EFFECTS OF QUARTZ FILTER TYPE ON SAMPLING AND ORGANIC CARBON/ ELEMENTAL CARBON ANALYSIS OF $PM_{2.5}$

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EXECUTIVE SUMMARY

Currently, different types of quartz filters are used in the two national $PM_{2.5}$ monitoring networks. The EPA's Speciation Trends Network (STN) uses Whatman QMA quartz filters, and the National Park Service's Interagency Monitoring of Protected Visual Environments (IMPROVE) network uses Pall TissueQuartz filters. Whatman quartz filters contain a binder, which allows for a much thinner but more brittle filter. Pall quartz filters do not contain a binder, which makes the filters much thicker and fluffier. In an effort to make data from the two networks more comparable, EPA is considering switching from Whatman QMA quartz filters to Pall TissueQuartz filters.

RTI International's Organic Carbon/Elemental Carbon (OC/EC) Laboratory initiated discussions of a comparison study with EPA/NAREL personnel in Montgomery, AL. Ultimately the plan evolved into collection of eleven replicate filter samples, with five filters of one type and six of the other type, over the course of three sampling events of differing duration to obtain replicate filter sets with high (200 hours), medium (100 hours), and low (24 hours) $PM_{2.5}$ loading. EPA/NAREL staff collected the replicate filter sets and analyzed each filter using the STN thermal-optical transmittance (TOT) method and using the IMPROVE-A thermal-optical reflectance (TOR) method on NAREL's TOT and dual-mode Sunset Laboratory Inc. carbon aerosol analyzers. As a follow-up study, EPA/NAREL staff ran a fourth event with six sampler channels containing pairs (front and back) of quartz filters in sequence to test for breakthrough of carbon-containing species and with four sampler channels containing single filters (two of each type) loaded in a sampler but with no flow of sampled air to test adsorption of vapor-phase organic compounds not associated with air flow.

For replicate samples from the initial three-event study, a statistical T-Test was performed on Whatman and Pall filter measurements of each carbon fraction for each filter loading by each analysis method to compare the results obtained from the two types of quartz filters. For the STN/TOT method, air concentration measurements for eight carbon fractions were tested across the three filter loadings, and 18 of the 24 T-Tests indicated that the two filters give statistically different results at the 5% level of significance. For the IMPROVE-A/TOR method, air concentration measurements for eleven carbon fractions were tested across the same three filter loadings, and 26 of the 33 T-Tests indicated that the two filters give statistically different results at the 5% level of significance.

The most interesting finding was the additional OC collected by the thick fluffy Pall filters. The fact that the STN/TOT EC measurements are generally consistent (except for the 200-hr samples as noted below) across filter types suggests that the problem is with OC only. These presumed vapor phase organics apparently form char within the filter during analysis. The STN/TOT method correctly assigned this char to OC in all but the heaviest loaded (200-hr) filters, but the IMPROVE-A/TOR method incorrectly assigned the organic char remaining within the filter to EC in all but the lightest loaded (24-hr) filters.

The results of this study indicate that Pall filters collect or retain significant amounts of vapor phase organics that in all but the heaviest loaded samples get assigned to OC by the STN/TOT method and in all but the lightest loaded samples mostly to EC by the IMPROVE-A/TOR method. These findings make difficult the choice of a quartz fiber filter for collection and OC/EC analysis of $PM_{2.5}$. Whatman filters appear to cause earlier evolution of OC components during analysis but retain less vapor phase organic compounds; while Pall filters cause later evolution of OC components during analysis but retain significant quantities of vapor phase organic carbon compounds. Regardless of the filter type or heating profile, using transmittance to set the OC/EC split generally provides a better assignment of unwanted vapor phase organics to OC rather than to EC.

In summary, switching from Whatman QMA to Pall TissueQuartz filters with OC/EC analysis by the STN/TOT method would have little effect on reported EC measurements, but the switch would increase reported OC (and therefore total carbon, TC) measurements substantially. Switching from Whatman QMA to Pall TissueQuartz filters with OC/EC analysis by the IMPROVE-A/TOR method could result in a large increase in reported EC measurements and a significant increase in reported OC measurements.

