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Assessment of Potential Interferences and Technical Strategies to Minimize False Positive Bias in Analytical Testing for Organochlorine Pesticides Dieldrin, Endrin, and DDT in River Water Samples

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Abstract

Aldrin, Dieldrin, Endrin, Endrin Ketone, Endrin Aldehyde and DDT and its isomers are organochlorine pesticides (OCPs) widely used as pesticides between the 1950s and 1970s when concerns about toxicity and persistence in the environment resulted in regulatory bans. Residual concentrations of OCPs in soils, groundwater and agricultural runoff continue to contaminate surface water largely from soil erosion. This paper investigates ambient background of OCPs in the Atibaia River in Sao Paulo, Brazil where detections of OCPs (banned in 1985) became more frequent with the introduction of lower detection limit methods in 2021. This study investigates why OCPs were detected more frequently decades after agricultural application. Although reliable for pesticides analysis, USEPA Method 8081 (dual column GC/ECD) can be prone to interferences, particularly at low levels. The purpose of the investigation presented in this paper was to determine if other substances in the river water could bias the detection of organochlorine pesticides at low concentrations near the method detection limit. Analysis of the laboratory surface water data suggests detections of these OCPs at very low levels near the method detection limit are potentially caused by non-target analyte (NTA) interferences associated with other natural and anthropogenic substances that may result in false positives and positive bias. This paper recommends several possible mod-

ifications to the analytical method that could minimize this bias in samples collected during future sampling campaigns.

Keywords

Organochlorine Pesticides, Dieldrin, Endrin, DDT, EPA Method 8081, Chromatography, Surface Water Quality

1. Introduction

Aldrin, Dieldrin, Endrin, Endrin Ketone, Endrin Aldehyde, and DDT isomers (selected OCPs) were widely used as pesticides between the 1950s and 1970s [1]. Concerns about toxicity, persistence, and bioaccumulation of OCPs motivated bans in various locations around the world [2]. OCPs have high carbon/water partition coefficients, high hydrophobicity, strong affinity for organic matter, and rapid sorption kinetics with soil particulates. Residual concentrations of OCPs are commonly found in soils and groundwater at sites where pesticides have been formulated and stored and from agricultural runoff where soil erosion facilitates migration into proximal surface water bodies.

Table 1. Laboratory reporting limits pre- and post-2021 and regulatory limits.

	Pre-2021 Laboratory Reporting Limits, µg/L	Post-2021 Laboratory Reporting Limits, µg/L	Surface Water Regulatory Limits, CONAMA 357, µg/L
Dieldrin	0.01	0.001	0.005
Endrin	0.01	0.004	0.004
DDT	0.01	0.001	0.002

Figure 1. River water sample collection and packaging, February 2023.

This study examines ambient background of OCPs (specifically Dieldrin, Endrin, and DDT) in water samples collected from the Atibaia River in Sao Paulo, Brazil. Regular monitoring of the Atibaia River water quality demonstrated little to no historical OCP detections for several years [3]. Starting in 2021, the laboratory adopted more modern instrumentation and detectors for water analysis using EPA Method 8081B [4] for quantification of OCPs at lower reporting limits in order to comply with the regulatory surface water quality criteria (**Table 1**). The conventional quantification limits were reduced from 0.010 µg/L to 0.001 µg/L for Aldrin, Dieldrin and DDT and to 0.004 µg/L for Endrin. The lower detection limit method resulted in more frequent trace detections for OCPs among the surface water samples and motivated this study.

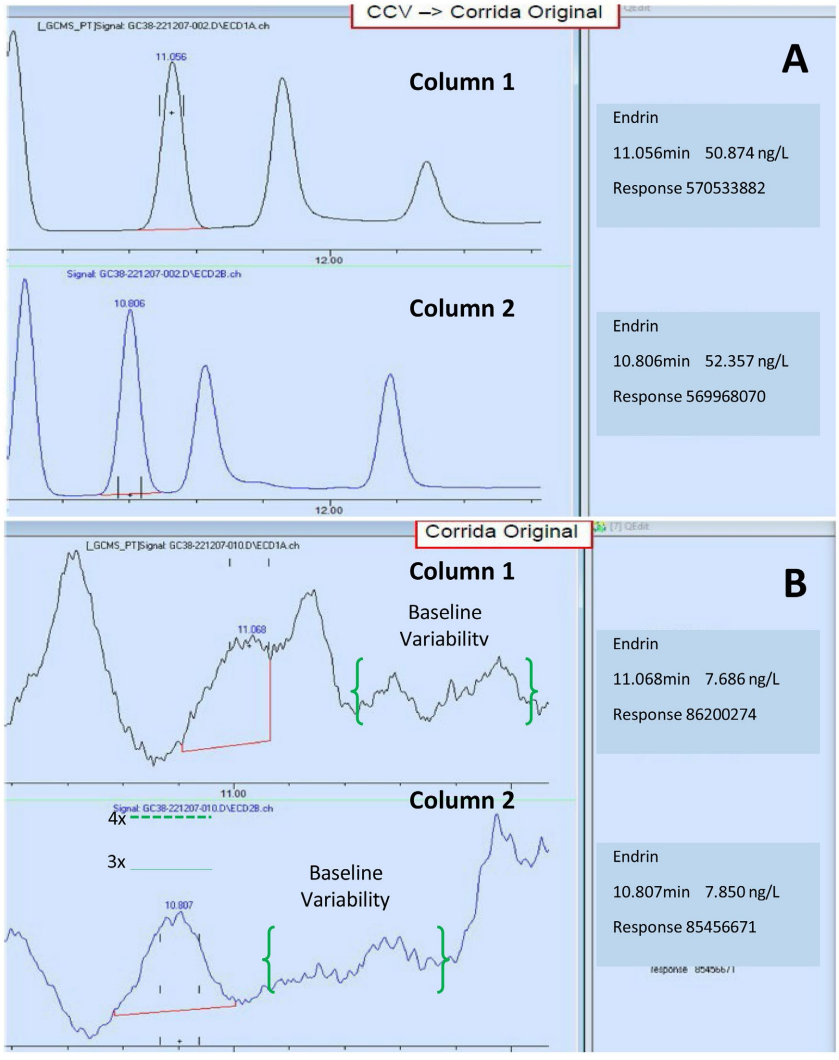


Figure 2. Lab 1 raw data displaying GC/ECD dual column analysis. A) Calibration standard for Endrin. B) Laboratory identification of low levels of Endrin in a river water sample.

