

# Potential Benefits of Nutrient and Sediment Practices to Reduce Toxic Contaminants in the Chesapeake Bay Watershed

## Report 2: Removal of Toxic Contaminants from the Agriculture and Wastewater Sectors

REVIEW DRAFT

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# Removal of Toxic Contaminants from Agriculture and Wastewater

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The following is a list of common acronyms used throughout the text:

AFO	Animal Feeding Operation
AMPA	Aminomethylphosphonic acid
BMP(s)	Best Management Practice(s)
BNR	Biological Nutrient Removal
CAFO	Combined Animal Feedlot Operation
CBP or CBPO	Chesapeake Bay Program Office
CBWM	Chesapeake Bay Watershed Model
CSO	Combined Sewer Overflow
EDC	Endocrine Disrupting Compound
EMC	Event Mean Concentration
GE	Genetically Engineered
HPCP	Household and Personal Care Products
HUC	Hydrologic Unit Code
LMW	Low Molecular Weight
MCL	Maximum Contaminant Level
MGD	Million Gallons Per Day
NPDES	National Pollutant Discharge Elimination System
OCP	Organochlorine Pesticides
OPP	Organophosphate Pesticides
OTC	Oxy-tetracycline
PEC	Probable Effects Concentration
PPCP	Pharmaceuticals and Personal Care Products
Rv	Runoff Coefficient
SAV	Submerged Aquatic Vegetation
SMX	Sulfamethoxazole
TC	Tetracycline
TEC	Threshold Effects Concentration
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TSS	Total Suspended Solids
WWTP	Waste Water Treatment Plant

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## Foreword

This project was developed by the Toxic Contaminant Work Group to evaluate whether best management practices (BMPs) used to reduce nutrient and sediment for the Bay pollution diet might also offer additional benefits such as reductions in toxic contaminants. The results of this one year research synthesis are summarized in two technical reports.

This report is the second installment in the series, and looks at how toxic contaminants are influenced by the agricultural and wastewater sectors in the Chesapeake Bay, with an emphasis on croplands, animal feeding operations and manure application, as well as discharges from wastewater treatment plants and land application of biosolids. This report focused on the following toxic contaminants:

- Pesticide applications (especially herbicides used for conservation till)
- Biogenic hormones generated by livestock, wastewater treatment and land application
- Antibiotics generated from livestock, wastewater and land application.

In compiling this memo, we tried to keep the technical jargon and organic chemistry to a minimum in order to make the findings more accessible to the general reader. Given the topics being explored, however, it is hard to avoid complexity or the often confusing terminology used to describe toxic contaminants, best management practices and wastewater treatment processes.

## Acknowledgements

This project was supported by a contract with the Chesapeake Bay Trust which developed the RFP in consultation of the Water Quality Goal Implementation Team and the Toxic Contaminants Work Group.

Special thanks to Jana Davis (CBT), Greg Allen (EPA), Scott Philips (USGS) and James Davis-Martin (VA DEQ) for their work in designing the project. Thanks are also extended to the members of the CBP Toxic Contaminant, Urban Stormwater and Agricultural Work Groups for their comments on the initial work plan and providing research citations. The assistance of David Wood and Emma Giese (both from CRC) was invaluable in getting the report done.

The massive literature review that supports this report could not have been completed without the tireless dedication, organization and hard work provided by Anna Youngk.

## Executive Summary

This report describes three stories on how market forces have changed the risks of toxic contaminants that are discharged from the agricultural and wastewater sectors of the Chesapeake Bay watershed.

### Conservation Tillage and Herbicides

The first story involves the profound change in the last three decades in how corn and soybeans are grown in the Chesapeake Bay watershed.

- The two row crops are planted in about 3 million acres in the watershed in any given year. The changes includes a major shift towards conservation tillage and genetically modified crops and greater use of glyphosate to control weeds.
- On balance, these changes appear to have improved both soil and water quality in the Bay watershed. Conservation tillage is a key practice to reduce sediment and nutrient loads from the agricultural sector. The shift away from herbicides used in past -- atrazine and metoachlor -- has also improved water quality, as measured by fewer groundwater advisories and fewer exceedances of aquatic life benchmarks in streams and rivers.
- Glyphosate and its degradate, AMPA, are mobile in the environment and are frequently detected in surface waters, but are not as persistent in soil or water as the herbicides they replaced.
- Testing has shown that glyphosate and AMPA are much less toxic to bird, fish and aquatic life, do not bioaccumulate in tissues, and have minimal impacts of human health.
- In addition, limited monitoring data suggest that vegetated buffers, constructed wetlands, biofilters and ponds all have a moderate to high capability to remove and degrade glyphosate and AMPA.
- Based on the evidence so far, the remarkable shift towards conservation tillage promoted in the Bay has helped improve water quality in the watershed, including reduced impacts from herbicides in stormwater runoff or groundwater.

## **Biogenic Hormones in Animal Manure and Municipal Biosolids**

The second story involves the increasing detection of biogenic hormones in surface waters of the Chesapeake Bay watersheds including the Choptank, Potomac and Shenandoah rivers.

- Biogenic hormones include estrogen, testosterone, estrone, estradiol and progesterone, and are of concern due to their potential endocrine disrupting properties.
- Scientists are still investigating the environmental risks associated with these emerging toxics of concern, but have found concentrations of biogenic hormones in the part per trillion range can negatively impact aquatic life and possibly cause intersex fish.
- Biogenic hormones are generated by animal feeding operations and wastewater treatment plants. Higher concentration are often associated with a high watershed density of either animal feeding operations or wastewater treatment plants.
- Research has shown that agricultural BMPs such as vegetated buffers, constructed wetlands and lagoons are highly effective in removing biogenic hormones in runoff from animal feeding operations.
- Likewise, wastewater treatment upgrades used for the Bay TMDL such as biological nutrient removal (BNR) have proven to be very effective in removing biogenic hormones in wastewater effluent.
- Research data suggests that that biogenic hormones can become concentrated in animal manure and municipal biosolids. When these treatment residuals are applied to crops as a fertilizer and soil amendment, they can potentially migrate back into the watershed. More research is needed to determine the significance of this loss pathway.
- The primary pollution prevention strategy is to keep unnecessary hormones out of the food supply chain. Many livestock producers, retailers and restaurant chains have recently adopted policies to eliminate the use of biogenic hormones in the meat, poultry and milk they purchase.
- This trend is strong reminder about the power of social marketing and economic forces that are focused on food quality and safety, as these policies should greatly reduce how many biogenic hormones are discharged from the animal feeding sector of the Bay economy.

## **Antibiotics in Animal Manure and Municipal Biosolids**

The third story involves a series of antibiotics that are detected in streams and groundwater in the Chesapeake Bay, which includes tetracycline, oxy-tetracycline and sulfamethoxazole.

