at a competitive disadvantage for mating, feeding, or evading predators. Such might go unrecognized by researchers until the mutation has fully manifested itself, at which point it will be as difficult to attribute to anthropogenic stimuli as it is to undo.

Of course, this discussion would be incomplete without mentioning the second mode of WWTP-mediated EC transport. As a treatment facility represents a fork in the influent road, ECs with an affinity to biosolids may eventually find themselves being applied to land, where they can provoke terrestrial and soil organisms. That land, too, may be a non-point source of surface and ground water contamination, as well as an uptake gateway for biota.

The text noted that WWTP removal efficiency, a common and misleading EC test parameter, merely expresses a compound's apparent mitigation as a ratio of influent-to-effluent concentrations. As such, it provides an incomplete picture of EC removal, failing to divulge the fate of the fraction gone missing from effluent, and whether it was actually degraded or merely diverted to biosolids, whose land application shifts its toxic burden from the aquatic to the terrestrial realm, and in more concentrated form.

Similar statements can be made about livestock manure (feces and urine), a potent EC source on the farm. Numerous studies have shown that lagoons are model EC reservoirs, containing high levels of hormones and veterinary pharmaceuticals, such as antibiotics and the corresponding resistant pathogens, which are transferred to soil when the manure is applied to cropland as fertilizer. Kumar et al. have demonstrated two additional ramifications; namely, that antibiotics applied to soil remain bactericidal (2005a) and are susceptible to uptake by food crops (2005b). But, while there are a number of mechanisms by which resistance can be manifested (such as selection for uptake barriers or efflux pumps) or transferred among bacteria, there is little data as to whether antibiotic transformation products are capable of inducing resistance to the parent compound.

Unique in their systematized reliance on microorganisms to mitigate organic matter, WWTPs are also both a gateway of antibiotics and a potential source of resistant pathogens, in biosolids and effluent. Furthermore, antibiotics, antimicrobials, and other ECs threaten the livelihood of in-house flora and the treatment subprocesses reliant on them.

The threat posed by the proliferation of ECs in the environment, then, is as vast and variegated as the compounds themselves. While the resulting threat to human health is indirect and direct, the former is likely to be the primary pathway.

Aquatic life-forms bear the brunt of EC exposure, and their integration in the food chain represents a indirect path by which surface water contaminants are conveyed back to humans.

Efficient and tireless sequestration agents, aquatic organisms bioaccumulate ECs according to their lipophilicity, and deliver them to humans in concentrated form. As noted in the text, a hydrophobic compound might be found in aquatic tissue at a concentration $10^{\log Kow}$ higher than that in the surrounding water. Ascending the food chain invites biomagnification, where bioconcentration increases with each trophic level by a factor of three for aquatic organisms and a factor of ten for birds and mammals (Mackay 1995).

Direct exposure to aquatic ECs is a lesser threat to humans, to an unknown degree. Primary contact is by domestic water supplies, and DWTPs are able to remove ECs with varying degrees of success. Stackelberg et al. (2007) reported that one such facility removed acetaminophen, caffeine, carbamazepine, cotinine, and DEET at rates of 98, 88, 85, 57, and 35 percent, respectively, while sulfamethoxazole, cholesterol, sitosterol, and stigmastanol were completely mitigated.[1] The cited study by Skadsen et al. (2004), however, included a DWTP that fully mitigated sulfamethoxazole, trimethoprim, carbamazepine, acetaminophen, caffeine, and dihydrocholesterol, but reduced ibuprofen, stigmasterol, sitosterol, and cholesterol by 29%, 50%, 30%, and 23%, respectively. The disparity in the two studies reveals that a common denominator among DWTPs and WWTPs is the uneven efficacy of inadvertent dilution agents. And, others are investigating the use of alternate mechanisms for degrading ECs; ultraviolet light is utilized in the final (disinfection) stages of some WWTPs, and Son et al. (2007) demonstrated its efficacy in photodegrading triclosan, albeit with the possibility of undesirable by-products.

The rivers investigated in the present study are not themselves public water sources, but each is a segment in a tributary cascade to eventual drinking water sources, namely the Illinois and Mississippi rivers. As an academic exercise, typical human exposure from direct and indirect channels can be calculated with the data.

A water column concentration of 16 ppt was found for triclosan at site SC. The appendix reports triclosan's octanol-water coefficient ($\log K_{OW}$) as being 4.76, resulting in a nominal aquatic tissue concentration of 0.921 ppm (equivalently, 0.921 mg/kg) at the lower trophic levels. A person who consumed 22 pounds (10 kg) of such fish annually would ingest a minimum of 9.21 mg of triclosan per year, the calculation being conservative in ignoring biomagnification inherent to larger fish.

In contrast, a human's direct exposure to surface water ECs in their native concentrations is much lower. For example, a lifetime exposure (2 liters of raw surface water per day for 75 years) to this study's most prevalent pharmaceutical analyte, sulfamethoxazole at site WB, would result in a cumulative ingestion of a mere 22.4 mg, less than ten percent of a typical single dose.

1. Four-stage purification process consisted of clarification (flocculation via ferric chloride [$FeCl_3$]), disinfection (via sodium hypochlorite [NaClO]), filtering (via sand and activated carbon), and final disinfection (via NaClO); while each analyte undoubtedly had a unique susceptibility to each stage, the general response was a progressive diminishing. A subsequent study by those authors demonstrated that residual chlorine from the final stage provided further, modest decreases in some ECs after ten days, a period of exposure that might be typical of an actual drinking water distribution system.

Admittedly, neither the toxicity nor the exposure levels calculated here are particularly striking, as the goal was simply to illustrate indirect and direct human exposure to an actual surface water EC encountered in this study. Other studies have investigated watersheds hosting ECs in greater concentrations, lipophilicities, and toxicities, to which these results can be scaled accordingly. Too, each calculation portrayed a single analyte for simplicity, and in doing so, neglected the additive effects of the cocktail of potentially synergistic compounds which comprise typical, impacted surface waters. While annual exposures in the milligram realm are likely innocuous, current pharmacology lacks the data to rule out deleterious effects of chronic, microdosed exposure.

And, these are not the only modes of indirect human exposure to surface water ECs. After uptake by an aquatic organism, an EC may assume the passive posture of a lipid-bound passenger, or find itself in the active role of a mutation agent. The human consumption of EC-mutated organisms has not been investigated. And, the proliferation of antibiotics in the environment may have consequences beyond the not insignificant danger of rendering them therapeutically impotent.

This is not to imply that micropollutants have a monopoly on mutagenicity, carcinogenicity, and other modes of environmental toxicity—priority pollutants have a rich and scintillating history of their own. But, with a knowledge base far exceeding that of their diminutive brethren, conventional contaminants have traditionally dominated pollution discourse, and efforts to broach ECs have failed to attract a broad audience. Speculating on the toxicity of pedestrian compounds in ultra-trace concentrations evokes lukewarm receptions, cautiously-worded support with skeptical undertones, implications of alarmism, and, in the competition for scarce research dollars, fear that EC budgets will displace those of priority pollutants and render their study an anachronism.

Just as research of traditional contaminants is not obsoleted by that of ECs, nor, too, must they compete for the same, shallow, grant pool. The enlarging of pollution research budgets to accommodate both objectives will allow EC research to supplement rather than supplant that of priority pollutants. At the same time, the expense of EC analysis can be expected to decrease with increases in technology, competition, and economies of scale.

Political attitudes toward environmental research has traditionally vacillated between antagonism and reticence, and constituencies have been only slightly less noncommittal. With budgets and taxes in perpetual tension, the need to reconcile them with a fair allocation to the environment is a critical one. One challenge is the persuasion of a public, already suffering from eco-fatigue, of the need to allocate greater attention and research dollars to the pursuit of prosaic product ingredients at concentrations one-ten-millionth of the proverbial drop-in-a-bucket. As society continues its retreat from the public sphere, where bottled water displaces tap, the lack of coordinated support for EC studies could cause them to backfire, increasing the distaste for tap water, the antipathy for the basins from which it is drawn and discarded, and the indifference toward continued research. In the meantime, the de facto solution to impaired waters will be sold in a box marked “kitchen water filter”.

The reluctance of policy makers, research bodies, and environmental organizations to broach ECs in the public realm, on the one hand, and the complacency of the public, on the other, has several roots.

In a society in which both lifestyle and employment are tightly coupled to consumption, the indictment of consumer products is akin to sedition. Attempts to regulate the production, use, or disposal of EC-laden products will meet with resistance, which has prompted some to speculate that the eventual EC solution will fall to WWTPs rather than the manufacturer or vector (consumer). Such an outcome is nonideal, as it represents a capitulation to the mislabelling of a treatment facility as a point source rather than a gateway, a distinction that goes beyond semantics in its displacement of culpability from the actual point sources.

It has been said that familiarity breeds contempt, but, more often, it merely induces passivity or complacency. Unlike priority pollutants, which owe much of their status to the respect that comes from unfamiliarity, consumer products—especially those that are swallowed—project a characteristic familiarity and wholesomeness that connotes harmlessness. The public perception of ECs, where it exists, is one of insipid ingredients in pedestrian products, based on the narrow perception of a pollutant as an unequivocally sinister chemical, often synthetic and industrial, with striking and specific modes of toxicity, such as teratogenicity or lethality, rather than the more banal predicament of general xenobioticity. The names of many ECs are not widely known outside of the scientific community, so it is both ironic and encouraging that vaguely distant priority pollutants have name recognition on par with many of the common household products harboring ECs. Still, as environmentally unregulated compounds in the ever growing body of consumer goods, ECs are evolving and proliferating at a faster rate than traditional pollutants. Sufficient resiliency is built into the term *emerging contaminant* that it can accommodate the newcomers—the newly discovered and the newly developed—which may include nontraditional pollutants as prosaic as plastics detritus, as esoteric as nanoparticles, or as enigmatic as new phytosterols from genetically modified plants.

Those being the obstacles to EC traction in the public sphere, there is also the personal—and apparently thorny—issue of their excretion gateway. The primary fount of many ECs is the toilet, and rather than risk the impropriety of the words *urine* and *feces*, some EC studies are content to perpetuate myths, such as that which attributes aquatic ECs to the improper disposal of medicines. Politeness is not a new hurdle in public discourse, but nor was it one demanded of priority pollutants.

In the public realm, ECs are allotted a few sidebars in the pollution discourse, creating a gap through which sensationalistic anecdotes of hormone-mediated, aquatic mutations have rushed in to fill the vacuum. While EDCs are indeed a legitimate concern, they are but one component—albeit an easily exploitable one—in the large and complex EC universe. As such, one downside to the preoccupation with EDCs by the public and media is that it displaces attention from other ECs and their modes of harm. Reproductive system mutations are a touchstone issue—accessible, headline ready, and sufficiently piquant—that the public can project onto themselves with little prompting. After all, it takes much less scholarship and imagination to evoke empathy for a caricatured intersex amphibian than for a metabolically impaired protist, and, while humor may make the subject more accessible for some readers, it is just as likely to do so at the expense of

urgency. The hope, of course, is that increasing awareness of EDCs will spread to the realization that other EC classes are capable of provoking unusual and as yet unidentified biological responses.

The research cited in this study is neither exhaustive nor definitive. The intent is merely to present a representative and multidisciplinary survey of a vast and growing field. The EC learning curve is steep, and while the past decade has witnessed great strides in its ascent, much remains to be discovered. As data accumulates, discourse widens, and the matter receives attention from a broader audience, palatable solutions will begin to make themselves apparent. In the meantime, as debris of contemporary life, ECs serve as a modern reminder of the ancient tension between humans and nature, and of the fundamental conflict between a resource's role as both a substrate for the food chain and as a medium of disposal. They also present an opportunity to begin educating consumers about the fate of their consumables. Much of the lay public, for example, would be surprised to learn that, in the context of ECs, a WWTP is less of a universal filter than an inadvertent one. Micropollutants do not announce themselves upon entering or exiting a facility, nor do compounds leaving the home attain a measure of post-consumer enlightenment and self-destruct as a final gesture of obeisance.

EC research is the newest chapter in the pollution narrative of developed nations, delving into the post-consumer fate of the manifold ingredients of contemporary life. As a nascent field of study, it can perhaps best be described not by what is known, but by what is not. To paraphrase a recent and unfairly parodied maxim: we know there are known unknowns, but there are also the unknown unknowns—the things we don't know we don't know.

7. Acknowledgements

Laboratory analysis for this study was co-funded by the Sierra Club's River Prairie Group (DuPage County, Illinois) and National Water Committee.

The author expresses gratitude to the following individuals for providing technical assistance and background data for this study:

Catherine O'Connor of the Metropolitan Water Reclamation District of Greater Chicago.
John Vargo of the University of Iowa Hygienic Laboratory.
Terri Arnold, David Dupre, Dana Kolpin, and John LaTour of the U.S. Geological Survey.
Jennifer Clarke of the Illinois Environmental Protection Agency.
Rodger Harvey of the University of Maryland Center for Environmental Science.
Brian Rice of Fleis & VandenBrink Engineering, Inc.
Vern Knapp of the Illinois State Water Survey, University of Illinois.
Gene Arbini and Steve Borowiak.

All opinions and conclusions expressed herein are those of the author.

Higher resolution versions of some appendix images are available upon request.