The Atibaia River basin drains an area of 2837.3 km^2 with the total population of the river basin of approximately 370,000 inhabitants [5]. The 7Q10 minimum

flow of this river is 902,016 m^3/d [5] with peak flows approaching 23,000,000 m^3/d after heavy rainfall [6]. The river basin supports a wide range of land uses ranging from relatively pristine natural environments to extremely urbanized areas, including industrial and agricultural land use [7]. Runoff and the high energy flow readily erodes soil and resuspends sediment, giving the surface water a "muddy" appearance with high suspended solids (**Figure 1(A-B)**). Preliminary inspection of the raw laboratory instrument data files from the 2022 sampling results (**Figure 2**) indicated a noisy chromatographic baseline that suggested the possible presence of non-pesticide interferences associated with chemicals in the resuspended river particles that recently became more apparent when the detection limits were lowered. In order to be considered a positive match**,** the peak of interest needs to be 3 - 5 times above the fluctuation of the instrument detector**,** which is referred to as the baseline variability of the instrument. The peak identified as Endrin on both columns is <3x the baseline noise (**Figure 2**). In addition, Endrin on Column 1 appears as a shoulder**,** indicating a possible matrix interference. Although reliable, Method 8081B can be prone to interferences, particularly at low levels, even when the laboratory conducts the analyses using commonly used standard processes [4].

The purpose of this study was to determine if substances in the river water could positively bias the detection of organochlorine pesticides at low concentrations.

2. Materials and Methods

A series of scientific experiments were designed to evaluate whether a matrix interference, present in the water and suspended particles (referred to herein as particulates), potentially creates increased and false positive pesticide detections. Water samples were collected from three locations in Rio Atibaia within the region of Campinas, Brasil.

- Sample AT01 located upstream.
- Sample AT07 located approximately 3 km downstream of AT-01.
- Sample AT09 located approximately 6.5 km downstream of AT07.

The river samples were collected on 6th February 2023 **(Figure 1),** and the samples were sent via courier to two separate laboratories for confirmatory pesticide analysis using multiple methods. The water samples were analyzed using a certified in-country laboratory (Lab 1), and split samples were collected by an additional external forensic laboratory (Lab 2).

The following procedure was performed by Lab 1 on the river water samples from each location:

- Extract the whole water (including that native mixture of water and particulates) without filtering. Concentrate the extract, perform florisil cleanup step (EPA Method 3620 [8]), and analyze sample extracts by EPA Method 8081 [4].
- Pass water through a 0.22 μm filter, extract the water and archive the filtered particulates. Concentrate, perform a florisil cleanup step [8], and analyze water sample extracts by EPA Method 8081 [4].

• Pass water through a 0.45 µm filter, extract the water, and archive the filtered particulates. Concentrate, perform a florisil cleanup step [8] and analyze water sample extracts by EPA Method 8081 [4].

All samples arrived at both laboratories intact and in good condition between 2˚ and 6˚C. Water samples were analyzed for organochlorine pesticides (**Table 2**) by EPA Method 8081B [4] by both laboratories; additionally, after passing the water samples through a 0.7 µm filter, the particulate matter from the filtrate was analyzed by Lab 2. The reporting limits achieved by the laboratories are presented (**Table 3**).

Table 2. Sample list.

River Water Sample ID	Lab	Analysis Performed				
		EPA Method 8081B (unfiltered water)	EPA Method 8081B (filtered 0.7 µm water)	EPA Method 8081B (particulate)	EPA Method 8081B (filtered 0.22 µm water)	EPA Method 8081B (filtered 0.45 µm water)
AT01	Lab 1	X		-	X	X
AT07	Lab 1	X		-	X	X
AT09	Lab 1	X		-	X	X
AT01	Lab 2	X	X	X	-	-
AT07	Lab 2	X	X	X	-	-
AT09	Lab 2	X	X	X	-	-

Table 3. Target compounds and reporting limits.

Pesticide	Reporting Limits		
	Lab 1 Water, µg/L	Lab 2 Water µg/L	Lab 2 Particulate µg/kg
Aldrin	0.001	0.0008	0.22
Dieldrin	0.001	0.00047	0.22
Endrin	0.004	0.00047	0.22
Endrin Aldehyde	0.010	0.00047	0.658
Endrin Ketone	0.010	0.00047	0.22
4,4'-DDT	0.001	0.00047	0.22

The capillary column configuration used by Lab 1 included a guard column (Agilent J & W DB-1 100% Dimethylpolysiloxane with length 2 m, diameter 0.53 mm, and film thickness 0.1 µm). Lab 1's primary column was Agilent J & W DB-35 MS 35%-Phenyl]-methyl polysiloxane with length 30 m × inner diameter 0.53 mm film thickness 1.0 µm. Its secondary column was Agilent J & W DB-5 with length 30 m × inner diameter 0.53 mm × film thickness 1.50 µm. The initial calibration curve acceptance criteria were $R^2 > 0.99$ or RSD < 20% depending on the analytes. Target analytes were quantified by external calibration factors. The quantitation limit was the sample equivalent of the lowest initial calibration stand-

ard.

The objective for Lab 2 was to analyze the particulate and dissolved water fractions as separate fractions to determine the contributions of each fraction to the total target analyte concentrations and NTA interferences, if detected. The water and particulates were separated by passing the water through a 0.7 μm filter and extracting each separately. Laboratory chemists fortified the water samples with surrogates to monitor extraction efficiency and were solvent-extracted at a neutral pH by EPA Method 3510 [9]. The filtered particulates (and filter paper) were fortified with surrogates and extracted by EPA Method 3570 [10]. The extracts were concentrated, cleaned using activated copper (EPA method 3660 [11]) and silica gel (EPA Method 3630 [12]), and spiked with internal standards. The water and particulate extracts were analyzed EPA Method 8081 [4] and reported separately.

Lab 2 utilized a deactivated fuse silica phenyl-methyl, 5 m × 0.32 mm ID Restek Guard Column followed by a RTX-5 Stationary Phase, 60 m length × 0.25 mm ID, 0.25 mm film thickness column. Its confirmatory column was RTX-CL Pesticide II Stationary Phase, 60 m length × 0.25 mm ID, 0.2 mm film thickness confirmation column. The calibration standard concentrations ranged from 0.5 μg/L to 200 μg/L and produced response factors with less than 20% relative standard deviation (RSD) acceptance criteria. Samples were quantified using average response factors, and analyte concentrations were determined versus internal standards, which were added prior to analysis.