- The main concern about these compounds is the potential for increased bacterial resistance to these drugs which could reduce their therapeutic effect on infectious diseases. Some research also indicates that some antibiotics can degrade the soil microbial community and reduce the rate of denitrification which is a critical process for reducing nitrogen.
- The analysis of antibiotics was very much limited by data quality problems. While we have learned more about the the sources and pathways of antibiotics in the watershed, we lack a basic understanding about whether they are effectively removed by agricultural practices and wastewater treatment upgrades, and whether leaching from animal manure or municipal biosolids are a significant problem or not.
- There is some evidence that BNR, which is increasingly used to achieve higher nutrient removal, may also be more effective in removing antibiotics from wastewater effluent. It remains unclear whether the municipal biosolids generated by this enhanced level of treatment can migrate back into the watershed after they are applied to croplands.
- An encouraging trend have been efforts to the phase out of antibiotics used in poultry, swine and cattle feeding operations. Several livestock producers, grocery stores and restaurant chains are now selling meat, poultry and dairy products that are grown without antibiotics. If these efforts to eliminate antibiotics from the food supply chain are expanded, it would represent a very effective strategy to reduce biogenic hormones from the watershed.
- Another key management strategy is to practice "antibiotic stewardship" to minimize the volume that are prescribed for humans and ensure that these pharmaceuticals are properly disposed to prevent their release to the environment.

## Next Steps and Research Recommendations

The overall findings in this report should be considered provisional because of the poor data quality associated with many of the toxicants (especially biogenic hormones and antibiotics).

- It is recommended that current expert panels launched to assess conservation tillage and manure management should also explicitly consider their unintended consequences in terms of potential discharge or removal of toxics to the environment.
- Likewise, wastewater expert panels should investigate whether treatment upgrades will increase the potential risk that biogenic hormones and antibiotics could be released when municipal biosolids are applied to cropland.
- Three specific research areas are recommended to resolve the uncertainties around these three groups of toxic contaminants. More research and monitoring are needed to:
  - Determine which practices can best reduce herbicide runoff from conservation tillage across the watershed.
  - Define the dynamics and pathways of biogenic hormones and antibiotics in the watershed, and to evaluate their risk to human health and aquatic life.
  - Test the best practices to store, handle and incorporate manure and municipal biosolids to minimize losses of biogenic hormones and antibiotics.



## **Section 1: Toxic Contaminants from the Agriculture and Wastewater Sectors**

### **1.1 Background for the Study**

One of the key outcomes under the Toxic Contaminant goal in the 2014 Chesapeake Bay Watershed Agreement was to "identify which best management practices (BMPs) might provide multiple benefits -- to not only reduce nutrient and sediment pollution but also remove toxic contaminants from entering waterways."

The key issue is whether BMPs and wastewater treatment upgrades used to comply with TMDL can also help to substantially reduce toxin inputs to local waterways and the Chesapeake Bay. Such multiple benefits could provide significant cost savings to the Chesapeake Bay Partnership to simultaneously meet the Bay TMDL and reduce toxic contaminants in the environment.

Therefore, the broad purpose of this study was to:

- (1) Investigate the potential toxic contaminant reduction benefits that could be associated with the implementation of BMPs for sediment and nutrient reduction under the Bay TMDL.
- (2) Provide water resource managers with better BMP data to develop more effective local TMDLs and action strategies to control toxic pollutants in the watershed.

### **1.2 Selection of Priority Toxins**

Thousands of potential contaminants exist in the water environment, so it was necessary to screen them down to a manageable number based on environmental risk in the Chesapeake Bay watershed. The degree of environmental risk was broadly defined based on three primary criteria, as previously established by CBP (2012).

- (a) Relative extent of the individual toxic contaminant in the Bay watershed based on prior monitoring data that indicate it has been detected in water, sediment, and/or tissue samples, as summarized in CBP (2012).
- (b) Relative severity of the human health and/or fish and wildlife impacts caused by the toxin in localized hotspots or across the entire Bay watershed.
- (c) Toxins that Bay states have directly linked to water quality impairments and/or fish consumption advisories in specific receiving waters within the Bay watershed.

Based on this screening analysis, a priority list of 45 toxic contaminants were selected for review (Table 1).

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<b>Table 1: Priority Contaminants Based on Environmental Risk<sup>1</sup></b>		
<b><i>Agricultural and Wastewater Contaminants</i></b>		
<b>#</b>	<b>Toxic Category</b>	<b>Individual Contaminants</b>
1	Cropland Herbicides	Atrazine, simazine, metolachlor, acetochlor, glyphosate
2	Biogenic Hormones	Estradiol, estrone, testosterone
3	Human and Livestock Antibiotics	Tetracyclines, oxy-tetracycline, sulfonamides (e.g., sulfamethoxazole)
<b><i>Urban Toxic Contaminants</i></b>		
4	PCBs	Total PCBs
5	PAH's	Total PAH, benzo(a)pyrene, naphthalene
6	Petroleum Hydrocarbons	TPH, oil and grease, benzene
7	Mercury	Hg, Me-Hg
8	Urban Trace Metals	Cd, Cu, Pb, Zn
9	Other Trace Metals	As, Cr, Fe, Ni
10	Pyrethroid Pesticides	Bifenthrin, permethrin
11	Legacy OC Pesticides <sup>2</sup>	DDT/DDE, dieldrin and lindane
12	Legacy OP Pesticides <sup>2</sup>	Chlordane, diazinon, chloropyrifos
13	Plasticizers	Phthalates
14	Flame Retardants	PBDE
15	Dioxins	Dioxins and furans
<p><b>Codes:</b> PCB's = Polychlorinated Biphenyls, PAH= Polycyclic Aromatic Hydrocarbons, HPCP= Household and Personal Care Products, PBDE = Polybrominated Diphenyl Ether, TPH = Total Petroleum Hydrocarbons. OC= organochlorine, OP = organophosphate.</p> <p><b>Notes:</b></p> <p><sup>1</sup> As defined by the extent and prevalence of the contaminant in the Bay watershed, as well as actual impairments or fish advisories, as defined in CBP (2012).</p> <p><sup>2</sup> Legacy pesticides refer to insecticides that have been banned or phased out, but have such long half lives that they are still detected in the environment; this list is based on a national assessment of pesticide prevalence in streams and groundwater by Gilliom et al (2006).</p>		

## 1.3 Scope of Literature Review

CSN conducted an international literature review to identify key research papers on the priority toxins. The review investigated:

- Key characteristics, sources, generating sectors and watershed pathways associated with priority toxins
- Measured concentrations in agricultural runoff, groundwater or wastewater effluents
- Measured or inferred removal of toxins associated with agricultural BMPs and WWTP upgrades.
- Measured concentrations and retention of toxins within BMP sediments and biosolids
- Additional practices that can prevent the toxins from being released into the environment

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Nearly 200 research papers and reports were discovered during the review, including several research databases and review papers that contained additional citations. A spreadsheet was developed to organize the papers by the toxin, author, title and geographic region, which is available upon request from the Chesapeake Stormwater Network.