Since 2000, RPG has performed nutrient, dissolved oxygen, and radionuclide testing in the three watersheds. Data, project description, and reports (including this one) available at
http://illinois.sierraclub.org/rpg/watermonitorproj.htm

Appendix A. Scope of the Term *Emerging Contaminants*

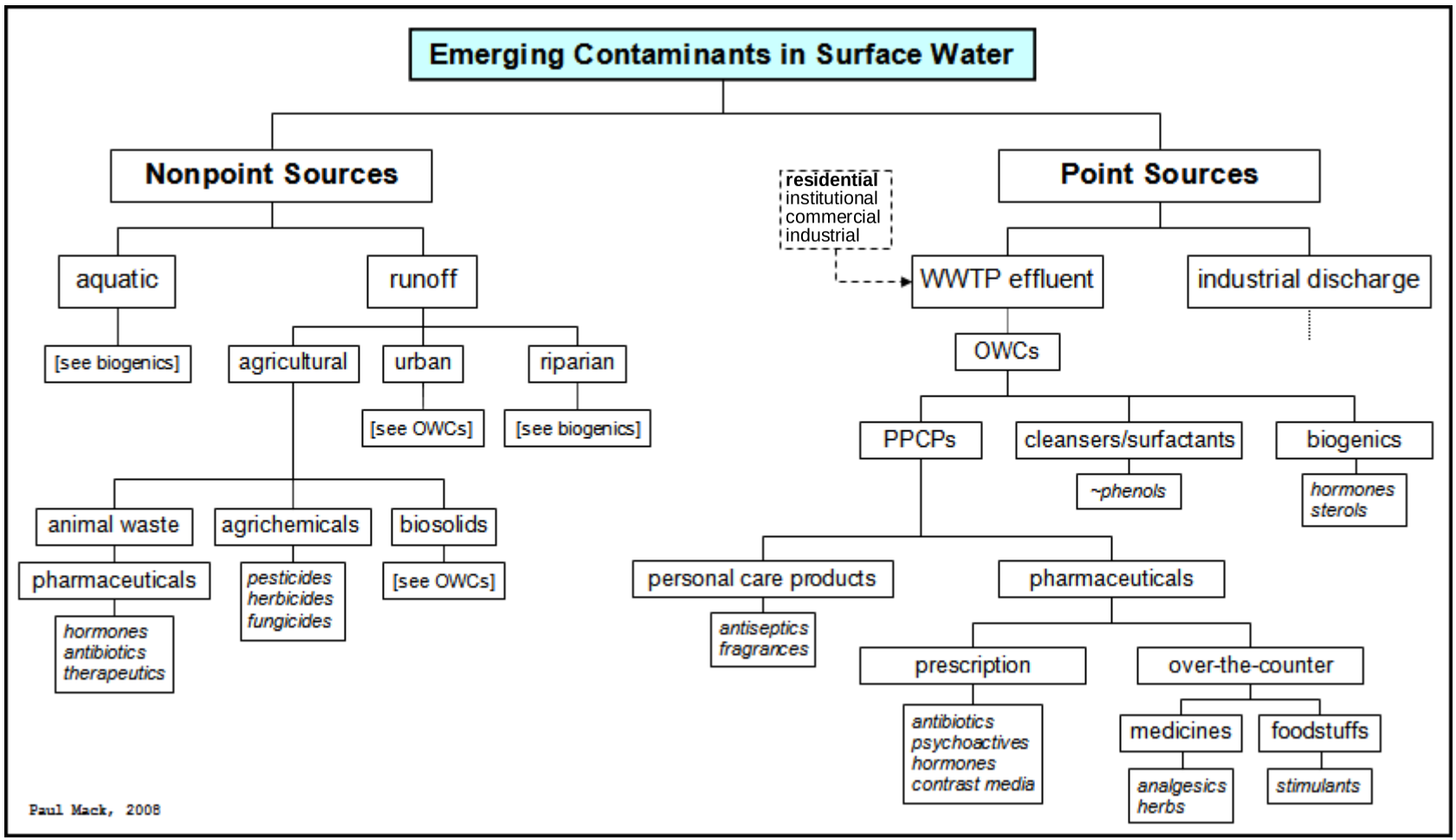

Figure A.1. Emerging contaminants in surface water. Neither exhaustive nor reflective of the scope of this investigation, this figure merely attempts to illustrate the breadth of the field and the primary sources. Descriptive categories, such as *endocrine disrupter,* traverse multiple headings and are not shown; nor are secondary point and nonpoint sources. Examples cited in italics. (Illustration by author.)

Appendix B. Primary EC Sources, Transports, and Fates: A Toilet-to-Tap/Table Analysis

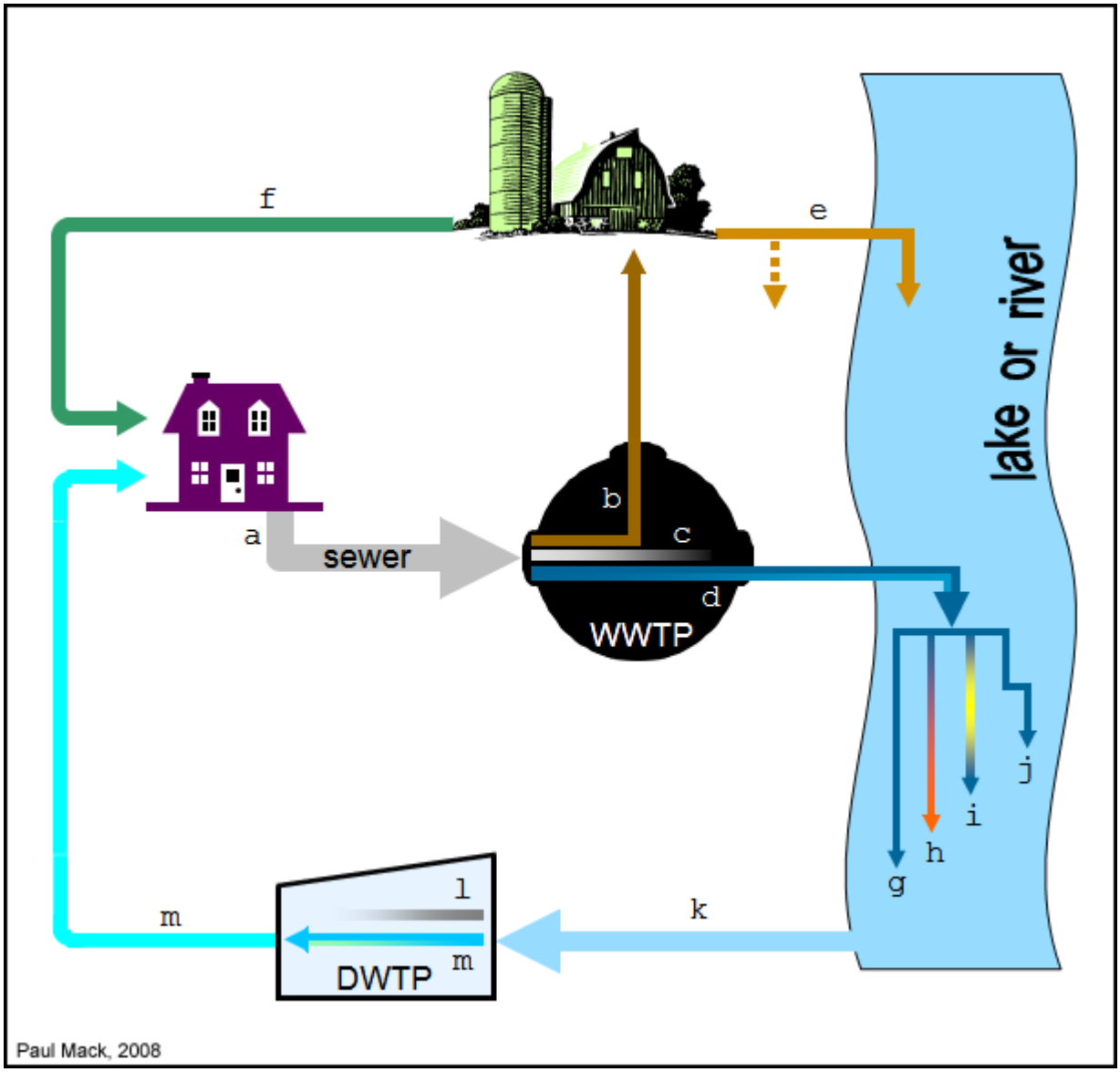

Figure B.1. EC sources, transports, and fates; a closed system. Primary point and nonpoint sources shown. See following pages for legend. (Illustration by author.)

Legend for Figure B.1.

Point source – the consumer:

- **a** – ECs are flushed down drains and toilets and travel through a sewer to a WWTP.

Fates of influent-borne ECs:

- **b** – Some ECs (e.g., hydrophobic compounds) gravitate towards biosolids (sludge), which may be landfilled or applied to cropland as fertilizer.
- **c** – Some ECs are inadvertently degraded by the WWTP or adsorbed to its sand filter.
- **d** – The remaining ECs, some of which have been inadvertently transformed by the WWTP, exit the facility in effluent into the discharge body.

Nonpoint source – agriculture; EC-tainted livestock manure and WWTP biosolids (**b**) applied to cropland as fertilizer represent a multifaceted and highly concentrated nonpoint source:

- **e** – Flora and fauna, including insects and soil microbes, are exposed to ECs directly, and indirectly (via the food chain). ECs go on to infiltrate ground and/or surface water; cross-infiltration is also possible (ground water to surface water or vice-versa, via ground water discharge or recharge, respectively).
- **f** – EC-tainted crops return to the home as food, completing the toilet-to-table cycle.

Fates of effluent-borne ECs (soil-borne fates are analogous):

- **g** – Some ECs persist in the water column.
- **h** – Some ECs are inadvertently transformed into other compounds.
- **i** – Some ECs are inadvertently degraded; however, they are effectively persistent, being continually replenished by WWTP effluent.
- **j** – Some ECs adsorb to streambed sediment and persist there.

Fates of water-borne ECs:

- **k** – Input to DWTP; **k = e + g + h + i + j**
- **l** – Some ECs are inadvertently degraded by the DWTP purification process or adsorbed to its sand filter. (Disinfection by-products, such as trihalomethanes and haloacetic acids, do not conform to the conventional definition of *emerging contaminant* and thus are not shown here.)
- **m** – The remaining ECs, some of which have been inadvertently transformed by the DWTP, exit the facility in drinking water and are pumped to the home, completing the toilet-to-tap cycle.

Notes:

- EC vectors are indicated by arrows labeled **a–m.**
- Toilet-to-tap analyses are inherently anthropocentric. EC affects on soil, terrestrial, and aquatic organisms are not explicitly illustrated here.
- For clarity, secondary point and nonpoint sources (such as industrial discharge and landfill leachate, respectively) are not shown. Note, too, that the anthropogenic definition of *EC* excludes native—albeit ultra-trace—pollutants such as algal toxins.
- The term *inadvertently* is used to highlight the accidental nature of EC mitigation, as none of the receiving systems are designed to detect or specifically mitigate ECs. For this reason,

a given EC will be spread across two or more vectors, based on its chemistry and the characteristics of the agents acting upon it (see figures B.2. and B.3.). The diversity of man-made and natural dilution agents, even within the limited confines of one watershed, precludes widespread agreement on the exact fate vectors of a given EC.

- Dilution agents in treatment facilities (WWTP and DWTP) and the environment (soil and discharge body) can be classified as biological, chemical, physical, thermal, and optical. The efficacy of a particular dilutive mechanism is influenced by exposure time, but in the environment, it is undermined by the EC replenishment rate. Note that sorption is a sequestration agent, not a transformative one. A comprehensive list of aquatic fate agents is listed in section 2.4.1.
- Without the diluting benefit of liquid, a given EC may appear in land fertilizer (livestock manure and WWTP biosolids) at concentrations several orders of magnitude higher than in surface water, exposing soil and terrestrial organisms to near-therapeutic doses of pharmaceuticals.

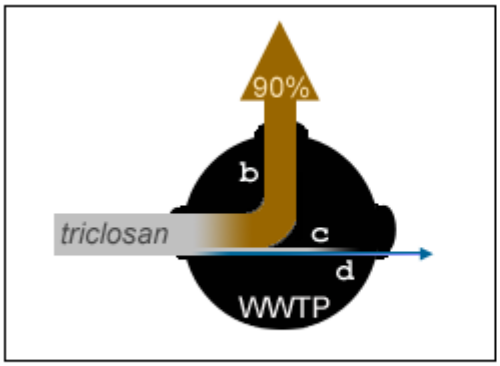

Figure B.2.

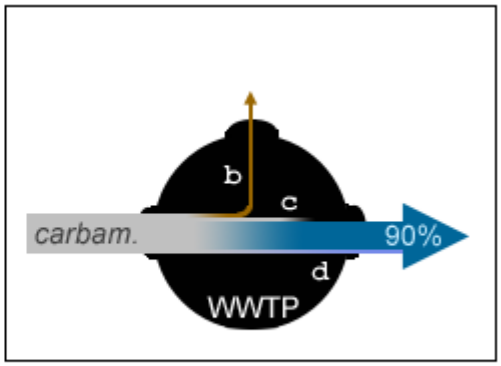

Figure B.3.

Figure B.2. and Figure B.3. Divergent fates of two ECs (triclosan and carbamazepine) in the WWTP of figure B.1. Values are approximate but representative of a typical WWTP. Triclosan serves as a reminder that EC concentrations in surface water are not indicative of WWTP degradation efficiency.