BACKGROUND

Two national monitoring networks provide chemical speciation data for carbon fractions found in atmospheric particulate matter (PM) with aerodynamic particle diameters of 2.5 microns and smaller ($PM_{2.5}$). The two networks are the Environmental Protection Agency's (EPA's) Speciation Trends Network (STN) and the Interagency Monitoring of Protected Visual Environment's IMPROVE Network. PM2.5 samples for carbon analysis are collected on Whatman QMA(?) quartz filters for the STN and on Pall TissueQuartz filters for the IMPROVE network.

Table 1 summarizes the most obvious differences in the two quartz filter types. The Whatman QMA quartz filter is a thin, hard, brittle filter that contains a binder, and the Pall TissueQuartz filter is a thick, fluffy, flexible filter that contains no binder. Total quartz fiber surface area actually exposed to sampled air appears to be much larger in the Pall TissueQuartz filter than in the Whatman QMA filter. The Pall TissueQuartz filter is several times thicker than the Whatman QMA filter, which suggests a longer residence time for sampled air as it passes through the Pall filter.

In a collaborative effort, RTI and EPA/NAREL staff developed a plan to evaluate potential differences in sample collection and OC/EC analysis results between the two types of quartz filters. This paper describes the results of that collaborative effort.

Table 1. Quartz Filter Comparison

	Whatman QMA	Pall Tissuequartz
Physical Description	Thin, hard, and brittle	Thick, fluffy, and flexible
Contains a Binder?	Yes	No

EXPERIMENTAL

RTI International and EPA/NAREL staff developed a plan to test the differences between the two types of quartz filters by collecting three groups of 11 replicate quartz filter samples at the EPA facility in Montgomery, Alabama. The three groups of replicate filter samples included one group each of heavily loaded, moderately loaded, and lightly loaded $PM_{2.5}$ quartz filter samples . Table 2 describes the three sampling events and the filter type used in each channel of each analyzer. To avoid any bias introduced by a particular sampling channel, the type of quartz filter was switched with each subsequent sampling event.

All collected quartz filter samples were analyzed by EPA/NAREL staff using the STN/TOT method and the IMPROVE-A/TOR method on their Sunset Laboratory Inc. TOT and dual-mode carbon aerosol analyzers, respectively. Analysis data were used to statistically test for differences between the two filter types for each carbon fraction measured by each of the two OC/EC analysis methods across all collected samples.

In a follow-on comparison, EPA/NAREL staff ran a fourth event with six sampler channels containing pairs (front and back) of quartz filters to test for breakthrough of carbon-containing species and with four sampler channels containing single filters (two of each type) loaded in a sampler but with no flow of sampled air to test adsorption of vapor-phase organic compounds. Sampling duration was 24 hours for the fourth event. Table 3 describes the fourth sampling event and the filter type(s) used in each channel of each analyzer.

RESULTS

Figures 1 through 4 provide visual representations of the distribution of carbon among the various fractions measured by the STN/TOT and IMPROVE-A/TOR methods. Filter loading is expressed in μgC/filter. Across all four figures and all three sample loadings shown in each figure, total carbon (TC) is typically noticeably larger for Pall filters than for Whatman filters.

Figure 1 gives OC and EC measurements by the STN/TOT method across all three groups of replicate filters. EC measurements are quite consistent across the two filter types, especially for the moderately loaded 100-hr replicate samples.

Figure 2 gives the OC Peaks and EC data for the same STN/TOT analyses. STN/TOT OC Peaks are defined by their contributions to OC. The pyrolyzed carbon fraction (PyrolC, which is OC evolved after the addition of oxygen to the analyzer atmosphere) is much larger for the Pall filters than for the Whatman filters. This could be due to the earlier evolution of organic carbon observed during analysis of Whatman filter samples or to additional adsorbed organic compounds within the much thicker Pall filters.