3. Results and Discussion

The water samples analyzed by Lab 1 contained no detectable pesticides above the reporting limit for whole water and filtered water samples from all locations (**Table 4**). The raw instrument data exhibited a variable baseline with many peaks eluting near the target analytes (**Figure 3**). Lab 1 GC/ECD pesticide chromatogram for AT07 whole water includes particulate and dissolved fractions (**Figure 3(A)**), and the filtered water passing through a 0.22 μm filter represents the dissolved fraction only (**Figure 3(B)**). The unfiltered water (**Figure 3(A)**) exhibited significantly more peaks than the filtered water (**Figure 3(B)**). This observation demonstrated that filtration helped remove significant interferences associated with suspended particulates. However, filtering did not eliminate all of the interferences. The remaining peaks (**Figure 3(B)**) are associated with interferences in the dissolved fraction. Little difference was observed between the level of interferences observed in the water filtered through the 0.22 and 0.45 μm filters. This observation demonstrated that either the 0.22 or 0.45 μm filters effectively reduced the particulate interferences, while allowing the dissolved phase interferences to remain in the filtered water sample. The variable baseline in the unfiltered and filtered samples indicated the presence of complex particulate-phase and dissolved-phase organics commonly observed in urban water samples [13] [14]. This same trend showing variable baseline in the unfiltered and filtered reduction also appears in AT01 and AT09 (**Figure 4**).

Table 4. Lab 1 analytical results whole water and filtered water samples from all locations.

Sample Name	AT-01								
	AT-01 (not filtered)			AT-01 (filtered 0.22 um)			AT-01 (filtered 0.45 um)		
Lab ID	213978/2022.1 - 0			213978/2022.2 - 0			213978/2022.3 - 0		
Matrix	Águas Acreditado			Águas Acreditado			Águas Acreditado		
Matrix Description	Água Superficial			Água Superficial			Água Superficial		
Reference Method	8081B			8081B			8081B		
Date Collected	Feb 6, 2023			Feb 6, 2023			Feb 6, 2023		
Units	µg/L			µg/L			µg/L		
Analyte	Result	RL	DL	Result	RL	DL	Result	RL	DL
Aldrin	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
4,4'-DDE	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Dieldrin	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin	<0.004	0	0.00133	<0.004	0	0.00133	<0.004	0	0.00133
4,4'-DDD	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin aldehyde	<0.01	0.01	0.00333	<0.01	0.01	0.00333	<0.01	0.01	0.00333
4,4'-DDT	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin ketone	<0.01	0.01	0.00333	<0.01	0.01	0.00333	<0.01	0.01	0.00333
Surrogates (% Recovery)									
Tetrachloro-m-xylene	41.2			37.5			34.8		
Decachlorobiphenyl	61.5			60			60.3		
Tetrachloro-m-xylene	41.2			37.5			34.8		
Decachlorobiphenyl	61.5			60			60.3		
Sample Name	AT-07								
	AT-07 (not filtered)			AT-07 (filtered 0.22 um)			AT-07 (filtered 0.45 um)		
Lab ID	213979/2022.1 - 0			213979/2022.2 - 0			213979/2022.3 - 0		
Matrix	Águas Acreditado			Águas Acreditado			Águas Acreditado		
Matrix Description	Água Superficial			Água Superficial			Água Superficial		
Reference Method	8081B			8081B			8081B		
Date Collected	Feb 6, 2023			Feb 6, 2023			Feb 6, 2023		
Units	µg/L			µg/L			µg/L		
Analyte	Result	RL	DL	Result	RL	DL	Result	RL	DL
Aldrin	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
4,4'-DDE	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Dieldrin	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin	<0.004	0	0.00133	<0.004	0	0.00133	<0.004	0	0.00133
4,4'-DDD	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033

Continued

Endrin aldehyde	<0.01	0.01	0.00333	<0.01	0.01	0.00333	<0.01	0.01	0.00333
4,4'-DDT	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin ketone	<0.01	0.01	0.00333	<0.01	0.01	0.00333	<0.01	0.01	0.00333
Surrogates (% Recovery)									
Tetrachloro-m-xylene	39.1			34.8			36.8		
Decachlorobiphenyl	62.4			54.9			56.7		
Tetrachloro-m-xylene	39.1			34.8			36.8		
Decachlorobiphenyl	62.4			54.9			56.7		
Sample Name	AT-09								
	AT-09 (not filtered)			AT-09 (filtered 0.22 um)			AT-09 (filtered 0.45 um)		
Lab ID	213980/2022.1 - 0			213980/2022.2 - 0			213980/2022.3 - 0		
Matrix	Águas Acreditado			Águas Acreditado			Águas Acreditado		
Matrix Description	Água Superficial			Água Superficial			Água Superficial		
Reference Method	8081B			8081B			8081B		
Date Collected	Feb 6, 2023			Feb 6, 2023			Feb 6, 2023		
Units	µg/L			µg/L			µg/L		
Analyte	Result	RL	DL	Result	RL	DL	Result	RL	DL
Aldrin	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
4,4'-DDE	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Dieldrin	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin	<0.004	0	0.00133	<0.004	0	0.00133	<0.004	0	0.00133
4,4'-DDD	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin aldehyde	<0.01	0.01	0.00333	<0.01	0.01	0.00333	<0.01	0.01	0.00333
4,4'-DDT	<0.001	0	0.00033	<0.001	0	0.00033	<0.001	0	0.00033
Endrin ketone	<0.01	0.01	0.00333	<0.01	0.01	0.00333	<0.01	0.01	0.00333
Surrogates (% Recovery)									
Tetrachloro-m-xylene	34.8			44.7			39.3		
Decachlorobiphenyl	55.8			56.2			53.8		
Tetrachloro-m-xylene	34.8			44.7			39.3		
Decachlorobiphenyl	55.8			56.2			53.8		

Lab 1 instrument chromatograms (column 1 and column 2) (**Figure 4**) for the retention time in the whole water (unfiltered) and filtered samples from all three sample locations for Dieldrin. The double vertical lines and shaded bars indicate the expected target analyte retention times based on the calibration standard. The symbol (*) identifies NTAs that co-elute with target analytes based on the retention time shifts, and the absence of these target analytes at the Method Detection Limit (MDL) in confirmation runs on a GC equipped with a mass spectrometer

(GC/MS). A similar behavior is observed for Endrin (Figure 5). These data demonstrate that baseline variability is caused by non-target analytes (*i.e.*, interferences) in the particulate-phase and dissolved-phase organics in the river samples, regardless of the location and filtering.