Appendix C. Region of Study

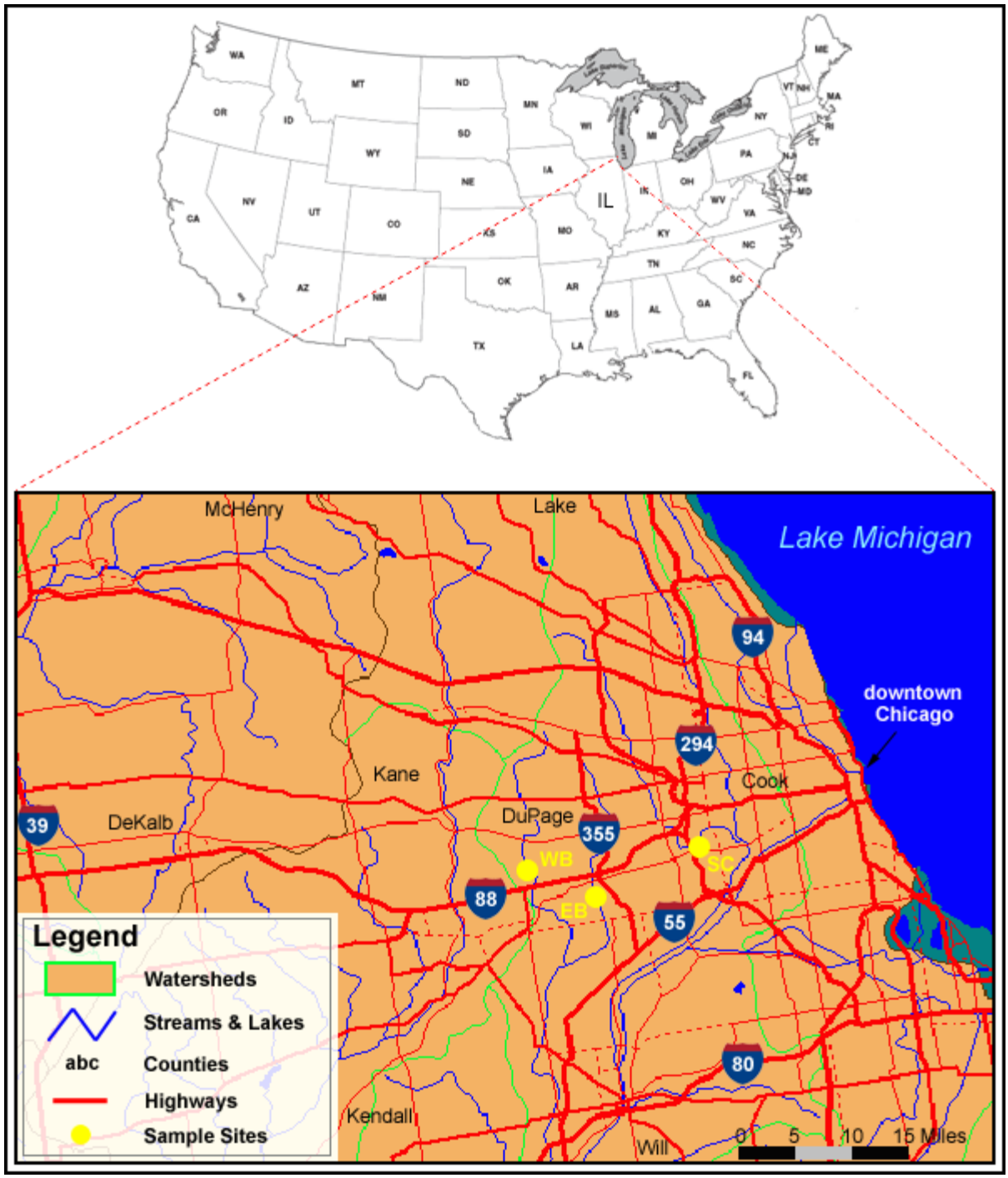

Figure C.1. Regional map showing sample site locations. (Adapted from Houghton Mifflin, *USA Postal Abbreviations*, http://www.eduplace.com/ss/maps/pdf/uspostal.pdf, and, U.S. Department of the Interior, *National Atlas of the United States*, http://nationalatlas .gov.)

Appendix D. Land Use in the Region

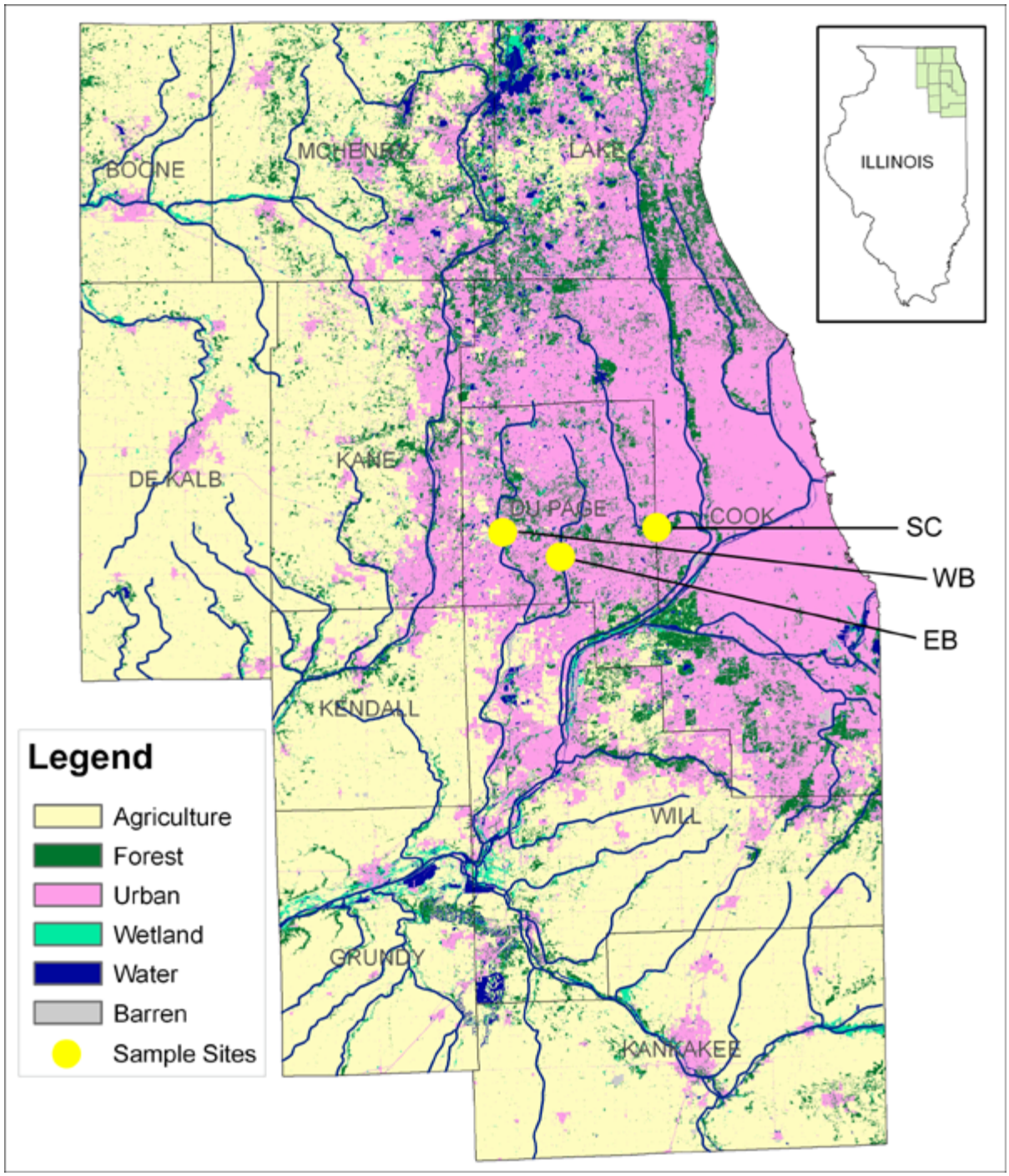

Figure D.1. Land use in the region, 2000. (Adapted from U.S. Geological Survey, Illinois land use map – 2000. Terri Arnold, personal communication with author.)

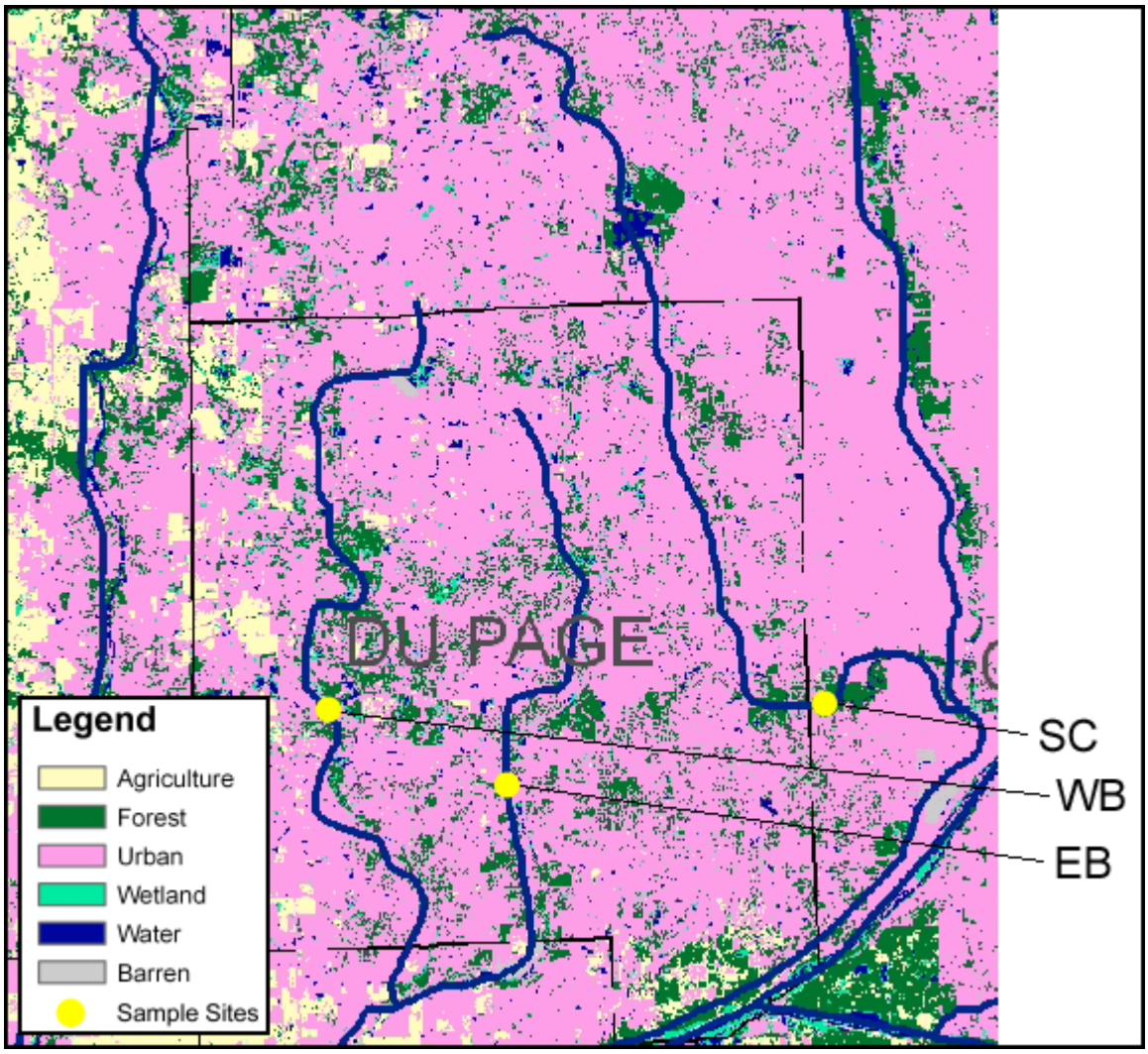

Figure D.2. Land use in the watersheds, 2000. (Ibid.)

Appendix E. Land Use Detail

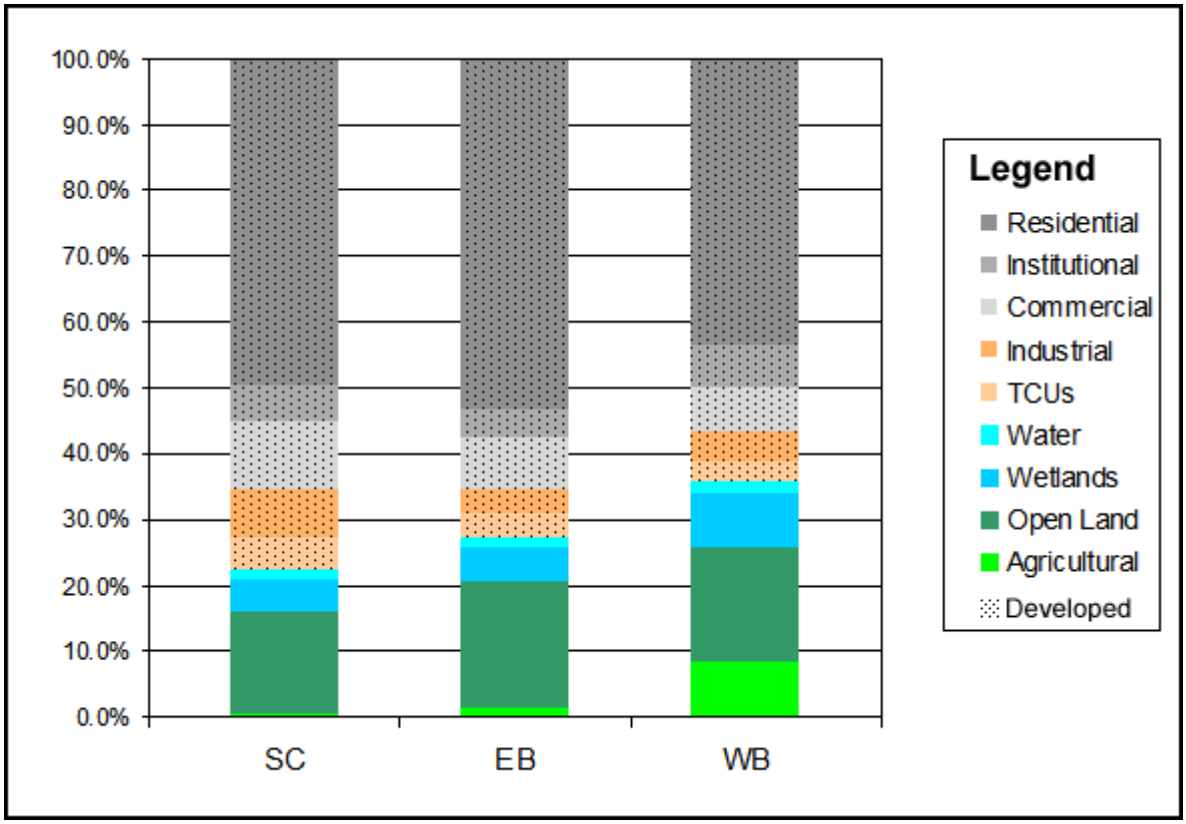

Figure E.1. Land use detail in the watersheds, 2001. *TCU* is transportation, communications, and utilities. (Derived from Illinois Environmental Protection Agency land use data. Jennifer Clarke, personal communication with author.)