## 1.4 Toxic Contaminants: Cross-Walk with Other Watershed Sectors

Many toxic contaminants are generated from multiple sectors in the Bay watershed. For example, a previous report by Schueler and Youngk (2015) focused on 12 toxic contaminants that were predominantly associated with urban land use, although other sectors in the watershed may play a role in generating some of them. For the benefit of the reader, Table 2 provides a short "cross-walk" on which sectors generate the toxins, and in which of the two reports they are discussed.

Name(s)	Report	Sector (s)	Notes
<i>Insecticides</i> Organochlorine Organophosphate Pyrethroids Neonictinoids Fipronil	1	Agricultural and Urban	Nearly every insecticide detected in urban watersheds is also applied to different crops in agricultural watersheds, although aquatic life benchmarks are exceeded more frequently in the urban streams
<i>Herbicides</i> Atrazine Metoachlor 2-4-D Prometon	2	Urban and Agricultural	The same herbicides applied to croplands are also applied in urban watersheds, although concentrations in urban streams are lower than in agricultural streams
<i>Pharmaceutical and Personal Care Products (PPCP)</i>	None	Wastewater, Stormwater and Municipal Biosolids	PPCPs that were <u>not</u> investigated included surfactants, antimicrobials, musks and fragrances, caffeine, biogenic steroids, insect repellent, anti-depressants and over the counter pharmaceuticals
<i>Other Trace Metals (OTM):</i> Arsenic	1	Urban and Agricultural	Associated with animal feeding operations, especially poultry
<i>PAH</i>	1	Urban and wastewater	Wastewater effluent is a common but minor source of PAH
<i>Plasticizers and Flame retardants</i>	1	Urban, wastewater and biosolids	Wastewater effluent and biosolid leaching appear to be a significant watershed source, but more data needed

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Of particular note were pharmaceuticals and personal care products (PPCP). More than a hundred have been detected in streams, wastewater effluent or municipal biosolids (Kolpin et al, 2002 and Focazio et al, 2008) and it was not possible to analyze them all in this study. Consequently, the analysis was restricted to antibiotics which have received the most study and are thought to pose the greatest risk to the environment.

A decision was also made to assign insecticides to the urban toxic contaminant category, although most of them are also applied in agricultural watersheds. More research is needed on pathways, persistence and toxicity of the newest generation of insecticides applied to crops and orchards, such as fipronil, dichlorvos, permethrin and the neonictinoids. Schueler and Youngk (2015a) provide more information on these insecticides.

Likewise, herbicides were assigned to the agricultural sector and included in this report, even though they are also applied in urban watersheds to control weeds on lawns, gardens and rights of ways. Some of the more common herbicides detected in urban watersheds include atrazine, metoachlor, 2-4-D and prometon (the latter two are primarily applied to control weeds in highway right of ways).

## **1.5 Comparative Data Quality for Toxins Reviewed in this Report**

One of the primary efforts in the review was to evaluate the quality of the available monitoring data for each class of toxic contaminants. Tables 3 to 5 provide a comparative summary of the data quality associated with herbicides, biogenic hormones and antibiotics, respectively.

The grey cells in each table indicates situations where the data quality is considered low or very low (i.e., less than five studies, most of which are not located in the Chesapeake Bay). As can be seen, limited data quality diminishes our understanding of the sources, pathways and concentrations of many potential toxins. The greatest data gaps for these toxins involve their impact to the aquatic environment and the capability of BMPs and WWTP upgrades to reduce those impacts.

The lack of monitoring data for these three toxics of emerging concern is not surprising, since it is only recently that monitoring technology has improved to the point where scientists can measure their presence in the environment at the part per billion or even part per trillion levels.

Based on these knowledge gaps, it is explicitly acknowledged that many of the key findings in this report should be considered provisional until more research is done to support them.

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**Table 3. Comparative Data Quality for Three Groups of Agricultural Herbicides**

Factor	Herbicide Group		
	Atrazine/Simazine	Metolachlor/Alachlor	Glyphosate/AMPA
Ag Runoff EMCs	M	L	L
Ag Groundwater	M	VL	M
Ag Streams	H	L	M
Degradation Rate	M	L	L
BMP Removal	L	VL	L
BMP Sediment	VL	VL	VL
VL = Very Low (<3 studies, none from CB) L = Low (< 5 studies, some from CB) M = Moderate ( 5 to 10 studies) H = High (10 to 25 studies) VH = Very High (>25 studies)		NA: Not Applicable EMC: Event Mean Concentration	

**Table 4. Comparative Data Quality for Biogenic Hormones**

Factor	Watershed Sources				
	WWTP Effluent	CSO Discharges	Municipal Biosolids	AFO Discharge	Manure Applied to Crops
Loading Data	L	VL	VL	VL	L
Runoff EMC	NA	VL	L	VL	L
Streams	M	L	L	L	VL
Groundwater	NA	NA	VL	VL	VL
Removal Rates	M	VL	VL	L	L
Sludge/Manure	L	VL	L	VL	L
VL = Very Low (<3 studies, none from CB) L = Low (< 5 studies, some from CB) M = Moderate ( 5 to 10 studies) H = High (10 to 25 studies) VH = Very High (>25 studies)			NA: Not Applicable EMC: Event Mean Concentration		

**Table 5. Comparative Data Quality for Antibiotics**

Factor	Watershed Sources				
	WWTP Effluent	CSO Discharges	Municipal Biosolids	AFO Discharges	Manure Applied to Crops
Loading Data	L	VL	VL	VL	VL
Runoff EMC	NA	VL	VL	VL	VL
Streams	M	L	VL	L	L
Groundwater	NA	NA	VL	VL	VL
Removal Rate	L	VL	VL	L	VL
Sludge/Manure	VL	NA	L	VL	VL
VL = Very Low (<3 studies, none from CB) L = Low (< 5 studies, some from CB) M = Moderate ( 5 to 10 studies) H = High (10 to 25 studies) VH = Very High (>25 studies)			NA: Not Applicable EMC: Event Mean Concentration		

## 1.6 The Agricultural Sector in the Bay Watershed

This section brief summarizes the agricultural sector in the Chesapeake Bay watershed with a focus on row crops, livestock and manure applications.

The three primary row crops in the Chesapeake Bay are corn, soybeans and wheat, which collectively cover about 3.6 million acres of land in the watershed. The precise acreage of row crops planted each year varies due to commodity prices, production costs and other market forces. According to the National Agricultural Statistics Service, corn and soybean production peaked in 2007 in the watershed at 2.05 and 1.2 million acres, respectively, when grain prices also reached their peak.

The major change in the last decade has been the remarkable shift toward genetically modified corn and soybeans in the watershed. According to the Agricultural Research Service, between 92 to 94% of all the corn and soybeans grown in the watershed are genetically modified for herbicide tolerance and/or insect resistance (up from 15 to 25% at the turn of the century). Glyphosate is now widely applied to corn and soybeans using conservation tillage since these crops have been specifically modified to tolerate this herbicide.