Figure 3 gives OC and EC measurements by the IMPROVE-A/TOR method across all three groups of replicate filters. Much of the additional carbon collected by the Pall filters is assigned to EC by the IMPROVE-A/TOR method. This indicates that much of the pyrolyzed carbon formed during the analysis is formed beneath the surface of the filter punch. When oxygen is added to the sample atmosphere, EC and pyrolyzed carbon on the surface of the filter burn off more quickly than pyrolyzed carbon formed within the filter. As soon as the reflectance of the filter surface reaches its initial reflectance, the OC/EC split is set and any pyrolyzed carbon remaining beneath the surface of the filter is assigned to EC.

Table 2. Sampling Details

Sampler Information		200-Hour Event			100-Hour Event			24-Hour Event		
Sampler ID	Module Position	Filter Type	Filter ID	Volume of Air Sampled	Filter Type	Filter ID	Volume of Air Sampled	Filter Type	Filter ID	Volume of Air Sampled
SuperSass 1	1	Pallflex	Q06-11847	80.62 m^3	Whatman	Q06-11858	40.27 m^3	Pallflex	Q06-11869	9.67 m^3
SuperSass 1	2	Pallflex	Q06-11848	80.67 m^3	Whatman	Q06-11859	40.31 m^3	Pallflex	Q06-11870	9.68 m^3
SuperSass 1	3	Whatman	Q06-11849	80.67 m^3	Pallflex	Q06-11860	40.30 m^3	Whatman	Q06-11871	9.68 m^3
SuperSass 1	4	Whatman	Q06-11850	80.66 m^3	Pallflex	Q06-11861	40.30 m^3	Whatman	Q06-11872	9.66 m^3
SuperSass 2	1	Pallflex	Q06-11851	80.73 m^3	Whatman	Q06-11862	40.34 m^3	Pallflex	Q06-11873	9.68 m^3
SuperSass 2	2	Pallflex	Q06-11852	80.64 m^3	Whatman	Q06-11863	40.33 m^3	Pallflex	Q06-11874	9.68 m^3
SuperSass 2	3	Whatman	Q06-11853	80.66 m^3	Pallflex	Q06-11864	40.30 m^3	Whatman	Q06-11875	9.69 m^3
SuperSass 2	4	Whatman	Q06-11854	80.65 m^3	Pallflex	Q06-11865	40.31 m^3	Whatman	Q06-11876	9.68 m^3
RegSass	1	Pallflex	Q06-11855	80.65 m^3	Whatman	Q06-11866	40.31 m^3	Pallflex	Q06-11877	9.67 m^3
RegSass	2	Pallflex	Q06-11856	80.66 m^3	Whatman	Q06-11867	40.32 m^3	Pallflex	Q06-11878	9.70 m^3
RegSass	3	Whatman	Q06-11857	80.66 m^3	Pallflex	Q06-11868	40.33 m^3	Whatman	Q06-11879	9.67 m^3
	Mean:			80.66 m^3			40.31 m^3			9.68 m^3
	Standard Deviation:			0.03 m^3			0.02 m^3			0.01 m^3
	%RSD:			0.035%			0.050%			0.114%

Table 3. Sampling Plan for Stacked and No-Flow Filter Samples

Sampler Information		24-Hour Event		
Sampler ID	Module Position	Filter Type and Position	Filter ID	Volume of Air Sampled
SuperSass 1	1-front	Pallflex front filter	Q06-11891	9.67 m^3
SuperSass 1	1-rear	Pallflex rear filter	Q06-11892	9.67 m^3
SuperSass 1	2-front	Whatman front filter	Q06-11893	9.68 m^3
SuperSass 1	2-rear	Whatman rear filter	Q06-11894	9.68 m^3
SuperSass 1	3	Pallflex quartz filter	Q06-11895	no flow
SuperSass 1	4	Whatman quartz filter	Q06-11896	no flow
SuperSass 2	1-front	Whatman front filter	Q06-11897	9.67 m^3
SuperSass 2	1-rear	Whatman rear filter	Q06-11898	9.67 m^3
SuperSass 2	2-front	Pallflex front filter	Q06-11899	9.67 m^3
SuperSass 2	2-rear	Pallflex rear filter	Q06-11900	9.67 m^3
SuperSass 2	3	Whatman quartz filter	Q06-11901	no flow
SuperSass 2	4	Pallflex quartz filter	Q06-11902	no flow
RegSass	1-front	Whatman front filter	Q06-11903	9.67 m^3
RegSass	1-rear	Pallflex rear filter	Q06-11904	9.67 m^3
RegSass	2-front	Whatman front filter	Q06-11905	9.68 m^3
RegSass	2-rear	Pallflex rear filter	Q06-11906	9.68 m^3
RegSass	3	Not Used	---	---