Appendix F. Population Density in the Region

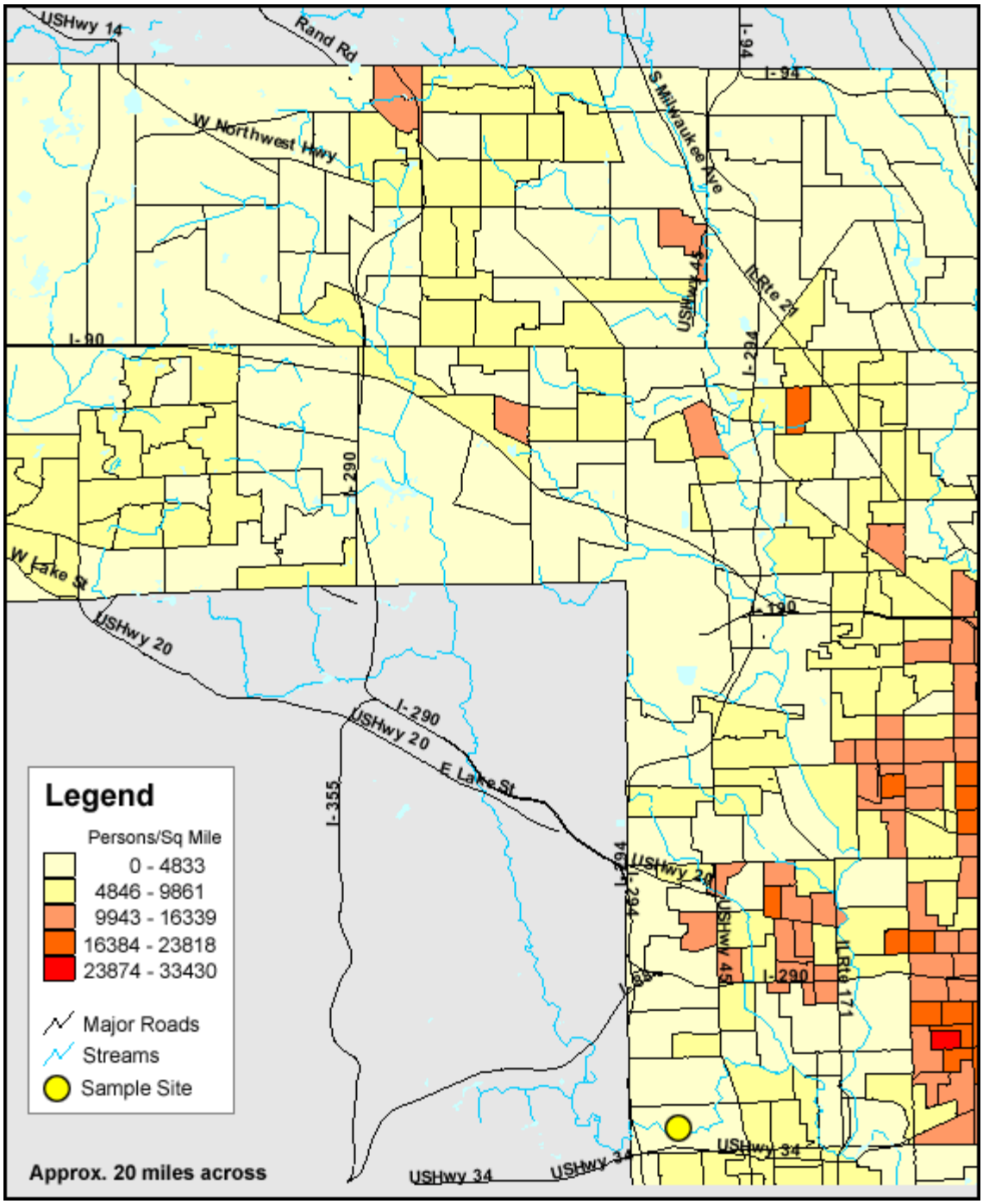

Figure F.1. Population density in Cook County by census tract, 2000. Vicinity of the Salt Creek watershed. (Adapted from U.S. Bureau of the Census, *American FactFinder Thematic Map - Persons per Square Mile 2000*, http://factfinder.census.gov.)

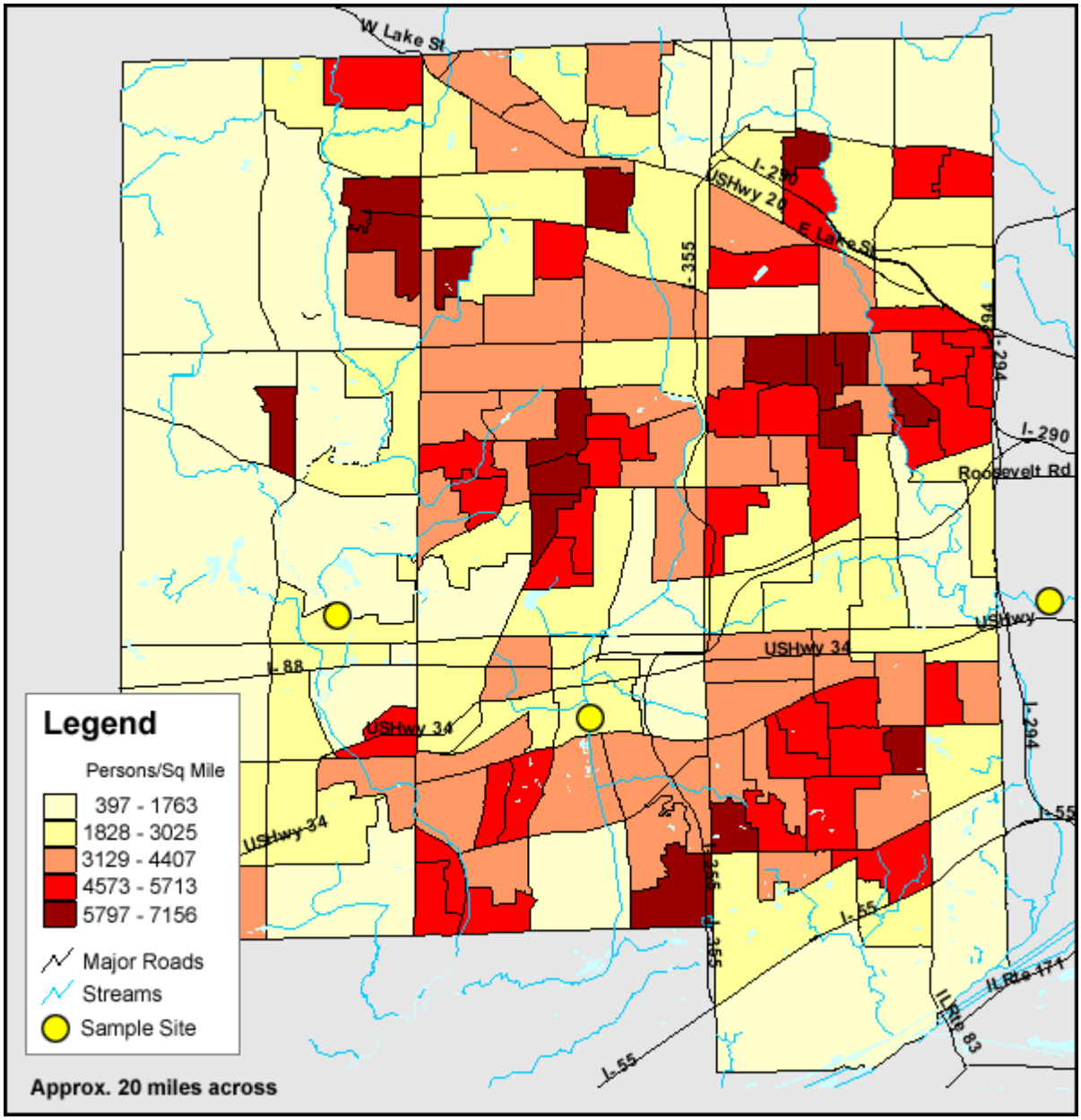

Figure F.2. Population density in DuPage County by census tract, 2000. (Ibid.)

Appendix G. The Three Watersheds of this Study

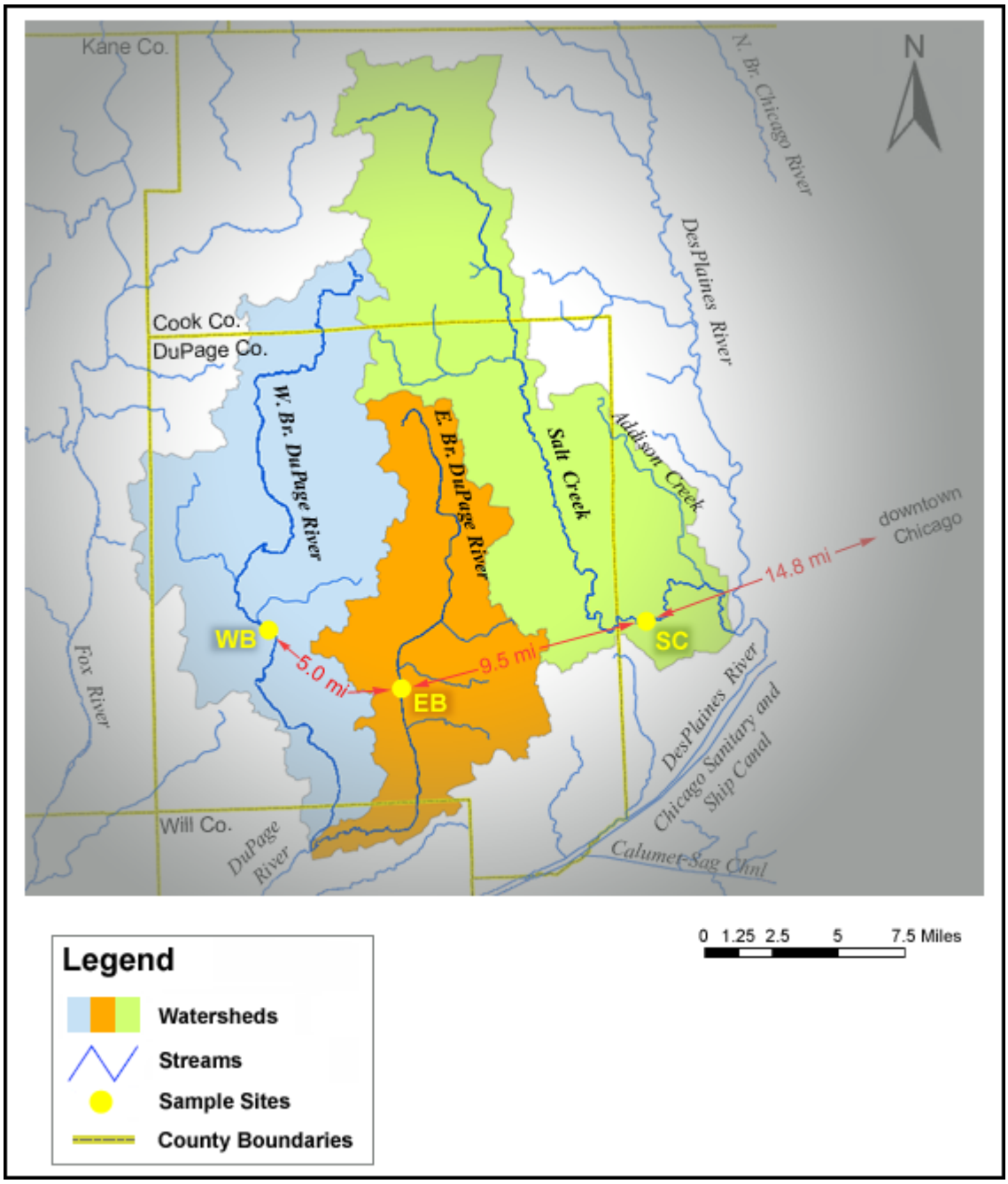

Figure G.1. Watersheds of Salt Creek and the East and West branches of the DuPage River, and their sampling sites. (Adapted from Illinois Environmental Protection Agency watersheds map. Jennifer Clarke, personal communication with author. Distances from John Byers, *Surface Distance Between Two Points of Latitude and Longitude*, http://www.chemical-ecology.net/java/lat-long.htm.)