Conservation tillage is now applied to about 88% of the row crops grown in the Bay watershed -- 48% as no till and 40% as either mulch till, strip till or some other form of reduced tillage (NRCS, 2011). Conservation tillage is a versatile practice, but it cannot be used everywhere in the watershed -- it is not always feasible for crops grown on steep slopes and/or heavy or poorly drained soils.

The shift to conservation tillage represents a major change in agronomy over the last several decades. Conservation tillage has been promoted as an effective agricultural BMP to reduce sediment and nutrient loads delivered to the Chesapeake Bay. Dinnes (2004) outlined the key mechanisms responsible for pollutant reduction by conservation tillage. They include:

- Reduced erosion and transport of nutrient-enriched sediments and particles
- Increased infiltration of runoff into the soil and adsorption of nutrients into the soil matrix
- Improved stabilization of surface soils that reduce wind or water erosivity
- Reduced runoff volumes delivered to the edge of field
- Temporary sequestration of nutrients in soil organic matter

CBP (2011) define conservation tillage as meeting two qualifying conditions -- a minimum of 30% of the soil surface must be covered by crop and/or organic residues immediately following planting operations and (2) the farmer must employ a non-inversion method of tillage. The NRCS has established specific technical standards and criteria for conservation tillage that must be met to qualify for sediment and nutrient reduction credits.

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Conservation tillage is currently represented in the Chesapeake Bay Watershed Model (CBWM) as a separate agricultural land use and not as a specific BMP. However, the CBP has established that conservation tillage produces nitrogen, phosphorus and sediment loads that are 8, 12 and 30% lower than conventional tillage, respectively.

The definition and qualifying conditions for conservation tillage may change in the coming years as the Phase 6 Chesapeake Bay Watershed Model is refined. The CBP has also launched an expert panel to re-evaluate sediment and nutrient rates for different forms of conservation tillage, which is expected to be completed during 2016.

Conservation tillage, along with winter cover crops, ranks among the most widely used agricultural BMPs in the Chesapeake Bay watershed. According to Sweeney (2015), conservation tillage was responsible for approximately 7 or 8% of the total nitrogen and phosphorus reduction achieved by the agricultural sector in 2014.

### *Livestock and Manure in the Watershed*

Klenman et al (2012) estimate that about 3.2 million animal units are raised in the Chesapeake Bay in a typical year (each animal unit is 1000 lbs) which collectively generate 36 million tons of manure each year, most of which is applied back to crops. Poultry and cattle generate most of the animal manure in the Chesapeake Bay watershed, as shown in Table 6.

Klenman et al (2012) provides an extensive review of current efforts to improve manure management in the Chesapeake Bay watershed. Significant progress has been made in manure handling and storage facilities on individual farms, and some progress has also been made in manure injection technology. The challenge remains on how to prevent manure applications from exporting nutrients, particularly in those regions of the Bay watershed where they are most extensively applied.

Livestock	% of Total Manure <sup>1</sup>	% TP Load	% TN Load	Notes
Poultry	24	49	44	
Dairy Cattle	26	20	24	
Beef Cattle	12	10	10	Small herds, pasture-based
Horses	11	8	8	
Swine	5	6	5	

Source: sources cited in Klenman et al (2012),  
<sup>1</sup> wet weight of manure generated in Bay watershed, does not sum to 100% due to other animal units and municipal biosolids.



## 1.7 The Wastewater and Biosolid Sector in the Watershed

As of 2010, 483 significant municipal and industrial wastewater treatment plants (WWTPs) operated in the Bay watershed that collectively discharged 3 billion gallons of effluent per day (CBP, 2012). Significant dischargers are operationally defined as individual WWTPs that exceed a design flow of 0.4 to 0.5 MGD, depending on the Bay state. More than 4,200 smaller "non-significant" wastewater facilities also exist in the Bay watershed.

In recent years, many Bay states have upgraded their WWTPs to provide greater nutrient removal, using a technology known as Biological Nutrient Removal or BNR. These BNR upgrades have produced much of the nitrogen and phosphorus removal from the Bay wastewater sector.

One byproduct of enhanced treatment is the production of sewage sludge, otherwise known as municipal biosolids, which are often applied to crops as a fertilizer and soil amendment. Reliable data could not be found on the acreage of cropland in the Bay watershed that are fertilized by municipal biosolids, or how their typical application rates compare to livestock manure application rates for the same crops.



## Section 2: Herbicides from Croplands

### 2.1 Trends in Herbicide and Tillage Practices Over Time

To fully understand the herbicide story in the Chesapeake Bay, it is helpful to review how trends in tillage practices and genetically engineered seeds have influenced the herbicides used on corn and soybean crops over the last 40 years. Table 7 summarizes these trends during three key eras in the Bay watershed, as described below

#### *ERA 1: The Atrazine Era (1970s and 1980s)*

In the first era, atrazine was the dominant herbicide applied to corn and soybeans, although conservation tillage was not yet routinely used to grow these crops. Indeed, atrazine was initially suspected to be one of the three pollutants that caused a Bay-wide decline in submerged aquatic vegetation (SAV) that occurred in the 1970s and early 1980s (the other two pollutants were suspended sediment and nutrients).

At that point in time, the application of atrazine to control weeds on corn and soybean fields was growing rapidly, and concerns were raised that it could harm SAV and phytoplankton given its mobility in the aquatic environment. Over time, SAV coverage in the Bay has partially recovered from its lows in the late 1970s, but not back to its historical levels.

**Table 7: Trends in Herbicides Applied to Corn and Soybeans <sup>1</sup>**

ERA	1970's -1980's	1990-2000	2001 to present
<b>Most Common Herbicides Detected</b>	<ul style="list-style-type: none"> <li>• Atrazine</li> </ul>	<ul style="list-style-type: none"> <li>• Atrazine</li> <li>• Metoachlor</li> <li>• Acetochlor</li> <li>• Alachlor</li> </ul>	<ul style="list-style-type: none"> <li>• Glyphosate</li> <li>• AMPA</li> <li>• Some Atrazine</li> </ul>
<b>Tillage Practices</b>	>25% of crops use conservation till	Climbs to about 50 to 60% of crop acres	Climbs to nearly 90% of row crops
<b>Genetically Engineered Crops</b>	None	GE corn and soybeans enter market in mid to late 1990's	GE seeds comprise 92 to 94% share of crop acres
<b>Environmental Risks</b>	Atrazine suspected in SAV loss, but later exonerated	Aquatic life criteria frequently exceeded for metoachlor and atrazine	Routinely detected in surface waters, but aquatic life criteria not exceeded
<b>Groundwater Concerns</b>	Major concern for rural drinking water wells	Declining levels measured toward end of the era	Rarely detected in groundwater or soil water at this time
<b>Sources:</b> Gilliom et al, 2006, Hartwell, 2011, Stone et al, 2014, Battaglin et al, 2014 and CTIC, 2011)			
<sup>1</sup> statistics, eras and time frames are all approximate, and may differ in the various agricultural regions of the Bay watershed.			