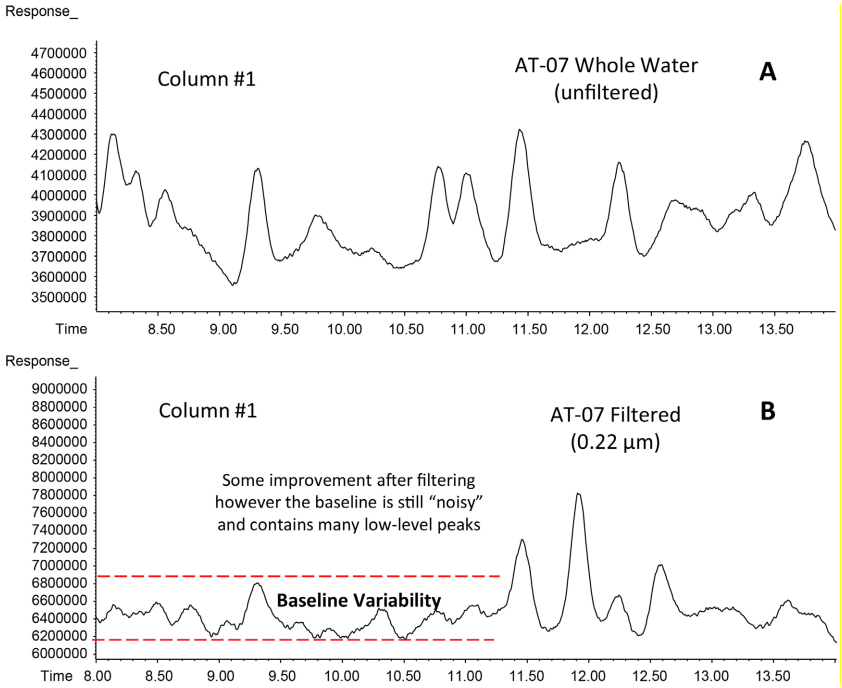


Figure 3. In-country laboratory GC/ECD pesticide chromatogram for AT07 whole water includes particulate and dissolved fractions (A) and filtered water passing through a 0.22 µm filter represents the dissolved fraction only (B).

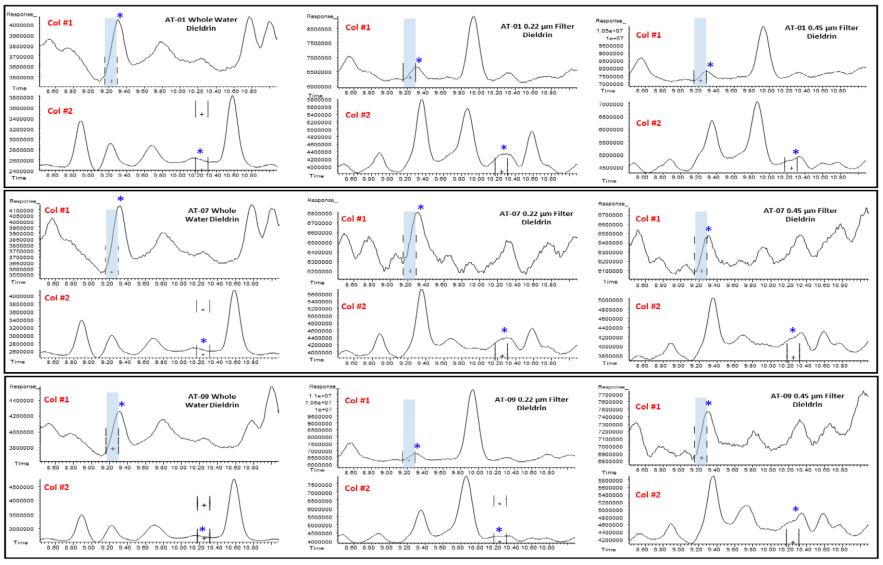


Figure 4. Lab 1 GC/ECD pesticide chromatogram for AT01, AT07, and AT09 whole and filtered water samples. Double vertical lines and blue shaded rectangle depict the expected retention time for Dieldrin based on the calibration standard. The (*) identifies possible interferences.

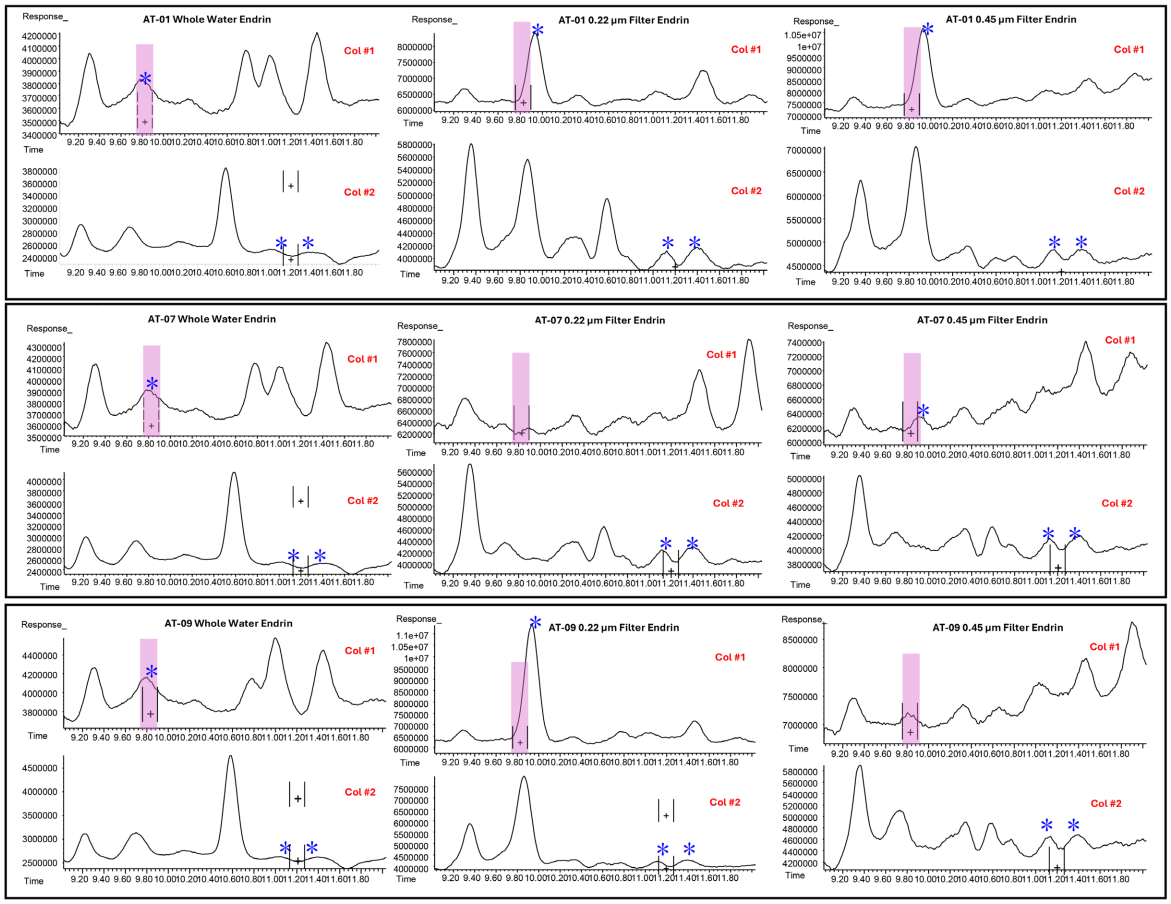


Figure 5. Lab 1 GC/ECD pesticide chromatogram for AT01, AT07, and AT09 whole and filtered water samples for Endrin. Double vertical lines and purple shaded rectangle depict the expected retention time for Endrin based on the calibration standard. The (*) identifies possible interferences.