Appendix H. Upstream Dischargers of Significance

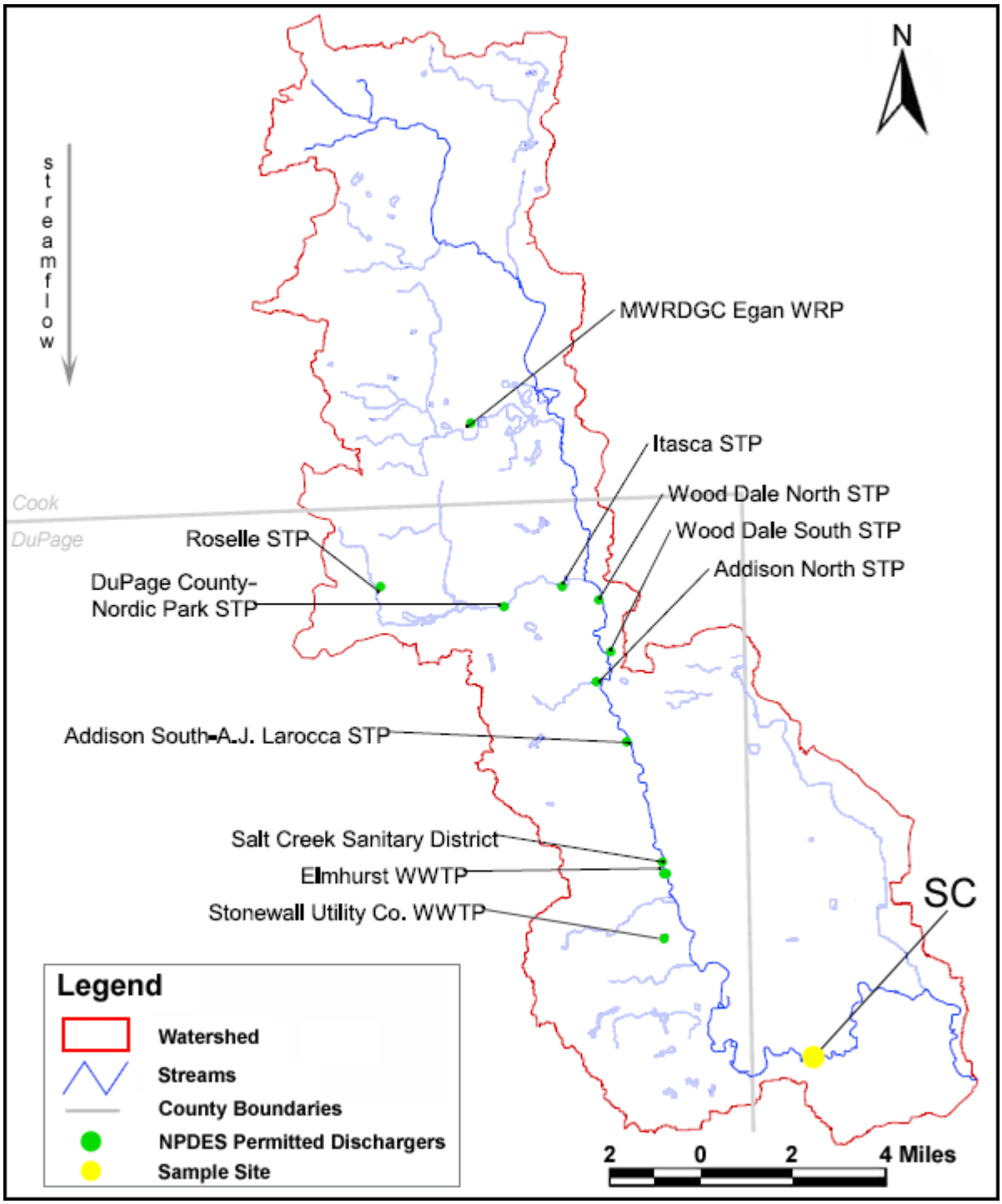

Figure H.1. Significant dischargers into Salt Creek, upstream of sample site *SC*. (Adapted from Illinois Environmental Protection Agency, *Total Maximum Daily Loads for Salt Creek, Illinois*, fig. 3-8.)

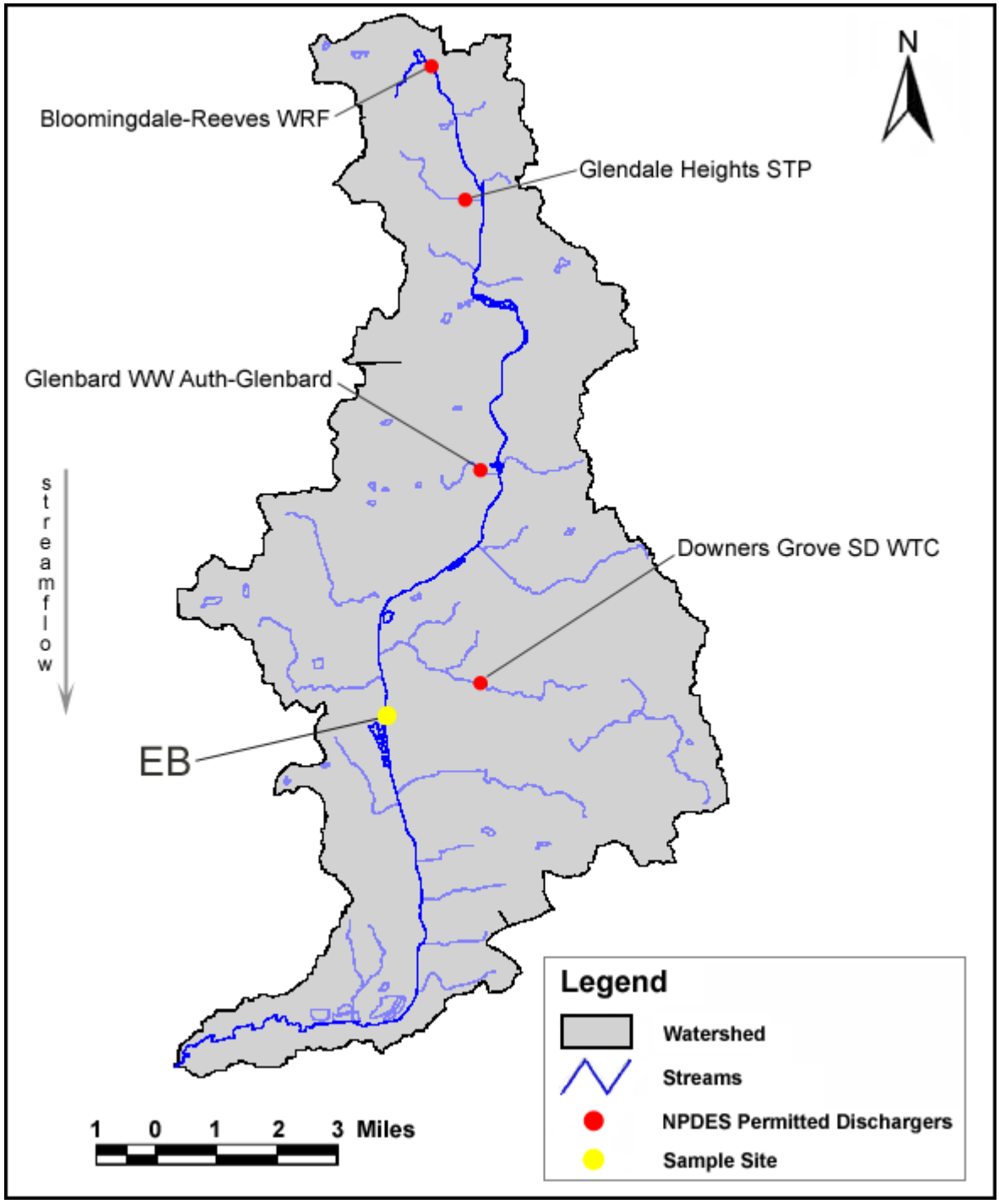

Figure H.2. Significant dischargers into DuPage River – East Branch, upstream of sample site *EB.* (Adapted from Illinois Environmental Protection Agency, *Total Maximum Daily Loads for the East Branch of the DuPage River, Illinois*, fig. 3-7.)

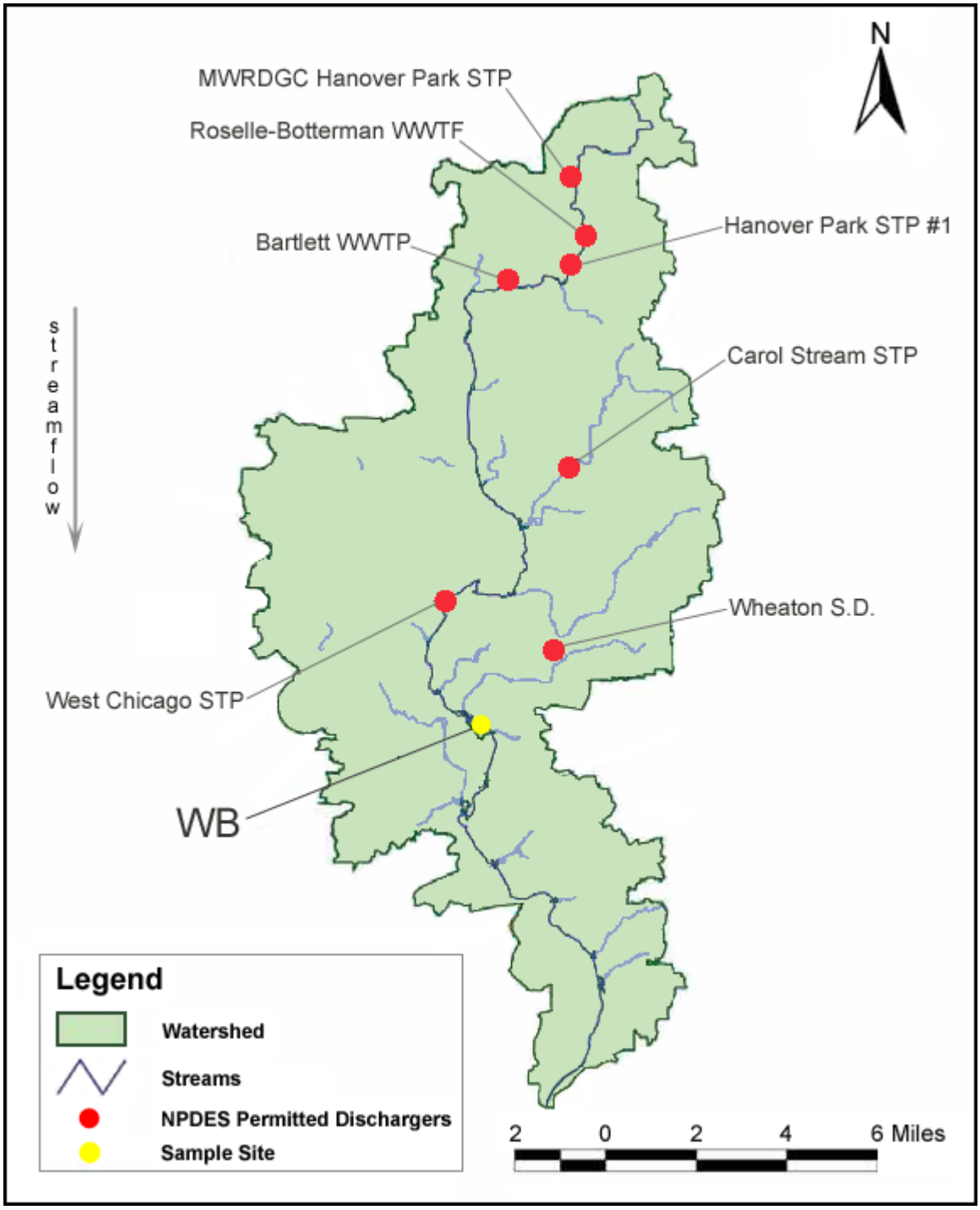

Figure H.3. Significant dischargers into DuPage River – West Branch, upstream of sample site *WB.* (Adapted from Illinois Environmental Protection Agency, *Total Maximum Daily Loads for West Branch DuPage River, Illinois*, fig. 3-8.)

Appendix I. Sample Site Photographs

Figure I.1. Sample site *SC*, facing upstream. August, 2008. (Photograph by author.)

Figure I.2. Sample site *EB*, facing downstream. August, 2008. (Photograph by author.)

Figure I.3. Sample site *WB*, facing downstream. Illinois Prairie Path pedestrian bridge is shown in background. August, 2008. (Photograph by author.)

Appendix J. Streamflow Preceding Sample Collection

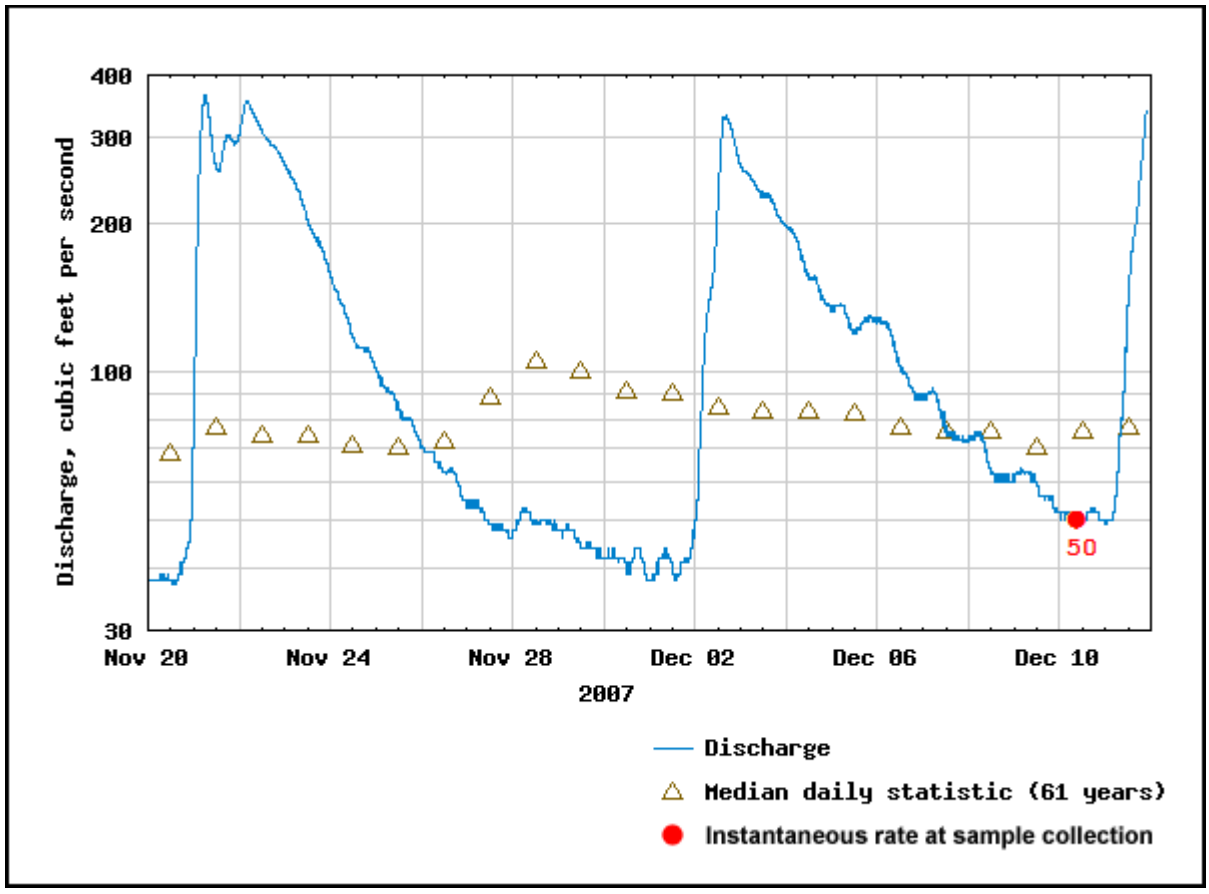

Figure J.1. Daily discharge data for Salt Creek at site *SC*, for three weeks preceding sample collection. (Adapted from U.S. Geological Survey, daily discharge data for Salt Creek gage 05531500, http://waterdata.usgs.gov/il/nwis/dv.)