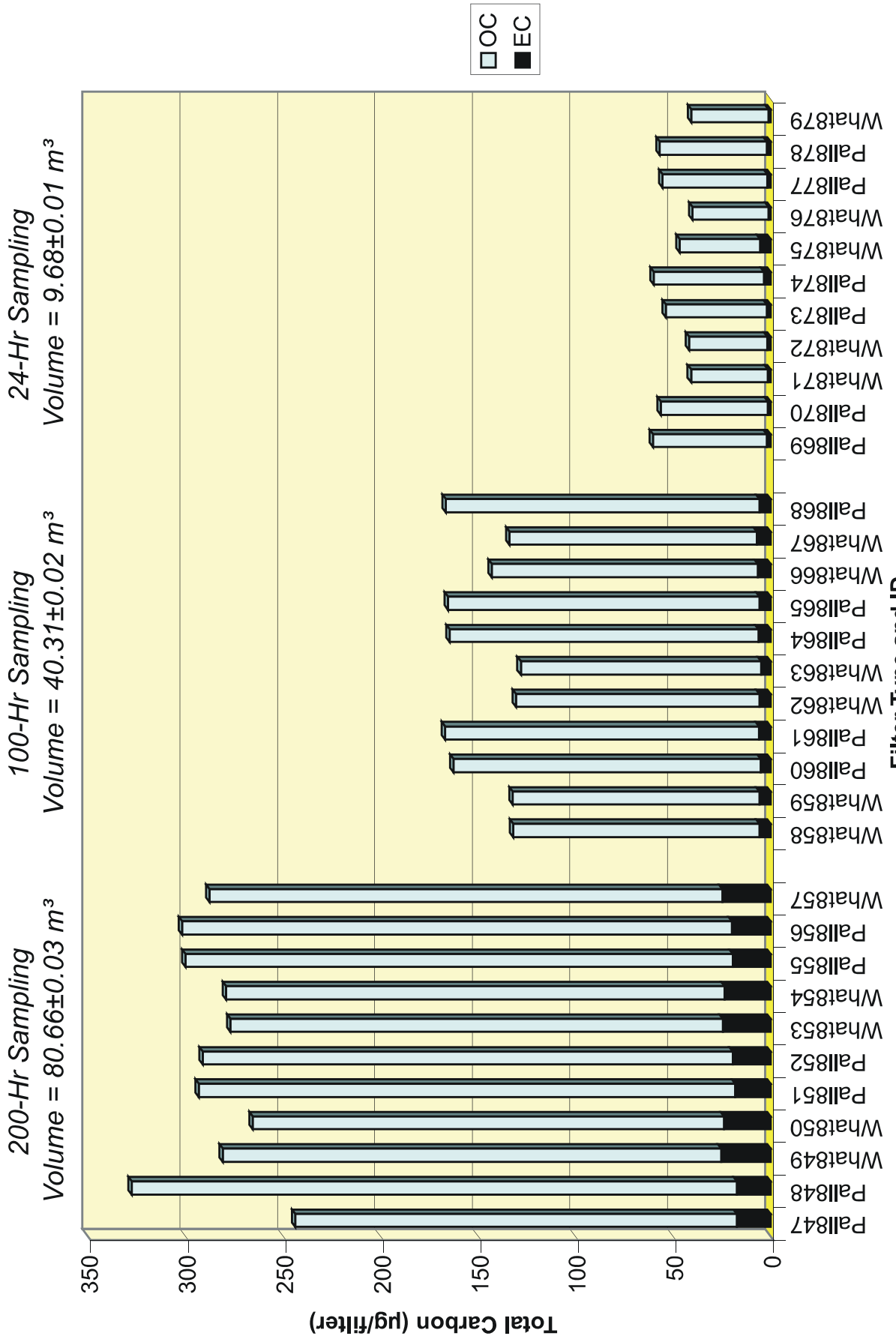

Figure 1. STN/TOT Analysis Results–OC and EC

