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Introduction

Unexplained fish kills have occurred in the North Fork of the Shenandoah River every spring since 2004. Smallmouth bass also have suppressed immune systems and males have immature eggs in their testes (intersex). In response to these fish health problems, the Friends of the North Fork sampled for trace organic chemicals in the river. Fifty-nine (59) manmade organic chemicals, including pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals, hormones, and caffeine were found in the North Fork. Samples were also evaluated for the presence of chemicals that imitate estrogen. That testing showed a high level of endocrine interference for the mixture of manmade chemicals found in our samples.

This paper presents information on the manmade organic chemicals we found in the river, the potential for them to be present in our drinking water and the impact they may have on the river and our health. Many questions remain as to the long term impacts of manmade organic chemicals in the river. By keeping the community informed, we seek to create and maintain a public dialogue on this emerging environmental issue.

BACKGROUND

In response to the seasonal fish kills throughout the Shenandoah River system, the Virginia Departments of Environmental Quality and Game and Inland Fisheries created the Shenandoah River Fish Kill Task Force. The Friends of the North Fork were placed on this Task Force. Determining the presence of manmade organic chemicals in the River was identified as a Task Force priority for several reasons. Studies of dead and dying fish indicated that their immune systems had been compromised. Manmade organic chemicals in the river can interfere with the effectiveness of fish immune systems. Additionally, nearly all male smallmouth bass in the North Fork have immature eggs in their testes (intersex). This condition has been linked to certain manmade organic chemicals that disrupt the normal functions of the endocrine system, which regulates hormones. With the presence of manmade organic chemicals implicated in both the fish kills and the intersex phenomenon, Friends set out to measure the level of manmade organic chemicals in the river during the spring and early summer when the kills have occurred. Our hypothesis was that there are chemical contaminants in the river that could contribute to autoimmune deficiency and endocrine disruption.

The Identified Manmade Organic Chemicals

In the spring of 2007, we deployed trace organic chemical samplers at two locations in the North Fork of the Shenandoah River¹. After the samplers were removed from the river, they were sent to a U. S. Geological Survey laboratory for analysis.

Fifty-nine manmade organic chemicals were identified in those samples:

Organic Chemicals in the North Fork of the Shenandoah River		
Herbicides	p,p-DDE	Pyrene
Atrazine	o,p-DDE	Chrysene
Simazine	Dieldrin	2-methylnaphthalene
Prometon	Endrin	1-methylnaphthalene
Desethylatrazine	cis-Nonachlor	1-ethylnaphthalene
Metolachlor	trans-Nonachlor	1,2-dimethylnaphthalene
Trifluralin	cis-Chlordane	2,3,5-trimethylnaphthalene
Hexachlorobenzene (HCB)	trans-Chlordane	1-methylfluorene
	Oxychlordane	dibenzothiophene
Insecticides	p,p-Methoxychlor	Perylene
cis-Permethrin	Heptachlor	2-methylphenanthrene
Trans-Permethrin		3,6-dimethylphenanthrene
Chlorpyrifos	Pharmaceuticals	
beta-Benzenehexachloride	Carbamazepine	Hormones
delta-Benzenehexachloride	Codeine	17a-Ethynylestradiol
Heptachlor Epoxide	Venlafaxine	
Endosufan-II		Other Chemicals
Endosulfan Sulfate	Polychlorinated Biphenyls (PCBs)	para-Cresol
p,p'-DDT		N,N-diethyltoluamide (DEET)
o,p'-DDT	Polycyclic Aromatic Hydrocarbons	Tri(2-chloroethyl)phosphate
p,p'-DDD	Acenaphthene	Tri(dichloroisopropyl)phosphate
o,p-DDD	Fluorene	Galaxolide
Carbaryl (Sevin)	Phenanthrene	Cholesterol
	Fluoranthene	Caffeine

¹ This monitoring program was carried out with financial support from the Virginia Environmental Endowment.

These chemicals come from a range of human activities and related chemical uses:

- **Herbicides** – These weed killers are used on crops common to the Shenandoah Valley, which are likely entering the river in runoff. The highest concentration for all the chemicals was for Atrazine, which is used on corn, soybeans and other crop fields.
- **Insecticides** – Several banned insecticides were found in the river, including DDT, dieldrin and endrin. These are likely present as residuals of earlier use, or as chemical by-products of similar chemicals that are still legal. Chlorpyrifos (currently used to control cutworms and other insects in corn) and Permethrin, which has many uses, including the control of insects in farm crops and the control of mites and lice on chickens were also present.
- **Pharmaceuticals** – A few common drugs were identified. Most samples contained Venlafaxine, an anti-depressant marketed under the name Effexor. Drugs are probably coming into the river through sewage treatment plants and septic systems as the result of their use by persons in the Valley.
- **Polychlorinated Biphenyls (PCBs)** – These are stable (persistent in the environment) chemicals that have been banned. Their presence is likely associated with past use.
- **Polycyclic Aromatic Hydrocarbons (PAHs)** – Most PAHs in the environment are from incomplete burning of carbon-containing materials like oil, wood, garbage or coal. Mothballs, blacktop, and creosote wood preservatives also contain PAHs. They are also found in some skin creams and anti-dandruff shampoos that contain coal tars..
- **Hormones** – One synthetic hormone used in oral contraceptives was identified. Like the pharmaceuticals, this hormone is likely coming from sewage treatment plants and septic systems, and is not fully removed during treatment.
- **Other Chemicals** – We found other indicators of human activity: the bug repellent DEET, caffeine, and two flame retardants, tri(dichloroisopropyl) phosphate and tri(2-chloroethyl) phosphate.