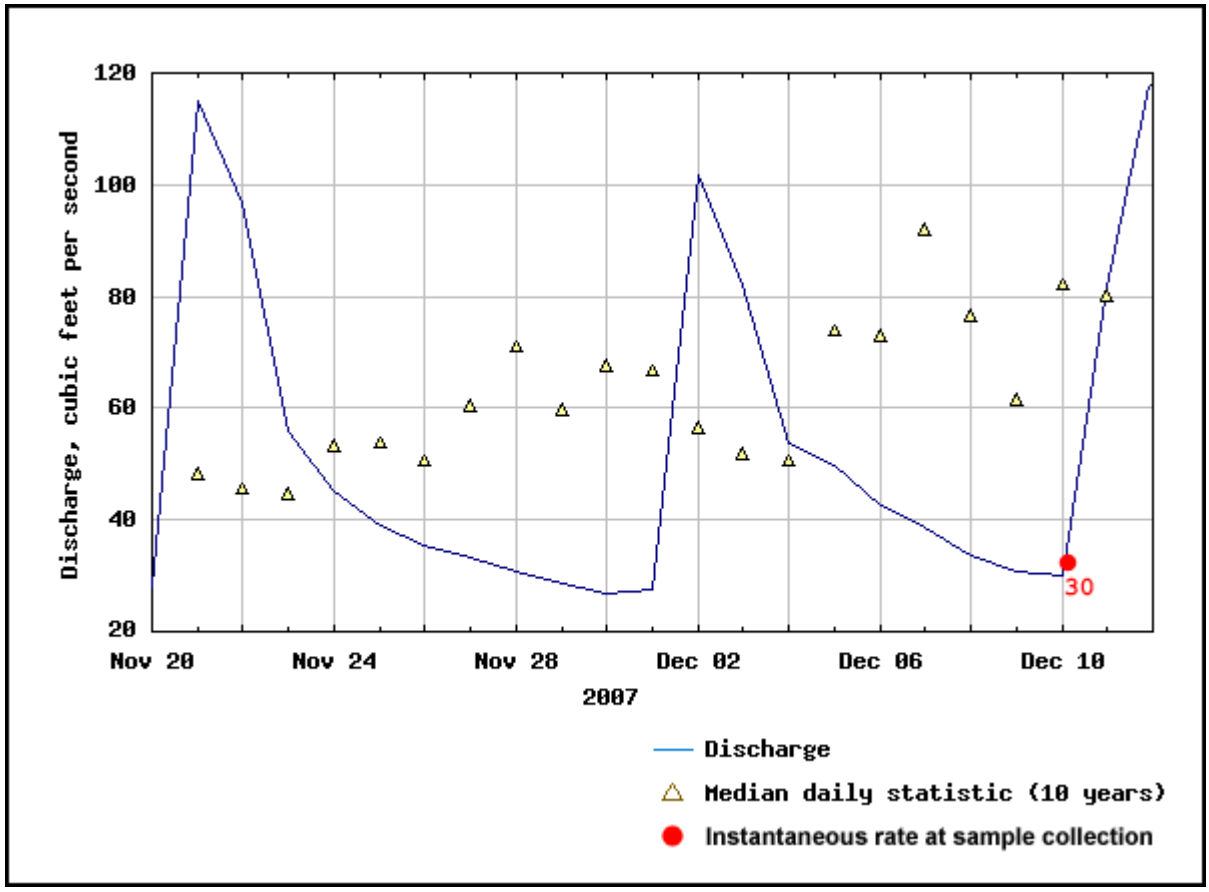

Figure J.2. Daily discharge data for DuPage River – East Branch at site *EB*, for three weeks preceding sample collection; approximate. (Adapted from U.S. Geological Survey, daily discharge data for DuPage River – East Branch gages 05540160 and 05540250, http://waterdata.usgs.gov/il/nwis/dv. As USGS gages in the immediate vicinity of site *EB* do not measure discharge rate, data in this figure were derived by averaging that of the two nearest flow gages: 05540160 [Downers Grove; four miles upstream] and 05540250 [Bolingbrook; five miles downstream]. Ten-year averages based on 1996–2005 data.)

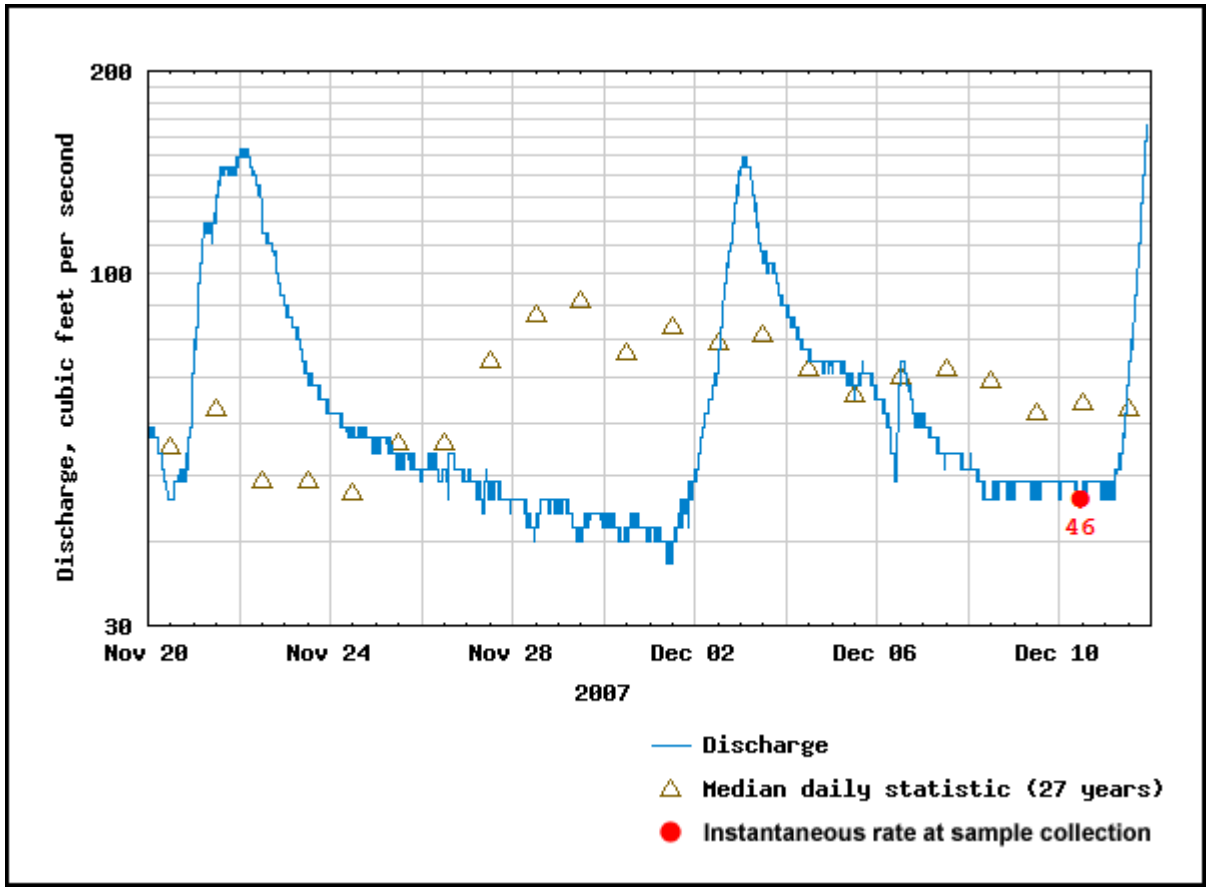

Figure J.3. Daily discharge data for DuPage River – West Branch, at site *WB*, for three weeks preceding sample collection. (Adapted from U.S. Geological Survey, daily discharge data for DuPage River – West Branch gage 05540095, http://waterdata.usgs.gov/il/nwis/dv.)

Appendix K. Biosolid and Sediment Comparison

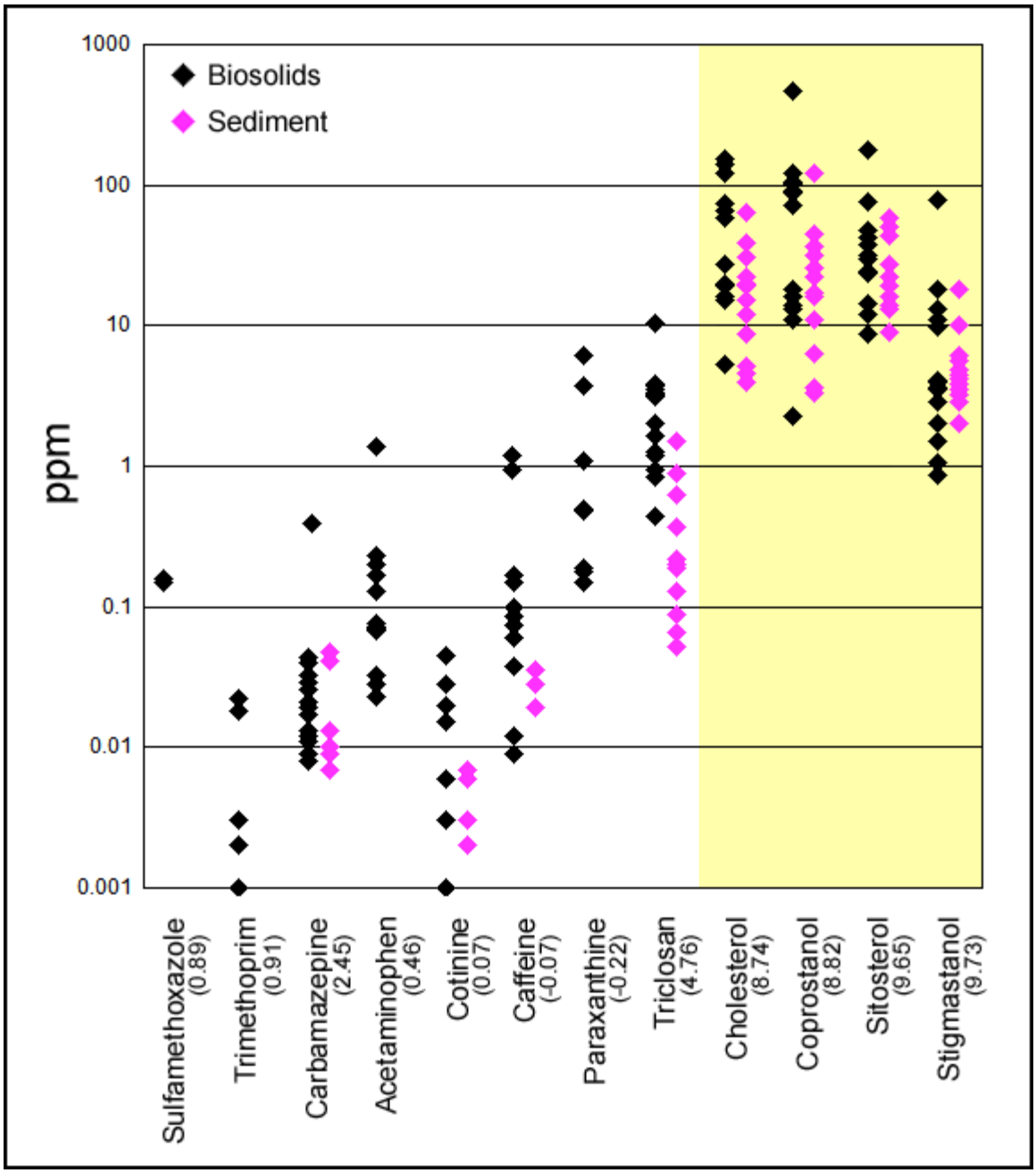

Figure K.1. Comparison of EC concentrations in biosolids and sediment; milligrams-per-kilogram dry weight. Log K_{OW} in parentheses; all values are empirical except biogenics. PPCPs and biogenics (yellow background) plotted on same graph to show disparity. (Derived from table S1 in Kinney et al. (2006) and tables 11 and 12 in Wilkison et al. (2005). Log K_{OW} data from Syracuse Research Corporation *KowWin*, http://www.syrres.com/esc/est_kowdemo.htm)