Lab 2 confirmed that no river samples contained pesticides above the reporting limit in both the particulate and dissolved fractions (**Table 5**). In this case, Lab 2 analyzed the water and particulate portion separately, which resulted in different reporting units for the particulates (0.22 µg/kg) and dissolved water (0.00047 µg/L) samples due to differing samples sizes (~1 g particulate and ~1000 mL water). These data complemented the Lab 1 results by directly comparing the particulate and dissolved fractions in separate extracts.

The Lab 2 raw instrument data file for dual column GC/ECD were analyzed with the calibration spike to estimate the magnitude of the false positive bias due to the baseline variability (**Figure 6**, **Figure 7**, **Figure 8**). **Figures 4-5** are an example of a matrix interference at low level detection for the AT07 water (**Figure 6**) and associated particulates (**Figure 7**). Although Endrin met retention criteria, the peak is shifted to the left on column #1 and to the right on column #2 of the calibration standard, as shown in **Figures 4-5**. This indicates the peak chosen as Endrin was an interferent compound.

Figure 8 showed interference for 4,4'-DDT in the water associated with sample AT01. The peak chosen for 4,4'-DDT matches on column #1, however the peak is

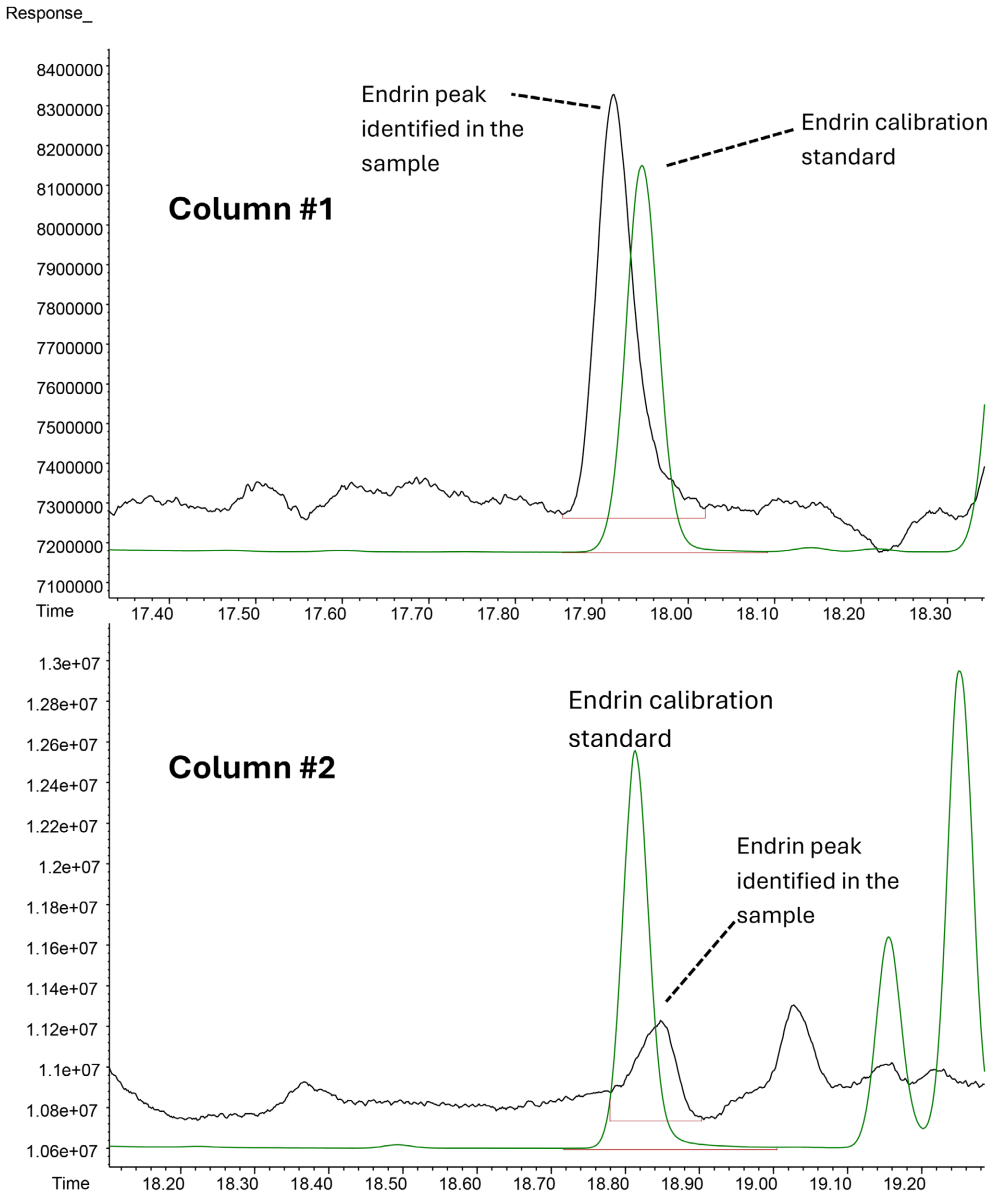
shifted to left on the confirmation column #2, indicating a possible interference is present at low levels and not verifying the column #1 match. 4,4'-DDT was not detected in the associated AT01 sample's particulates (Table 5).

Table 5. Lab 2 Analytical Results particulate and dissolved fractions samples from all locations. RL = Reporting Limit.