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Researchers ultimately concluded that excess nutrients and sediments that diminished estuarine water clarity were the primary cause of the decline in SAV in the Bay, and not atrazine (Schwarzchild et al, 1994). Atrazine was found to exceed aquatic life benchmarks in streams and groundwater advisories were also issued for some drinking water wells in agricultural watersheds.

### *ERA 2: The Rise of Conservation Tillage (1990 to 2000)*

The second era extended from about 1990 to 2000 and witnessed several important developments. First, conservation tillage was adopted on a widespread and also coincided with the advent of genetically engineered corn and soybeans by the middle of the decade. Another important driver for the increased acreage of conservation tillage were the efforts by the Chesapeake Bay partnership to promote (and cost-share) the practice to reduce sediment and nutrient nitrogen loads in the Bay watershed. During this era, Bay states such as Maryland and Virginia actually adopted conservation tillage at a faster rate than the traditional corn-belt states in the midwest.

The second development involved a changing mix of herbicide products applied to corn and soybeans. Hartwell (2011) documented how herbicide applications changed in the Bay watershed during this era. In the early 1990s, atrazine, metoachlor and alachlor were the top three herbicides used in the watershed. Acetochlor was introduced as an herbicide for corn in the mid 1990s and largely replaced alachlor by the turn of the century. The use of atrazine and metoachlor began to decline sharply in the Bay watershed by the turn of the century. These herbicides were largely replaced by a sharp rise in the use of glyphosate.

The changing mix of herbicides are reflected in the surface water and groundwater monitoring data that was collected during this era. For example, Gilliom et al (2006) reported on a national assessment of herbicide levels in streams and groundwater from 1992 to 2001. For agricultural streams, the top five herbicides that were detected included atrazine (80% detection), metoachlor (75%), cynazine (40%) and acetochlor (30%) and trifluralin (15%). Glyphosate was just coming into use at the end of their study period, and was not measured.

Gilliom et al (2006) observed that atrazine and metoachlor, which were applied extensively to corn during this era, were highly soluble and mobile in agricultural watersheds. Atrazine tended to be more persistent than metoachlor, which is not surprising given its longer half life in soil and water (see Table 8). In general, both atrazine and metoachlor were found at higher concentrations in agricultural streams compared to urban streams.

Metoachlor exceeded aquatic life benchmarks in 40% of agricultural streams sampled across the nation from 2002 to 2011 -- a higher rate than all other agricultural pesticides -- herbicide or insecticide -- that were sampled in a USGS study (Stone et al, 2014). By contrast, atrazine was only found to exceed the aquatic life benchmarks in 5% of agricultural streams during the same time period, and appears to be declining to even lower levels as its use continues to fall.

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Only two herbicides -- atrazine and metoachlor -- were widely detected in groundwater, which occurred in both agricultural and urban watersheds (Gilliom et al, 2006). Debrewer et al (2008) looked at trends in herbicide levels in groundwater in the mid-Atlantic region during this era. Debrewer sampled groundwater concentrations in wells across the Great Valley of the Shenandoah and the Delmarva peninsula. Herbicides were detected in 89% of the wells of the Great Valley and 93% of the wells in Delmarva, although groundwater concentrations seldom exceeded 0.1 ug/L.

The main herbicides used at the time for corn and soybeans were all detected -- atrazine, alachlor and metachlor (Debrewer et al, 2008). In general, the concentration of herbicide degradates typically exceeded that of their parent compounds, and the concentration of atrazine in groundwater declined from the mid-1990's to 2003.

### *ERA 3: The Rise of Glyphosate and Genetically Engineered Crops (2001 to present).*

This era saw three intersecting trends -- the dominance of acres planted in conservation tillage and genetically engineered crops, and a pronounced shift towards glyphosate as the principal herbicide for corn and soybeans.

The rapid shift in the herbicides applied to genetically modified corn and soybeans has been documented by Stone et al (2014). Starting around the turn of the century, farmers shifted away from atrazine and acetochlor and now rely almost exclusively on glyphosate. Hartwell (2011) also reported that the use of atrazine and metoachlor had declined sharply in the Bay watershed by the turn of the century, and alachlor was completely phased out by then. These herbicides were largely replaced by a sharp rise in the use of glyphosate, which began around the year 2000 and has accelerated throughout the last decade (Hartwell, 2011).

The changes in tillage practices in this era also changed in what herbicides were detected in surface water and groundwater. Initially, the high cost and difficulty of sampling glyphosate prevented scientists from routinely sampling for its presence in the water environment, but this problem has been largely solved.

Battaglin et al (2005) conducted the first intensive survey of glyphosate and AMPA levels in Midwestern streams located in watersheds where genetically modified corn and soybeans were grown. In general, they found that the two herbicides were detected less frequently and at lower concentrations than the herbicides that they had replaced (e.g., atrazine, acetochlor and metachlor).

More recent studies indicate that glyphosate and its degradation product, AMPA, are widely prevalent in aquatic environments, as its use has steadily increased. For example, Battaglin et al (2014) reported on a comprehensive national assessment of glyphosate mobility based on more than 3,700 samples collected in the last decade. They found that AMPA was detected more frequently than glyphosate in most environmental settings, except for lakes and wetlands. Glyphosate was detected in more than 50 percent of all soil and sediment samples, as well as 50% of the water samples collected from rainwater, ditches, drains, streams and rivers. Battaglin et al (2014) also reported that

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glyphosate and AMPA were detected much less frequently within groundwater or soil water (only 8% of all samples).

## 2.2 Herbicide Properties

The chemical properties of different herbicides can explain a lot about their dynamics, persistence and mobility in the watershed, as well as their potential toxicity in the environment. Table 8 compares the different properties of herbicides that were historically applied within the Bay watershed (white cells) with those that are applied now (grey cells). Current herbicides tend to have a lower risk to either contaminate groundwater or exceed aquatic life benchmarks in streams, and are generally less persistent in soils and water in the watershed. Appendix A provides more data on key herbicide coefficients that influence the mobility and partitioning of the current and historically applied herbicides.

Herbicide	Groundwater Contamination Advisory?	Exceeds Aquatic Life Benchmarks ?	MCL	Half-life in Soils	Half-life in Water
			(ug/l)	Days	
Atrazine	Yes	Yes	3	146	742
Simazine	Yes	Yes	4	91	32
Metoachlor	Yes	Yes	100	26	410
Alachlor	Yes	Yes	2	21	640
Glyphosate *	No	No	700	35	96
AMPA*	No	No	nd	7-14	76-240

**Sources:** Gilliom et al (2006), Battaglin et al (2005) and Zhang et al (2014)  
 nd = no data \* some inconsistency in reported values in the literature, especially for half life data

### *Focus on Glyphosate and AMPA*

Given that glyphosate is now the most widely used herbicide on corn and soybeans that are conservation tilled in the Chesapeake Bay watershed, it is helpful to take a closer look at its mobility and potential toxicity in the watershed.