Appendix L. Streamflow Preceding SC_{1999}

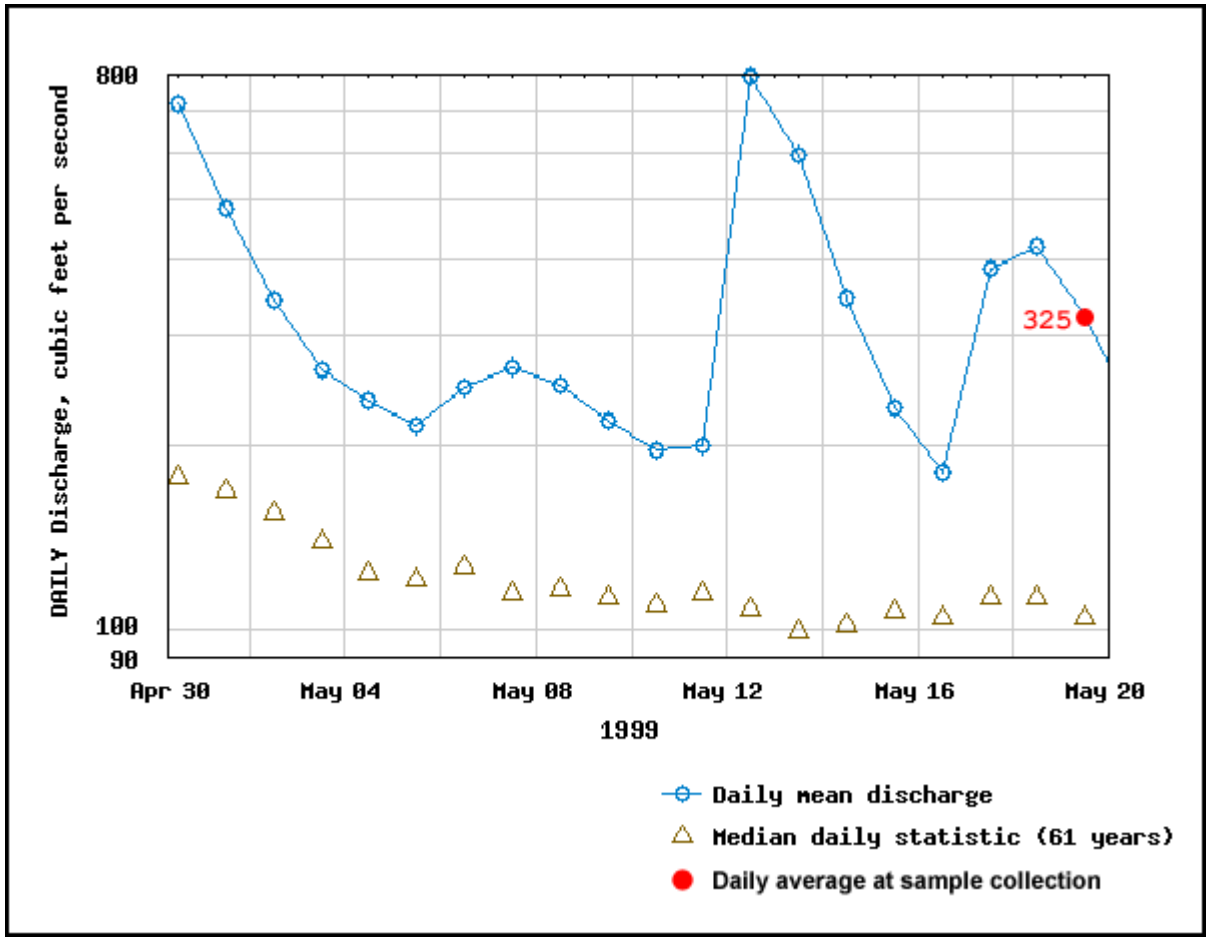

Figure L.1. 1999 daily discharge data for Salt Creek at site *SC*, for three weeks preceding sample collection. (Adapted from U.S. Geological Survey, daily discharge data for Salt Creek gage 05531500, http://waterdata.usgs.gov/il/nwis/dv.)

Appendix M. Fifteen Year Prescribing Trend of Co-trimoxazole

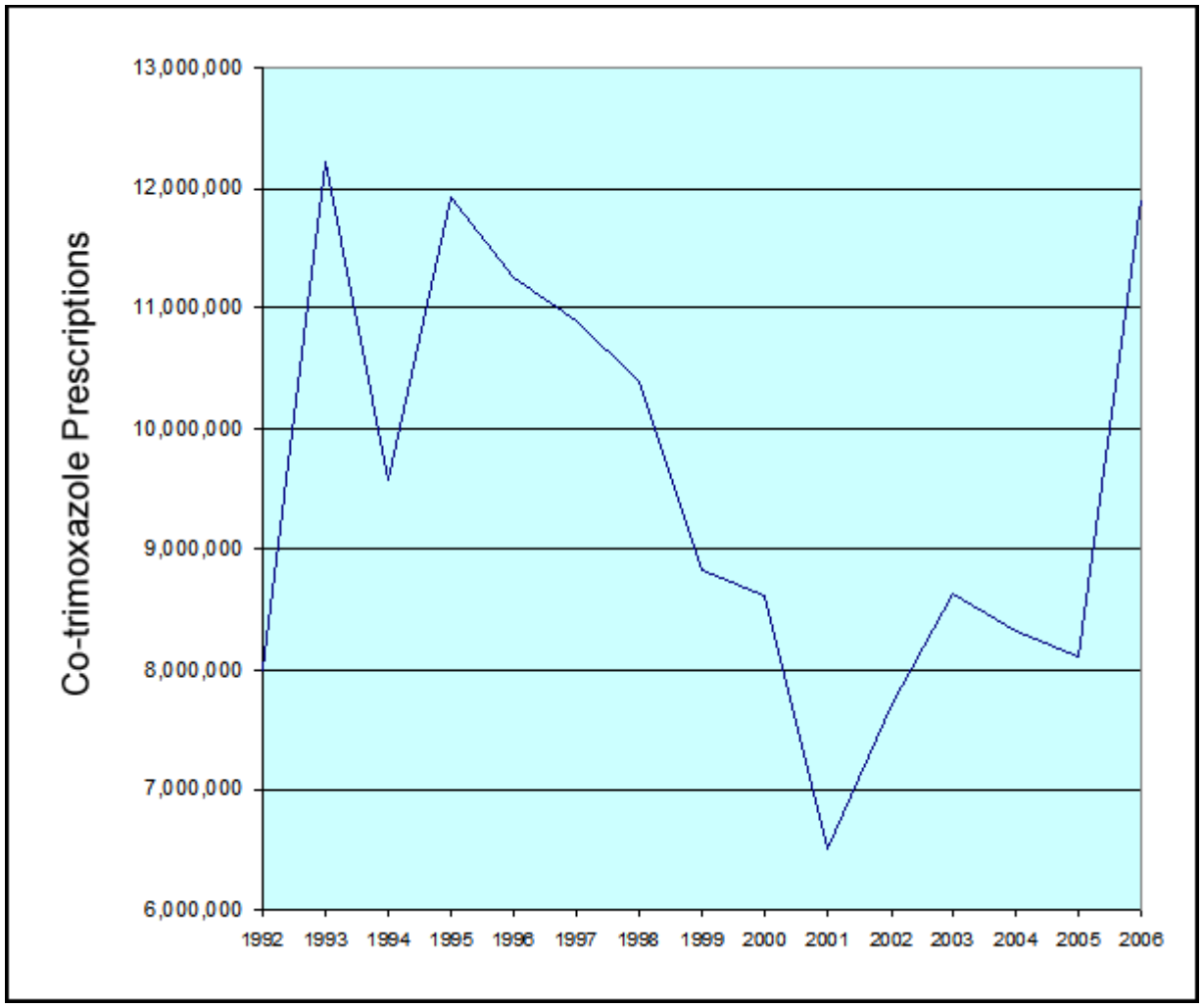

Figure M.1. Fifteen-year prescribing trend of co-trimoxazole. (Derived from National Center for Health Statistics, *TMS Drug Visit Rate.* Linda McCaig, personal communication with author.)

Appendix N. Interregional Comparison

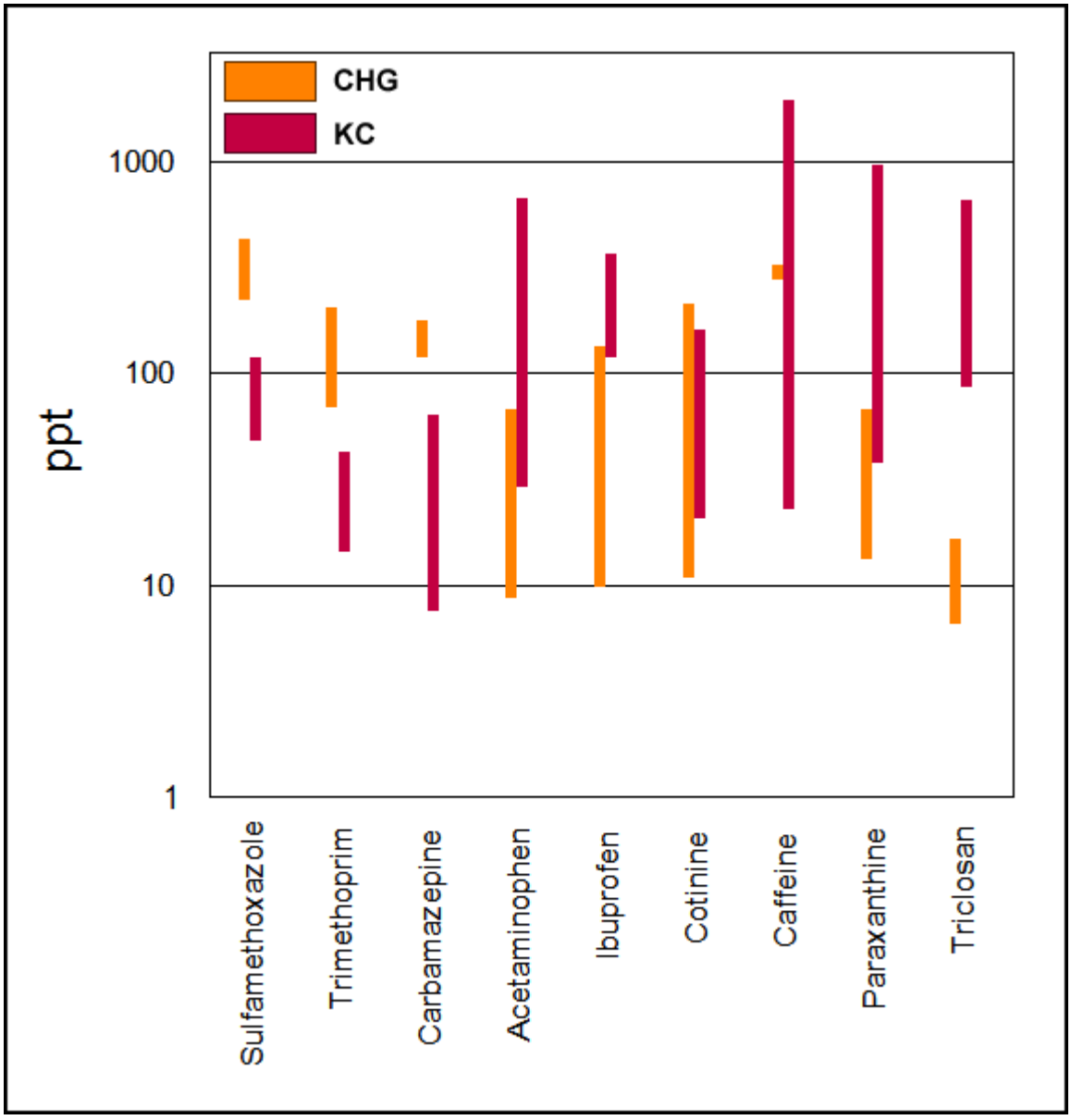

Figure N.1. Comparison of data from metropolitan areas of Chicago (CHG) and Kansas City (KC); PPCPs. (Derived from table 11 on page 38.)

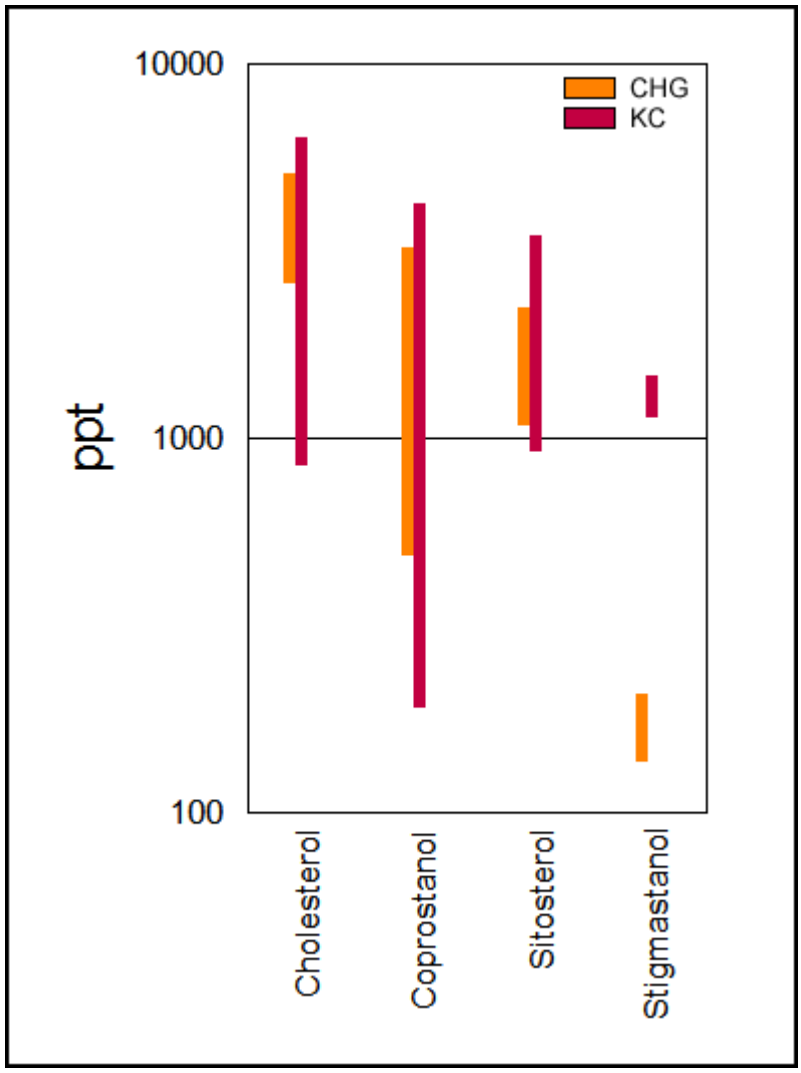

Figure N.2. Comparison of data from metropolitan areas of Chicago (CHG) and Kansas City (KC); sterols. (Derived from table 12 on page 39.)