Because of the Task Force interest in the smallmouth bass intersex phenomenon, extracts from the samples were also evaluated for the presence of chemicals that imitate estrogen. That testing showed a high level of endocrine interference for the mixture of organic chemicals in our samples. To date, the fish kills and intersex in the Shenandoah River have not been attributed to any single cause. The United

State Geological Survey (USGS) continues to study the causes of these fish health problems and the role of manmade organic chemicals is still being evaluated in that context.

We should also note that many of the same chemicals have been found in the South Fork of the Shenandoah River and other parts of the Potomac River watershed.

When river water is used for drinking water supply, manmade organic chemicals are present in the raw water.

After we completed our study, we wondered if the chemicals that we found in the river might pass through the drinking water treatment systems and show up in home drinking water supplies. While no specific study has been done to relate Shenandoah River water contamination to the drinking water in the Valley, the USGS has completed a study of the raw water and treated drinking water for Washington DC. The USGS studied water withdrawn from the Potomac River, downstream of us, and used to produce drinking water for the greater DC area. USGS found 26 manmade organic chemicals in the raw water. Many were the same chemicals that we found in the North Fork, including five of the herbicides, one of the insecticides, the two flame retardants and three of the PAHs.

Conventional drinking water treatment does not remove all of the chemicals we found in the river.

In this same study, the USGS analyzed the finished drinking water to see if the DC drinking water treatment system was effective in removing these manmade organic chemicals. They found that certain types of manmade organics were not removed and were still present in the drinking water. In particular, certain of the herbicides and herbicide by-products remained in the drinking water at low levels, including Atrazine, Desethylatrazine, Metolachlor and Simazine, all of which were found in the North Fork during our study.

A number of communities in the Shenandoah Valley use river water to produce their drinking water. Others use well water. In particular, Woodstock, Strasburg, Broadway and Winchester use water from the North Fork. We wondered whether the same chemicals USGS found in the DC area drinking water may be present in

the drinking water of these communities. We contacted each town to find out what testing had been done and the results of that testing. Here is what we learned:

Winchester The town of Winchester provided us with testing reports for a range of chemicals. Of the five herbicides, we found in the river and USGS found in the drinking water, Winchester had test results from 2009 for three of them: Atrazine, Simazine and Metolachlor. Each was reported to be below the detection limit of their test method which was 0.5 parts per billion. This means that if they are present, they are present at levels below 0.5 parts per billion. For two of the three, EPA has set acceptable concentration limits and those limits were not exceeded. However, as discussed below, this does not mean these chemicals are not present in the water (they may be present at lower levels) and the EPA standards do not address all the potential effects of these chemicals. We should note that the Winchester documents do show detectible levels of Chloroform, Dibromomethane and Bromodichloromethane in their drinking water. The presence of these three chemicals is likely the by-product of the chlorination of the water which is done to control bacteria. These kinds of organics were also found in the DC drinking water. The potential impact of these chemicals is not the subject of this report which focuses on contaminants coming from the river water itself.

Woodstock The town of Woodstock provided us with a testing report for certain organic chemicals from 2009 and 2010. Of the five herbicides, we found in the river and USGS found in the drinking water, Woodstock had test results for three of them: Atrazine, Simazine and Metolachlor. Each was reported to be below the detection limit of their test method which was 0.5 parts per billion. This means that if they are present, they are present at levels below 0.5 parts per billion. For two of the three, EPA has set acceptable concentration limits and those limits were not exceeded. Like Winchester, they reported levels of Chloroform, Dibromochloromethane, and Bromodichloromethane that are likely by-products of chlorination.

Strasburg Strasburg provided us with a testing report specific to their testing for herbicides and similar compounds from early in 2010. Of the five herbicides, we found in the river and USGS found in the drinking water, Strasburg had test results for three of them: Atrazine, Simazine and Metolachlor. Each was reported to be below the detection limit of their test method which was 0.5 parts per billion. This means that if they are present, they are present at levels below 0.5 parts per billion.

Broadway The town of Broadway provided us with reports on testing done in 2009. Their report did not include test results for any of the five herbicides found by the USGS.