Glyphosate is highly water soluble and mobile in aquatic systems. Glyphosate binds strongly to cations that are adsorbed to soils. Much like phosphorus, glyphosate binds fairly tightly to soils and not organic matter (Battaglin et al,2005). Glyphosate is degraded by microbes into AMPA, which is less toxic than glyphosate, but also degrades at a slower rate in soil and water. Ultimately, AMPA degrades into inorganic phosphorus, ammonium, and carbon dioxide.

A nationwide assessment conducted by Battaglin et al (2014) reported that glyphosate concentrations were well below existing benchmarks to protect aquatic life or human health, and no samples exceeded EPA MCLs or Canadian short or long term standards to protect aquatic life (Battaglin et al, 2014). Glyphosate is not very toxic to birds, fish or aquatic life, exerts minimal impacts to human health and does not pose a risk of bioaccumulation in fish or avian tissues.

Battaglin et al (2014) did observe that glyphosate and AMPA were more persistent and mobile in the aquatic environment than had been previously thought, and expressed concern that their possible impacts on aquatic and terrestrial ecosystems had not been fully resolved.

### **2.3 Estimated Removal by Agricultural BMPs**

The available research on herbicide runoff losses under conservation tillage is fairly limited. The conventional wisdom has been that herbicide losses should be minimized under no till conditions, given that surface runoff and corresponding soil erosion are reduced. Warnemunde et al (2007) conducted experiments to test that assumption, and found that both atrazine and glyphosate concentrations were actually higher in no till test plots than conventional till plots. Warnemunde et al (2007) reported that glyphosate levels from no till plots never exceeded its high MCL (700 ug/l), whereas atrazine levels occasionally exceeded its much lower MCL of 3 ug/l (See Table 8).

A handful of other studies have looked at the capability of agricultural buffers, constructed wetlands and ponds to reduce herbicide losses. For example, Burken and Schnoor (1997) studied test plots to evaluate the phytoremediation effect of hybrid tulip poplar trees to biodegrade atrazine. Poplar trees were found to be effective in biodegrading soils that were contaminated with atrazine, and suggested that edge of field forest buffers could play a role in reducing herbicide loss.

Australian researchers reported 20 to 60% reductions of diuron and simazine in a constructed wetland (Page et al, 2014). Imfield et al (2012) monitored the capability of a constructed wetland to remove herbicides from vineyard runoff in France over three seasons. Depending on the year, the constructed wetland removed 75 to 99% of the loads of glyphosate and AMPA. Interestingly, neither herbicide was detected in the wetland sediment samples, which indicates that they rapidly biodegrade in sediments within a few days. Imfield et al (2012) also found that the two herbicides did adsorb to wetland vegetation which turned out to be responsible for much of the herbicide attenuation.

Zhang et al (2014) evaluated the capability of biofilters to remove a range of herbicides in an urban catchment in Australia. They found the biofilters were very effective in removing glyphosate (80+%), but were only moderately effective at removing atrazine and simazine (20 to 50%). Zhang et al (2014) concluded that prolonged dry periods and aerobic soil conditions promoted greater biodegradation and enhanced herbicide removal rates.

Sebastian et al (2014) monitored the performance of a retention pond in removing pesticides from a 457 acre industrial watershed in Lyon, France. The pond was able to trap about 66% of the glyphosate delivered to it, but released its biodegradation product AMPA (negative 189% removal). In addition, low (>20%) or even negative removal rates, were reported atrazine, diazinon and chlorpyrifos.

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Fischer et al (2003) measured herbicide levels in monitoring wells adjacent to stormwater infiltration basins in the New Jersey coastal plain. They discovered elevated levels of metoachlor and prometon in the infiltration basin wells (these two herbicides were used to control grassy weeds in the highway right of way that drained to the basin). While atrazine was also detected, the levels were the same as background groundwater levels for the region. Overall, Fischer et al (2003) concluded that the risk of herbicide contamination in the groundwater below infiltration basins was low, and that the stormwater runoff diverted to the basins helped to dilute the herbicide concentrations.

## **2.4 Other Herbicide Management Strategies**

Conservation tillage is one of the cornerstone BMPs that can effectively reduce sediment and nutrient losses from the agricultural sector to the Chesapeake Bay. The shift to newer and less persistent herbicides appears to have reduced their potential toxicity to aquatic life, although some concerns remain. More research is needed to investigate how to maximize the efficiency of herbicide treatments to croplands that could prevent edge of farm herbicide losses. More effective techniques to incorporate them into soils could simultaneously protect aquatic resources and produce economic benefits to the farming community.



## Section 3: Biogenic Hormones from Agricultural and Wastewater Operations

### 3.1 Background on Biogenic Hormones

Biogenic hormones are routinely detected in rivers and streams and are of concern due to their potential endocrine disrupting properties. Biogenic hormones include estrogen, testosterone, estradiol and progesterone, which are suspected to harm aquatic life and possibly cause intersex fish. Bradley (2009) found that concentrations in the part per trillion range can have a negative effect on some aquatic species.

Kolpin et al (2013) sampled for numerous micro-pollutants at six stations in the Potomac River basin near smallmouth bass nesting areas. Kolpin et al (2013) reported a significant positive relationship between intersex fish and total hormone/sterol levels measured in bed sediments at the fish nests.

These hormones are naturally created and excreted through the human body, but are also routinely added to livestock feed. The three main sources of biogenic hormones in the watershed are:

- Discharges from animal feeding operations (AFOs)
- Wastewater treatment plant (WWTP) effluent
- Land application of manure or municipal biosolids to crops

Together, these sources can contribute high loads of biogenic hormones into both agricultural and urban streams and rivers (Esperanza et al, 2012). Higher detection of biogenic hormones is often related to the intensity of either agricultural or urban land use, especially as it relates to the density of animal feeding operations and/or the volume of wastewater effluent produced in a watershed (Ciparis et al, 2012).

Biogenic hormones are nonvolatile, highly adsorptive and bind to aquatic sediments. Although they are slightly hydrophilic, they are more likely to be found in the particulate phase (Esperanza et al, 2007; Hanselman et al, 2003; Jacobsen et al 2005; Salierno et al 2012).

In most cases, biogenic hormones are sorbed to soils or creek sediments, and are mobile in surface waters, and to a lesser degree, groundwater. Most biogenic hormones are not very persistent in the environment, with measured soil half lives of 1 to 5 days (Hansleman et al, 2003 and Jacobsen et al, 2005).