References Cited

Alliance for Environmental Technology (AET). 1997. Environmental Fate Process. http://www.aet.org/science_of_ecf/eco_risk/sap97toc.html.

Arbini, G. 2008. Pharmacist, Webster Groves, Missouri. Personal communication with author.

Batt, A. L., K. Sungpyo, and D. S. Aga. 2006. Enhanced biodegradation of iopromide and trimethoprim in nitrifying activated sludge. *Environmental Science and Technology* 40:7367–7373.

Batt, A. L., K. Sungpyo, and D. S. Aga. 2007. Comparison of the occurrence of antibiotics in four full-scale wastewater treatment plants with varying designs and operations. *Chemosphere* 68:428–435.

Borowiak, S. 2008. Veterinarian, Wheaton, Illinois. Personal communication with author.

Clarke, J. 2008. Illinois Environmental Protection Agency (IEPA). 2001 CMAP land use spreadsheets. Personal communication with author.

City of Ann Arbor, Michigan (CoAA), Earl Kenzie. 2008. February04.xls. Personal communication with author.

Derksen, J. G., G. B. Rijs, and R. H. Jongbloed. 2004. Diffuse pollution of surface water by pharmaceutical products. *Water Science and Technology* 49:213–221.

Desbrow, C., E. J. Routledge, G. C. Brighty, J. P. Sumpter, and M. Waldock. 1998. Identification of estrogenic chemicals in STW effluent. *Environmental Science and Technology* 32:1549–1558.

Glenbard Wastewater Authority (GWA), Erik Lanphier. 2008. Glenbard_2007DailyFlow.xls. Personal communication with author.

Harvey, Roger. 2008. Chesapeake Biological Laboratory. University of Maryland Center for Environmental Science. Personal communication with author.

Holt, K. K., ed. 1997. *Veterinary pharmaceuticals and biologicals: The veterinarian's PDR.* 10th ed. Lenexa, KS: Veterinary Medicine Publishing Group.

Holt, K. K., ed. 1998. *Veterinary values.* 5th ed. Lenexa, KS: Veterinary Medicine Publishing Group.

Huerta-Fontela, M., M. T. Galceran, J. Martin-Alonso, and F. Ventura. Occurrence of psychoactive stimulatory drugs in wastewaters in north-eastern Spain. *Science of the Total Environment* 397:31–40.

Illinois Environmental Protection Agency (IEPA). Bureau of Water. 2004a. *Total maximum daily loads for Salt Creek, Illinois: Final report.* http://www.epa.state.il.us/water/tmdl/report/salt-creek/salt-creek.pdf.

———. 2004b. *Total Maximum Daily Loads for the East Branch of the DuPage River, Illinois: Final report.* http://www.epa.state.il.us/water/tmdl/report/dupage/east-branch-dupage.pdf.

———. 2004c. *Total Maximum Daily Loads for West Branch DuPage River, Illinois: Final report.* http://www.epa.state.il.us/water/tmdl/report/dupage/west-branch-dupage.pdf.

Illinois State Water Survey (ISWS). 2003. *7-Day 10-Year Low Flows: Map 2 Northeastern Illinois Streams; February 2003 Revision.* http://www.sws.uiuc.edu/docs/maps/lowflow/images/maps/map2.tif.

Jenkins, R. L., E. M. Wilson, R. A. Angus, W. M. Howell, and M. Kirk. 2003. Androstenedione and progesterone in the sediment of a river receiving paper mill effluent. *Toxicological Sciences* 73:53–59.

Kinney, C. A., E. T. Furlong, S. D. Zaugg, M. R. Burkhardt, S. L. Werner, J. D. Cahill, and G. R. Jorgensen. 2006. Survey of organic wastewater contaminants in biosolids destined for land application. *Environmental Science and Technology* 40:7207–7215.

Kolpin, D. W., E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber, and H. T. Buxton. 2002a. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: A national reconnaissance. *Environmental Science and Technology* 36:1202–1211.

Kolpin, D. W., K. K. Barnes, M. T. Meyer, E. M. Thurman, E. T. Furlong, S. D. Zaugg, and L. B. Barber. 2002b. *Water-quality data for pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000.* http://toxics.usgs.gov/pubs/OFR-02-94/index.html.

Kolpin, D. W. 2004. *Pharmaceuticals, EDCs, and other OWCs in water resources of the United States.* Plenary lecture at Environmental Side Effects Symposium.

Kumar, K., Y. Chander, S. M. Goyal, and S. C. Gupta. 2005a. Antibacterial activity of soil-bound antibiotics. *Journal of Environmental Quality* 34:1952–1957.

Kumar, K., S. C. Gupta, S. K. Baidoo, Y. Chander, and C. J. Rosen. 2005b. Antibiotic uptake by plants from soil fertilized with animal manure. *Journal of Environmental Quality* 34:1952–1957.

Kumar, K., A. K. Singh, S. C. Gupta. 2006. *Estrogens and estrogenic activity in swine manure.* Paper presented at ASA–CSSA–SSSA International Annual Meeting.

LaTour, J. 2008a. U.S. Geological Survey (USGS). Water Resources Discipline. Personal communication with author.

LaTour, J. 2008b. U.S. Geological Survey (USGS). Water Resources Discipline. National Water Information System: Discharge Measurement spreadsheets for gages 05531500, 05540160, 05540250, 05540095. Personal communication with author.

Lee, K. E., L.B. Barber, E.T. Furlong, J.D. Cahill, D.W. Kolpin, M.T. Meyer, and S.D. Zaugg. 2004. *Presence and distribution of organic wastewater compounds in wastewater, surface, ground, and drinking waters, Minnesota, 2000–02:* U.S. Geological Survey Scientific Investigation Report 2004–5138.

Lelo, A., J. 0. Miners, R. A. Robson, and D. J. Birkeit. 1986. Quantitative assessment of caffeine partial clearances in man. *British Journal of Clinical Pharmacology* 22:183–186.

Loffler, D., J. Rombke, M. Meller, and T. Ternes. 2005. Environmental fate of pharmaceuticals in water/sediment systems. *Environmental Science and Technology* 39: 5209–5218.

Loper, C.A., J. K. Crawford, K. L. Otto, R. L. Manning, M. T. Meyer, and E. T. Furlong. 2007. *Concentrations of selected pharmaceuticals and antibiotics in south-central Pennsylvania waters, March through September 2006:* U.S. Geological Survey Data Series 300.

Mackay, D. 1995. A perspective on the chlorine controversy. *Great Lakes Research Review* 1:5–12.

Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). 2000. *Egan Outfall 1990–2000.* http://www.mwrd.org/RD/IEPA_Reports/WRP%20Data/WRP%20Effluents/WRP%20Outfall%201990-2000/Egan%20Outfall%201990-2000.xls.

———. 2006. Terrence O'Brien to US EPA, letter.

———. 2007a. *Egan Outfall 2001–2007.* http://www.mwrd.org/RD/IEPA_Reports/WRP%20Data/WRP%20Effluents/WRP%20Outfall%202001-%202010/Egan%20Outfall%202001-%202007.xls.

———. 2007b. *Hanover Park Outfall 2001–2007.* http://www.mwrd.org/RD/IEPA_Reports/WRP%20Data/WRP%20Effluents/WRP%20Outfall%202001-%202010/Hanover%20Park%20Outfall%202001-%202007.xls.

———. 2008. Catherine O'Connor. Personal communication with author.

National Oceanic and Atmospheric Administration (NOAA). National Weather Service. 1999. Chicago O'Hare Daily Climate Data (F6). www.crh.noaa.gov/lot/climate/F6ORD/ordmay99.txt.

———. 2007. Chicago O'Hare Daily Climate Data (F6). www.weather.gov/climate/index.php?wfo=lot.

Plumb, D. C. 2005. *Plumb's Veterinary Drug Handbook.* 5th ed. Ames, IA: Blackwell.

RxList. 2008a. Gantanol: Clinical pharmacology. http://www.rxlist.com/cgi/generic/gantanol_cp.htm.

———. 2008b. Trimpex: Clinical pharmacology. http://www.rxlist.com/cgi/generic/trimeth_cp.htm.

———. 2008c. Tylenol: Clinical pharmacology. http://www.rxlist.com/cgi/generic/apap_cp-page2.htm.

———. 2008d. Motrin: Clinical pharmacology. http://www.rxlist.com/cgi/generic/ibup_cp-page2.htm.

Seelig, B. 2005. *Water Resource Impacts from Medicines and Other Biologically Active Substances, WQ–1278.* North Dakota State University Extension Service.

Sekimoto, H., O. Shimada, M. Makanishi, T. Nakano, and O. Katayama. 1983. Interrelationship between serum and fecal sterols. *Japanese Journal of Medicine* 22:14–20.

Skadsen, J. M., B. L. Rice, and D. J. Meyering. 2004. *The Occurrence and Fate of Pharmaceuticals, Personal Care Products and Endocrine Disrupting Compounds in a Municipal Water Use Cycle: A Case Study in the City of Ann Arbor.* Water Utilities, City of Ann Arbor, Michigan.

Skadsen, J. M., J. Wierenga, S. Allen, B. L. Rice, and D. J. Meyering. 2006. *The Occurrence and Fate of Pharmaceuticals, Personal Care Products and Endocrine Disrupting Compounds in a Municipal Water Use Cycle: A Case Study in the Cities of Ann Arbor, Grand Rapids, and Monroe.* Water Utilities, City of Ann Arbor, Michigan.

Son, H. S., S. B. Choi, K. D. Zoh, and E. Khan. 2007. Effects of ultraviolet intensity and wavelength on the photolysis of triclosan. *Water Science & Technology* 55:209–216.

Spring, A. J., D. M. Bagley, R. C. Andrews, S. Lemanik, and P. Yang. 2007. Removal of endocrine disrupting compounds using a membrane bioreactor and disinfection. *Journal of Environmental Engineering and Science* 6:131–137.

Stackelberg, P. E., J. Gibs, E. T. Furlong, M. T. Meyer, S. D. Zaugg, and R. L. Lippincott. 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Science of the Total Environment* 377:255–272.

U.S. Bureau of the Census (USBC). 2000. American FactFinder Fact Sheet, 2000 Total Population. http://factfinder.census.gov.

U.S. Department of Agriculture (USDA). Animal and Plant Health Inspection Service (APHIS), et al. [1999] 2007. *Antimicrobial Resistance Issues In Animal Agriculture.* Ed. Reginald Johnson.

U.S. Environmental Protection Agency (USEPA). Office of Solid Waste. 1999. *Aquatic Food Web Module: Background Implementation for the Multimedia, Multipathway, and Multireceptor Risk Assessment (3MRA) For HWIR99.*

U.S. Environmental Protection Agency (USEPA). 2005. *Code of Federal Regulations: Title 40 – Protection of the Environment,* section 799.6756.

U.S. Geological Survey (USGS). 2007a. *Water Data Report 2007: 05531500 Salt Creek at Western Springs, IL.* http://wdr.water.usgs.gov/wy2007/pdfs/05531500.2007.pdf.

———. 2007b. *Water Data Report 2007: 05540160 East Branch Du Page River near Downers Grove, IL, Water Data Report 2007: 05540250 East Branch Du Page River at Bolingbrook, IL*. http://wdr.water.usgs.gov/wy2007/pdfs/05540160.2007.pdf, http://wdr.water.usgs.gov/wy2007/pdfs/05540250.2007.pdf.

———. 2007c. *Water Data Report 2007: 05540095 West Branch Du Page River near Warrenville, IL.* http://wdr.water.usgs.gov/wy2007/pdfs/05540095.2007.pdf.

Werner, J. J., A. L. Boreen, B. Edhlund, K. H. Wammer, E. Matzen, K. McNeill, and W. A. Arnold. 2005. Photochemical transformation of antibiotics in Minnesota waters. *Univ. of Minnesota Center for Urban and Regional Affairs* 35:1–5.

Wilkison, D. H., D. J. Armstrong, R. E. Brown, B. C. Poulton, J. D. Cahill, and S. D. Zaugg. 2005. *Water-Quality and Biologic Data for the Blue River Basin, Kansas City Metropolitan Area, Missouri and Kansas, October 2000 to October 2004:* U.S. Geological Survey Data Series 127.

Wilkison, D. H., D. J. Armstrong, R. D. Norman, B. C. Poulton, E. T. Furlong, and S. D. Zaugg. 2006. *Water Quality in the Blue River Basin, Kansas City Metropolitan Area, Missouri and Kansas, July 1998 to October 2004:* U.S. Geological Survey Scientific Investigations Report 2006–5147.

Xia, K., A. Bhandari, K. Das, and G. Pillar. 2005. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. *Journal of Environmental Quality* 34:91–104.

Yang, L. H., G. G. Ying, H. C. Su, J. L. Stauber, M. S. Adams, and M. T. Binet. 2008. Growth-inhibiting effects of 12 antibacterial agents and their mixtures on the freshwater microalga Pseudokirchneriella subcapitata. *Environmental Toxicology and Chemistry.* 27:1201–1208.

To live is so startling, it leaves little time for anything else.

Emily Dickinson

This report is dedicated to the memory of Timothy Brian O'Hearn.

1967–2007