Sample Name	AT-01		AT-01_SOLID		AT-07		AT-07_SOLID		AT-09		AT-09_SOLID	
Lab ID	L2306975-01		L2306975-02		L2306975-03		L2306975-04		L2306975-05		L2306975-06	
Matrix	Water		Solid		Water		Solid		Water		Solid	
Matrix Description	Dissolved Fraction		Particulate Fraction		Dissolved Fraction		Particulate Fraction		Dissolved Fraction		Particulate Fraction	
Reference Method	8081B		8081B		8081B		8081B		8081B		8081B	
Date Collected	Feb 6, 2023		Feb 6, 2023		Feb 6, 2023		Feb 6, 2023		Feb 6, 2023		Feb 6, 2023	
Units	µg/L		ug/kg		µg/L		ug/kg		µg/L		ug/kg	
Analytes	Result	RL	Result	RL	Result	RL	Result	RL	Result	RL	Result	RL
Aldrin	U	0.0008	U	0.21	U	0.0008	U	0.22	U	0.0008	U	0.23
2,4'-DDE	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
4,4'-DDE	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
Dieldrin	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
2,4'-DDD	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
Endrin	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
4,4'-DDD	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
2,4'-DDT	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
Endrin Aldehyde	U	0.0005	U	0.64	U	0.0005	U	0.65	U	0.0005	U	0.69
4,4'-DDT	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
Endrin Ketone	U	0.0005	U	0.21	U	0.0005	U	0.22	U	0.0005	U	0.23
Surrogates (% Recovery)												
Tetrachloro-Meta-Xylene	70		71		66		69		64		68	
Decachlorobiphenyl	44		57		44		53		41		52	
Tetrachloro-Meta-Xylene	63		64		62		65		58		67	
Decachlorobiphenyl	50		66		51		63		50		60	

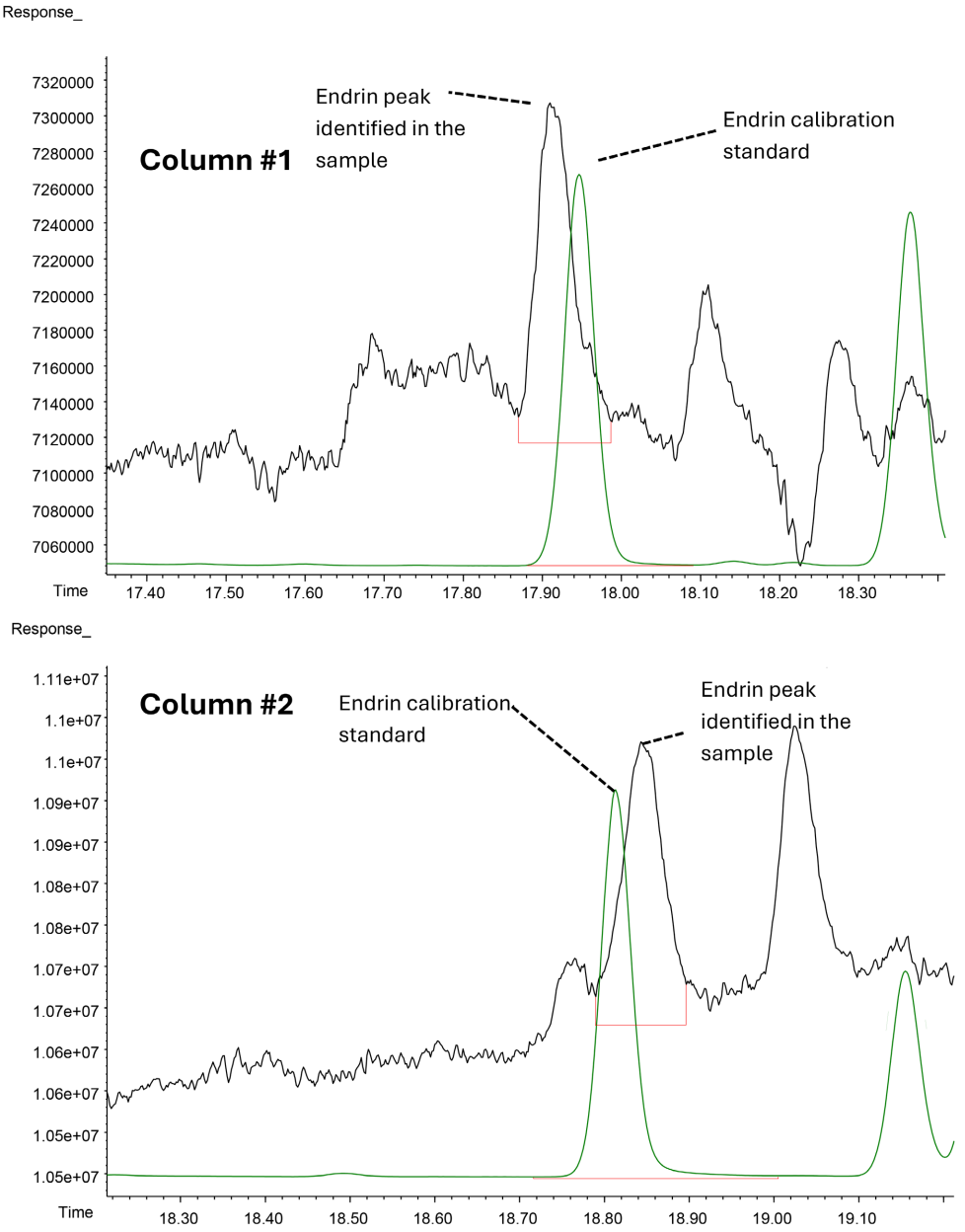
Further interferences examples can be found (Figure 9), which depicts the Lab 2 raw instrument chromatograms (column 1 and column 2) for the retention time of Endrin in the filtered water and filtered particulate samples from all three river

sampling locations. The double vertical lines on Figure 9 chromatograms indicate Endrin's expected retention time based on the calibration standard. The red lines are the integration boundaries for the non-target interference peak used to estimate the magnitude of the false positive bias. The symbol (*) identifies potential interferences with a target analyte, Endrin. Regardless of the location and whether the samples represent dissolved phase or particulates, the baseline variability indicates the presence of unidentified organic substances at low levels.



Note the peak chosen for Endrin (although meets retention criteria) is shifted to left on column #1 and to the right on column #2 indicating a possible interference present at low levels. The green lines are raw instrument data for dual column GC/ECD for the Endrin calibration standard. The red lines are the integration boundaries for a peak eluting with-in the retention time window of the target analytes.

Figure 6. Lab 2 raw instrument data for dual column GC/ECD for the water associated with AT07.



Note similar to the water (Figure 6) the peak chosen for Endrin (although meets retention criteria) is shifted to left on column #1 and to the right on column #2 indicating a possible interference present at low levels. The green lines are raw instrument data for dual column GC/ECD for the Endrin calibration standard. The red lines are the integration boundaries for a peak eluting within the retention time window of the target analytes.