While the data that exist do not indicate the presence of herbicides in the finished drinking water from these towns, the methods used in the analyses, while good, are not as sensitive as the ones used by the USGS in their study of DC water where the chemicals were found at lower levels. For example, the detection limit of the method used by the towns for Atrazine was 0.5 parts per billion but the one used by USGS was 0.007 parts per billion. Only testing with the more sensitive methods will let one know if the findings in DC carry over to the Valley drinking water supply. Please note that our investigation and this paper focus on drinking water supplied from the river. We have not looked into drinking water systems that rely on well water. Given the geology of the valley, it is possible that the well water and river water have common interconnections underground and the same chemicals may be in some of the well water in the Valley.

There is growing concern that certain of these manmade organic chemicals, even at very low levels, are harmful to human and animal health.

EPA has established drinking water standards for a few of the 59 organic chemicals that we found in the river and USGS found in the raw water and drinking water in DC but the existing standards are limited in two ways:

Current drinking water standards do not reflect an adequate understanding of the impact of these chemicals on our endocrine and immune systems.

Accordingly, in April of 2009, US EPA launched an investigation of the effect of some of these chemicals on our endocrine and hormonal systems. Producers of 67 chemicals have been ordered to test their chemicals for hormone system (endocrine) effects. The list focused on pesticides with the greatest potential for human exposure. On that list are five chemicals we found in the river; Atrazine, Endosulfan, Metalochlor, Simazine and Trifluralin. And three of these five were found in the drinking water system in DC. EPA officials have said this work is significant, long overdue and necessary to assuring the safety of these chemicals in our environment and in our bodies. These studies are the necessary starting point for setting drinking water standards that address these kinds of effects.

The importance these chemicals may have for our health is reflected in the testimony at a recent Congressional hearing. In testimony before Congress, the Director of the National Institute of Environmental Health Sciences at the US Department of Health and Human Services made the following statement:

“The detection of numerous pharmaceutical agents and chemicals with endocrine disruption potential in surface waters around the country has raised concern about drinking water as a significant route of exposure.”

The Director went on to say:

- Endocrine disruption can occur at very low exposures;
- There can be a wide range of effects, including cancer, reproductive; problems, immune suppression, developmental problems and diabetes;
- The effects can occur long after the actual exposure; and
- Human exposure to the chemicals in question is widespread.

Current drinking water standards do not address the cumulative effect of the multiple chemicals that may be present in drinking water. In the USGS report on the drinking water system for DC, the agency said:

“An important consideration in assessing the potential effects for human health is the common occurrence of mixtures of organic compounds... The potential human-health effects of mixtures of co-occurring organic compounds are largely unknown and have not been extensively studied. The effect of one compound on another’s toxicity may be additive, antagonistic or synergistic. ... Continued research is needed ... human-health benchmarks generally are based on toxicity data for individual compounds, and the effects of specific mixtures of compounds at low levels are not well understood.”

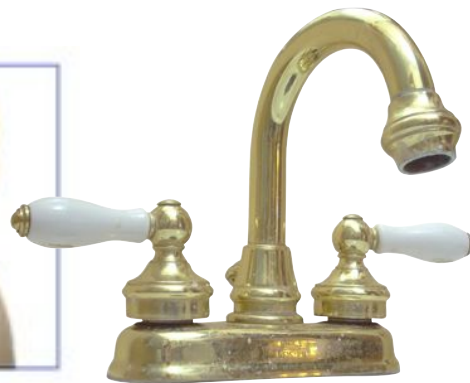
In this context, the US Department of Health and Human Services has announced a new set of studies on the impact of the mixtures of chemicals that occur in drinking water on prenatal and postnatal child development.

Characterizing the presence of these chemicals in our environment and the effects they are having needs to be a high priority for our communities.

Investigating and understanding of the role that these manmade organic chemicals have in the river and on our community is a priority for the Friends of the North Folk. We are advocating at the Federal, State and Local levels for better monitoring of their presence in the river and the water supplies of the Valley. We are advocating for more research into their effects on wildlife and human health. We will continue to inform our members and the public through postings on our website. We ask that you join us in this effort.

There are things you can do:

- Support actions at the local, state and national level to reduce the use of pesticides by farmers and lawn care professionals and support programs to prevent the runoff of these chemicals into the river
- Ask the US EPA to research the effects of low level manmade chemicals in our water
- Ask EPA to reconsider the current drinking water standards so that our drinking water suppliers know what standards must be met to provide healthy water to all of us.
- Ask your drinking water supplier to test periodically for manmade chemicals using methods with the lowest possible detection limits and share the findings with their customers.
- Take action in your own life to keep manmade chemicals out of the river:
- Avoid using anti-microbial cleaners and soaps or harsh chemicals around the house. Even though they may go to a sewage treatment plant, some residuals can end up in the river.
- Support drug take back programs by manufacturers and pharmacies. Dispose of unused drugs and chemicals properly rather than flushing them down the toilet
- Reduce the use of herbicides and other pesticides in your yard
- Consider home treatment of your drinking water to remove manmade chemicals
- Become an active member of the Friends of the North Fork!



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