It also appears that biogenic hormones can be transported for long distances in streams and rivers before they break down. Cohen et al (2005) sampled biogenic hormones from fish pond and wastewater discharges along a 65 mile reach of the Jordan River. They noted biogenic hormones were transported for considerable distances without significant biodegradation -- at concentrations frequently exceeded 1 ng/l. Cohen et al

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(2005) indicated that biogenic hormones half lives were on the order of 2 to 46 days in water and 2 days or less in soils.

It is not clear whether biogenic hormones leach into groundwater -- their chemical properties suggest they should not, but a few monitoring studies indicate a limited potential for migration.

## **3.2 Discharges from AFOs and Manure Applications**

Ciparis et al (2012) sampled 18 reaches of the Shenandoah river for biogenic hormones that were influenced by wastewater discharges and animal feeding operations (mostly poultry and cattle). Ciparis et al (2012) found a strong relationship between the watershed density of AFOs and higher concentrations of both nutrients and biogenic hormones. These trends were most pronounced during high flow events. In particular, higher estrogen levels were observed in reaches that had more than 1 AFO per thousand acres. By contrast, smaller WWTPs present in the Shenandoah river did not appear to have a strong influence on estrogen levels in the river.

Arikan et al (2008) conducted a detailed investigation of biogenic hormones and antibiotics at 15 subwatershed and 7 main-stem stations in the Choptank River in MD. The watershed was 62% agricultural, and included extensive poultry production. While the study detected biogenic hormones in some subwatersheds, they were more frequently below detection limits.

Several studies indicate that the two main agricultural sources of biogenic hormones are direct AFO discharges and manure applications to crops. Soto et al (2004) evaluated biogenic hormones in cattle feedlot effluent in eastern Nebraska over a three year period. Estrone was detected in every sample and represented over 46% of estrogenic activity.

Hanselman et al (2003) evaluated the risk that biogenic hormones could migrate from manure applied to crop lands. They concluded that the risk was low since most biogenic hormones have low aqueous solubility, are moderately hydrophobic, relatively non-volatile and have short half lives.

Finlay-Moore et al (2000) evaluated potential edge of field losses of biogenic hormones from poultry litter used to fertilize grasslands in Georgia. The research team found high initial losses of both estradiol and testosterone shortly after the litter was applied to the fields, but dropped back to background levels within 3 months. Salierno et al (2012) measured the biogenic hormones in poultry litter leachate from the eastern shore of MD. Estradiol and testosterone were frequently detected, as were arsenic and other metals used in feed additives.



### 3.3 Discharges from WWTPs, CSOs and Municipal Biosolids

Several recent reviews have looked at the capability of wastewater treatment processes to remove biogenic hormones (CDM, 2011 and Furlong et al 2012). Ogunlaja et al (2013) evaluated how well three different wastewater treatment processes were able to reduce estrogenicity. While conventional activated sludge and nitrifying activated sludge processes reduced estrogenicity by at least 80%, BNR was found to have the highest removal of all WWTP processes. Ogunlaja and Parker (2015) determined that the aerobic zones of the pilot BNR bioreactor were responsible for the majority of the removal of biogenic hormones.

Most of the major WWTPs in the Chesapeake Bay watershed have shifted to enhanced biological nutrient removal (BNR) in order to achieve nutrient reductions to comply with the Bay TMDL. These upgrades appear to have had the additional benefit of reducing biogenic hormones and overall estrogenicity in wastewater effluent by as much as 95% (Koh et al 2009, Li et al, 2011 and Ogunlaja et al, 2013).

Esperanza et al (2007) measured biogenic hormone removal from municipal wastewater treatment plants on the range of 80 to 99% for estrone and estradiol. The hormones were expected to partition to the solids generated during the wastewater treatment process. Bradley et al (2009) monitored biogenic hormones in three streams receiving wastewater effluent in Colorado and Iowa, and concluded that aerobic biodegradation within the streams was an important mechanism to remove biogenic hormones.

Phillips et al (2012) evaluated the significance of CSOs as a potential source of biogenic hormones to Lake Champlain in Burlington, VT. They concluded that untreated CSOs contributed 40 to 90% of a group of biogenic hormones to the lake, despite the fact that the CSO flow volumes represented only 10% of the total flows from the WWTP that were discharged to the lake.

A recent WERF study by Furlong et al (2010) examined the potential for biosolids to transport estrogenic compounds into the environment. They found that more than 90% of the compounds were removed during typical activated sludge treatment, and that concentrations of most (but not all) estrogenic compounds decreased through the wastewater treatment train. The stabilization process that reduced estrogenicity the most was aerobic digestion. High removals were also reported when anaerobic digestion was combined with biological processes, such as composting. Esperanza et al (2007) concluded that substantial estrogenicity may still occur in biosolids that are applied to crop lands, even if it is effectively removed from wastewater effluent.

## **3.4 Estimated Removal by Lagoons and Constructed Wetlands**

Most of the research on biogenic hormone removal has focused on treatment by constructed wetlands and lagoons at animal feeding operations.

Shappel et al (2007) evaluated the impact of a lagoon/constructed wetland system to treat swine wastewater from a CAFO located in the coastal plain in North Carolina. The facility had multiple cells, oxygenation and a residence time of 20 to 50 days. Overall, Shappel et al (2007) found that the facility had decreased estrogenic activity by 83 to 93%, with estrone the most persistent of the biogenic hormones.

Cai et al (2012) evaluated the impact of a constructed wetland in treating estrogen and androgens in dairy wastewater in Ireland. The constructed wetland, which had retention times of up to 100 days, was found to remove more than 92% of the estrogen and androgens in the dairy wastes. While these rates are high, they were not always able to achieve effluent concentrations below the levels of environmental concern established by the European Union.

Arnon et al (2008) used both monitoring and modeling data to evaluate the effect of clay-lined wastewater lagoons to treat dairy farm waste in Israel. Arnon et al (2008) discovered that estrogen and testosterone had migrated to a depth of 10 to 20 meters below the clay-lining of the wetland, and that they were accumulating over time.

Scheurer et al (2015) evaluated the impact of a retention soil filter (a form of constructed wetland with a long hydraulic retention time) in removing biogenic hormones delivered in combined sewer overflows in a German watershed. Scheurer et al (2015) reported that 94 to 98% of biogenic hormones were removed by the constructed wetland.

## **3.5 Other Biogenic Hormone Management Strategies**

The primary pollution prevention strategy is to keep unnecessary hormones out of the food supply chain. In recent years, many livestock producers, retailers and restaurant chains have adopted policies to eliminate the use of biogenic hormones in the meat, poultry and milk they purchase. It is not clear what the precise impact of these policies has been in keeping biogenic hormones out of the food supply chain, but it is a powerful reminder on how quickly social and market forces can change farm practices.

Fewer options exist to prevent human hormones from entering the wastewater treatment system, especially when they are concentrated into municipal biosolids that are subsequently applied to crops. Consequently, more research is needed on the best practices to (a) incorporate manure and biosolids into cropland soils that minimize losses of biogenic hormones by leaching and/or runoff (b) the potential for composting and other techniques to reduce hormones during the period where manure/biosolids are stored prior to land application.