Figure 7. Lab 2 raw instrument data for dual column GC/ECD for the particulates associated with AT07.

Lab 2 data were reintegrated, combining water and particulates in the associated water, to recalculate pesticide concentrations on a µg/L basis by using the associated water sample size (1.05 L), which is reported for each sample location (Table 6). On Table 6, analytes shaded in blue exhibited noisy chromatographic baselines signifying matrix interference as shown in Figures 4-9. To be clear, these

data (Table 6) are not detected pesticides; but rather, an estimate of the magnitude of the combined interfering peak in the particulate and dissolved samples. This procedure differs from Lab 2's standard operating procedure (SOP) because it integrates peaks that are below the detection limit to make this evaluation of potential interferences at low levels. Based on the combined particulate and water results, sample AT07 would have reported 4,4'-DDT (0.00058 µg/L) and sample AT09 would have reported Endrin (0.00055 µg/L), all above the reporting limit (Table 2); however, as discussed, these concentrations are positively biased by the presence of NTA interferences. This observation strongly suggests the need for careful inspection of the peak retention time and baseline variability if low level detections occur.

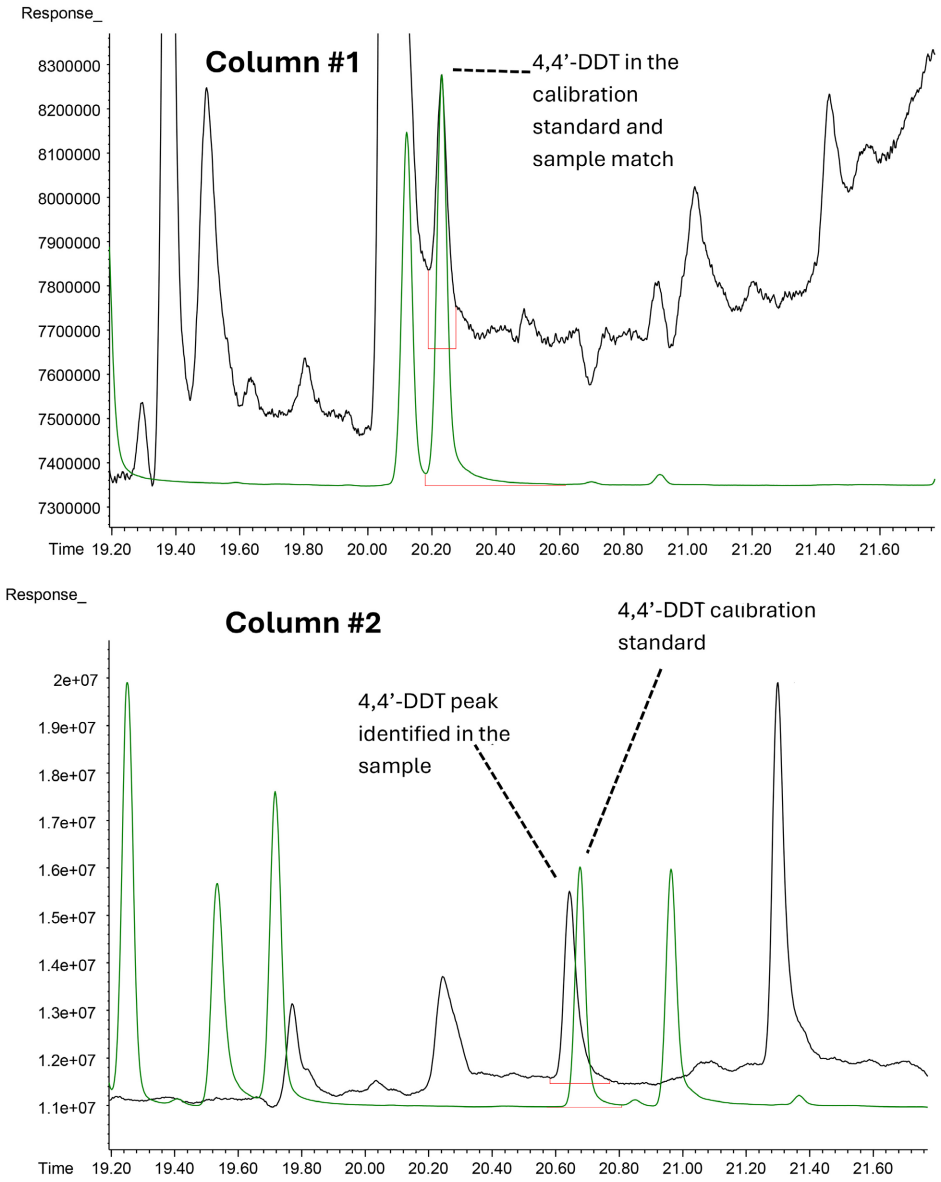
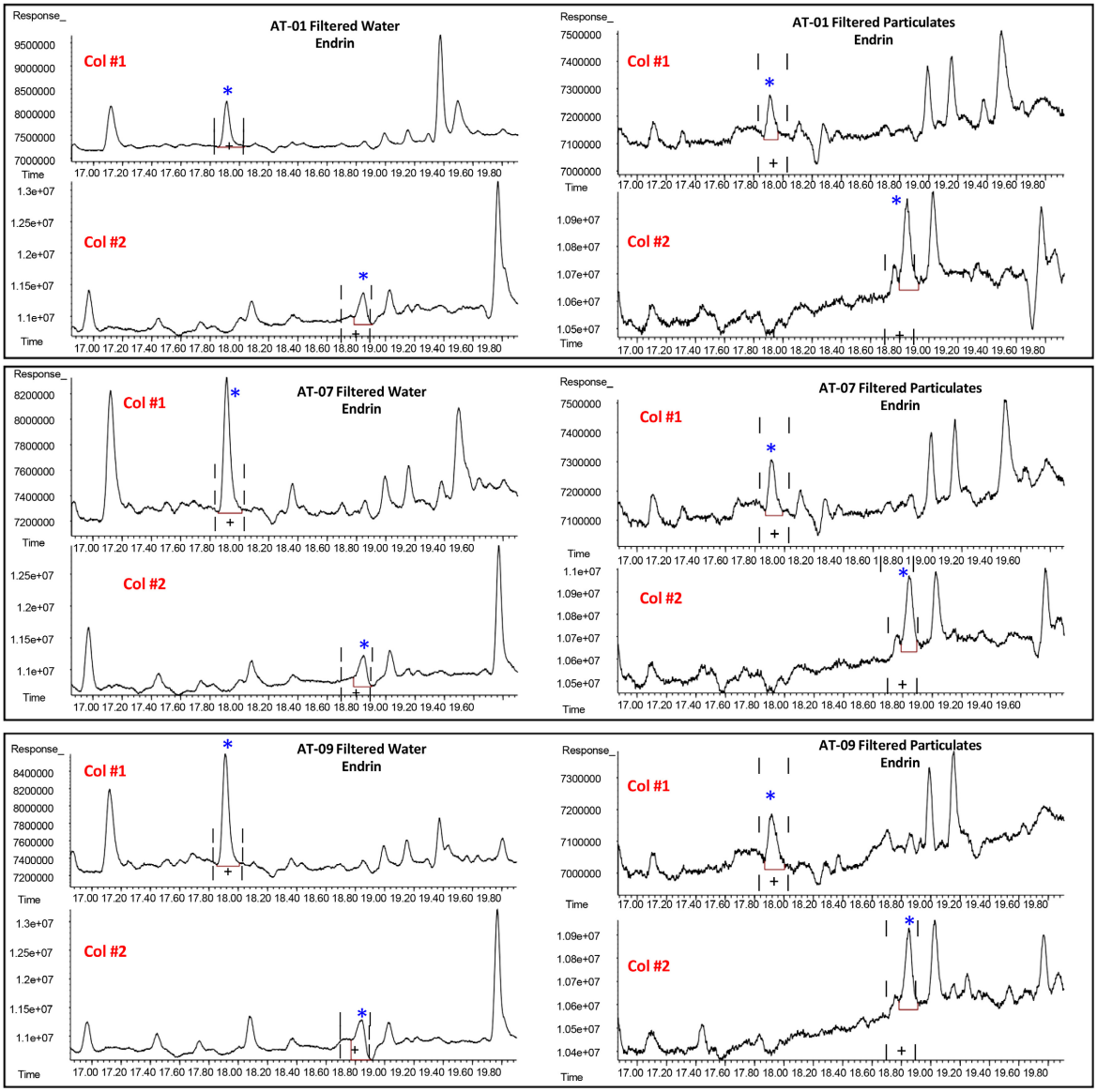


Figure 8. Example of Lab 2 raw instrument data for dual column GC/ECD for the water associated with sample AT01.



Note Double vertical lines depict the expected retention time for Endrin based on the calibration standard. The (*) identifies possible interferences.

Figure 9. Lab 2 GC/ECD pesticide chromatogram for AT-01, AT-07, and AT-09 filtered water (left, dissolved fraction) and filtered water (right, particulate fraction).

Table 6. Low level interferences observed for selected pesticides in reintegrated dissolved water and particulate samples below the reporting limit at lab 2 (reference method 8081B).

Sample	AT01		AT07		AT09	
Units	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Analytes	Result	Reporting Limit	Result	Reporting Limit	Result	Reporting Limit
Dieldrin	0.00012	0.00047	0.00011	0.00047	0.00024	0.00047
Endrin	0.00038	0.00047	0.00034	0.00047	**0.00055**	0.00047
DDT	0.00033	0.00047	**0.00058**	0.00047	U	0.00047

Note: U = Non-detected at 3 - 5 times signal to noise.

Bolded analyte concentration is above the water reporting limit for the reintegrated dissolved water and particulate sample. Note that the dissolved water results were below the reporting limit for all samples.

4. Conclusions and Recommendations

This study reviewed the electronic instrumental data files for the whole and filtered surface water samples for spilt samples sent to two laboratories for evidence of matrix interferences that could result in false positive and/or biased high results and to evaluate the effects of filtering. This review confirmed the potential for matrix interferences associated with low levels for organochlorine pesticides (*i.e.*, Endrin, Dieldrin, and isomers of DDT) at all three river sampling locations evaluated (AT-01, AT-07, and AT-09). In addition, the interference can be seen in the whole water as well as both filtered samples (0.45 and 0.22 μm), which indicates these interferences are not specifically isolated to the particulates but are also present in the dissolved water fraction. EPA Method 8081 [4], as normally applied, generates accurate and precise data with sufficient sensitivity to confidently measure pesticide analytes with detection limits below the applicable regulatory compliance limits, and it is well suited for future analyses of river water. However, as demonstrated in the previous sections, it may exhibit a false positive bias at low levels due to the presence of natural and anthropogenic substances in urban waterways. This bias can be reduced by the application of the following procedures:

- **Filtration**. The Lab 2 results demonstrated the presence of interferences from suspended particulates. These interferences can be reduced by passing the water sample through 0.22 μm or 0.45 μm filter paper as carried out by Lab 1. Both filter papers produced similar results, which suggested that either filter size would work well.
- **EPA method 3620 Florisil Cleanup [8], EPA method 3660 Sulfur Cleanup [11], EPA method 3630 Silica Gel Cleanup [12]**. Both Lab 1 and Lab 2 data also demonstrated significant interferences in the dissolved phase (filtered water sample). These interferences cannot be removed completely using the GC/ECD analytical method. However, the polar organic interferences were removed by application of the florisil and silica gel cleanup methods. The activated copper cleanup (method 3660 sulfur cleanup) should also be performed because sulfur presence can also create interference with the pesticides through the normal extraction and cleanup techniques. The combination of filtration and these cleanup techniques substantially reduced particulate and polar interferences.
- **Chromatographic Inspection**. Small peaks in a variable baseline should not exhibit retention time shifts compared to the associated continuing calibration standard run before and after the sample. Anomalous retention time shifts on one or both columns may be grounds for flagging the analyte as a false positive or detection with a high bias. Review by experienced chemists is recommended to confirm positive detections, especially those near or above the applicable regulatory limit.

Mass Spectrometry Confirmation Analysis. Sample extracts can be re-analyzed on a GC/MS instrument if future analyses using EPA Method 8081 [4] detect pesticides with a variable baseline. High-resolution GC/MS instruments work best when NTAs coelute with low level OCPs. However, a conventional quadrupole GC/MS operated in scanning and selected ion monitoring (SIM) modes may also confirm pesticide detections at moderate to high concentrations. Most environmental laboratories possess quadrupole GC/MS instruments for the analysis of semivolatile hydrocarbons using EPA Method 8270 [15]. It is recommended that the instrument run time be no shorter than 30 minutes with a constant temperature ramp from approximately 65˚C to 300˚C to maximize analyte separation. These operating conditions will promote peak separation, minimize coelutions with NTA interferences, and enable retention time indexing. The scanning mode can help identify the identity of interfering compound or class of NTA interferences, while the SIM run can confirm the identity of the target pesticide analyte. This analysis should include the analysis of the low calibration standard from the initial calibration curve to accurately identify the target analyte retention time and approximate response factor.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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