## Section 4: Antibiotics

### 4.1 Background on Antibiotics

Antibiotics and other pharmaceuticals have become ubiquitous in the environment due to their increased use by individuals and in animal feed. The majority of antibiotics are excreted in human or livestock urine. Antibiotics are fairly persistent, hydrophilic and very soluble; consequently, they may not be effectively removed by conventional wastewater treatment plants. Antibiotics can be directly discharged to waterways by WWTPs (Jelic et al, 2011) and can also leach from manure or biosolids that are applied to crops (Deo and Halden, 2013).

The routine detection of antibiotics in receiving waters has prompted concerns they may increase bacteria resistance to these drugs that fight off infections, as well as potential harm to human health and aquatic life. The levels of most antibiotics in streams, groundwater and drinking water tend to be extremely low, and are many orders of magnitude below their therapeutic dose.

The Center for Disease Control recently evaluated the threat of antibiotic resistance in United States (CDC, 2013). Two of their main findings were that (1) data on antibiotic use in human health care and in agriculture are not systematically collected or tracked and (2) up to half of human antibiotic use, and most of the antibiotic use for livestock "is unnecessary, inappropriate, and makes everyone less safe" (CDC, 2013).

### 4.2 Discharges from AFOs and Manure Applications

Yang and Carlson (2003) sampled for the presence of antibiotics at five reaches in the Cache la Poudre River in Colorado, some of which were pristine and others that were influenced by wastewater and animal feeding operations. They did not detect antibiotics in the pristine reaches, but detected them in the reaches influenced by wastewater and animal feeding operations. While WWTPs were confirmed as a source of antibiotic discharge, they were also found to be very effective at removing antibiotics from effluent. Veterinary uses at animal feeding operations were found to be the most significant antibiotic source.

Arikan et al (2008) conducted a detailed investigation of antibiotics at 15 subwatershed and 7 main-stem stations in the Choptank River in MD. The watershed was 62% agricultural, and included extensive poultry production. Antibiotics were frequently detected at both river and subwatershed stations, which was attributed to application of poultry litter to croplands in the Choptank watershed.

Kay et al (2004) performed a soil plot experiment that showed that more antibiotics were lost in runoff (i.e., soluble) than in the particulate phase. As much as 0.4% of the mass of manure applied to cropland was lost after it rained shortly after the surface applications.

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Davis et al (2006) measured the loss of antibiotics in runoff and sediments from agricultural fields that received manure applications in Colorado. Crop BMPs that minimized erosion appeared to be effective in reducing antibiotic losses.

Underwood et al (2011) reported that antibiotics could impair the capability of bacteria to denitrify nitrates and nitrites in the soil layer, which is a critical process to remove nitrogen before it is delivered to the Chesapeake Bay. More specifically, Underwood et al (2011) reported that sulfamethoxazole (SMX) concentrations in aquatic environments as low as 1 µg/L could delay the start of cell growth, limit denitrification, and alter soil bacterial community composition. SMX is a sulfonamide antibiotic that is commonly used to treat a variety of bacterial infections. Barnes et al (2008) documented that SMX is frequently detected in the nation's streams and groundwater, and that wastewater treatment plants, septic tanks and livestock are its primary sources.

### **4.3 Discharges from WWTPs, CSOs and Municipal Biosolids**

The ability of WWTPs to remove antibiotics varies greatly depending on the treatment mechanism used to treat wastewater effluent and dispose of the sludge created as a result (Deo and Halden, 2013). Most removal WWTP strategies target the degradation or sorption of antibiotics (Jelic et al, 2011). The most effective WWTP treatment process appears to be activated carbon, with up to 90% removal of antibiotics reported. Yi et al (2009) presented data that antibiotic resistance bacteria increased as they traveled through a drinking water treatment and distribution system, although at very low levels. Pal et al (2010) notes the single greatest source of antibiotics are wastewaters derived from hospitals and other medical facilities.

The presence of antibiotics in urban streams is usually an indication of sewage contamination somewhere in the watershed (e.g., leaking sewers, combined sewer overflows, failing septic systems). Boyd et al (2004) detected antibiotics in stormwater canals and bayous in New Orleans, LA and noted that they were a useful marker of sewage contamination from this aging sewage system. Several urban BMPs are effective at finding and eliminating leaking sewers, most notably the discovery of nutrient discharges from grey infrastructure (NDGI EP, 2014).

### **4.4 Other Antibiotic Management Strategies**

In the last few years, the trend has been to phase out the use of antibiotics in poultry, swine and cattle feeding operations. Several livestock producers, grocery stores and restaurant chains are now selling meat, poultry and dairy products that are grown without antibiotics. One notable example was the 2014 announcement by Perdue that it was eliminating the use of antibiotics from all of its chicken products, and many other producers have followed suit. If these efforts to eliminate antibiotics from the food supply chain are adopted on a more widespread basis, it would represent an extremely effective strategy to reduce their impact on the environment.

Another key management strategy is to practice "antibiotic stewardship" to minimize the volume that are prescribed for humans and ensure that these pharmaceuticals are

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properly disposed (CDC, 2013). This may entail better outreach on the proper disposal of unused antibiotics and the creation of new drugs that are more rapidly degraded in the environment.

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## Appendix A: Key Properties of Herbicides Applied in the Chesapeake Bay

Several coefficients are used to assess the solubility, mobility and persistence of pesticides in the environment, as shown in Table A-1.

$K_H$  is Henry's law constant, and measures the partitioning of the compound between air and water. The higher the  $K_H$  value, the more likely that the pesticide will volatilize into the atmosphere.

$K_{oc}$  represents the soil organic carbon water partition coefficient, which describes how the pesticide partitions between water and organic matter in sediments or soil. Pesticides with a high  $K_{oc}$  are considered hydrophobic and have a strong affinity for sediments, whereas a low  $K_{oc}$  indicates they are hydrophilic and therefore more mobile in water.

The water solubility indicates how mobile the herbicide is, whereas the estimated half lives indicate how persistent they are in soil and water.

<b>Table A-1 Comparing the Properties of Common Agricultural Herbicides</b>					
Herbicide	log $K_{oc}$	log $K_H$	$S_w$ Water Solubility	Half-life soil	Half life water
UNITS	Log	log	mg/l	days	days
Atrazine	2.0	-3.54	30	146	742
Simazine	2.18	-3.46	5	91	32
Metoachlor	3.13	-2.63	430	26	410
Alachlor	2.8	-2.7	240	21	640
Glyphosate	3.1	nd	12,850	35	96
AMPA	Nd	nd	Nd	7-14	76-240
<b>Sources:</b> Gilliom et al (2006), Battaglin et al (2005) and Zhang et al (2014)					
nd = no data					