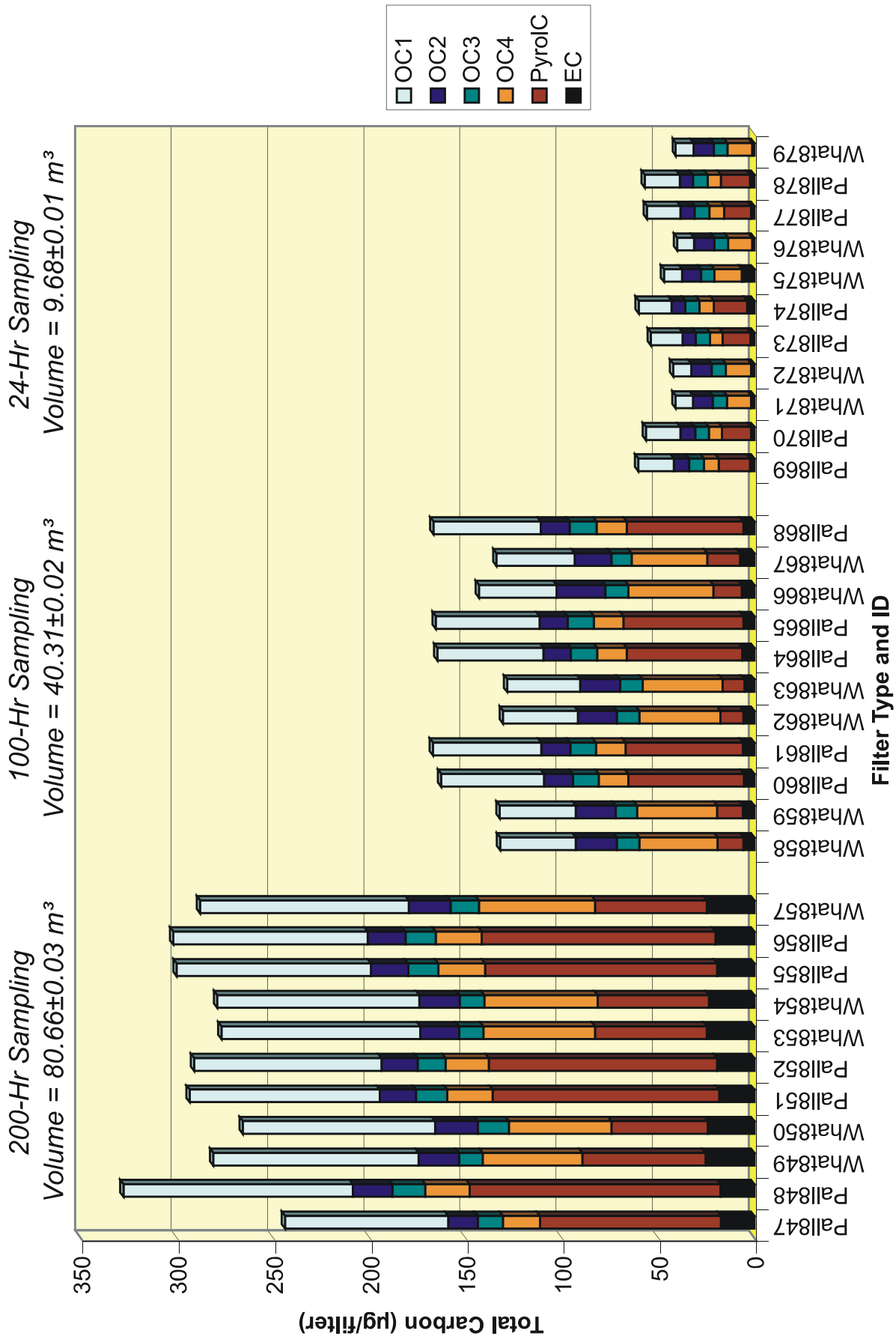

Figure 2. STN/TOT Analysis Results–OC Peaks and EC

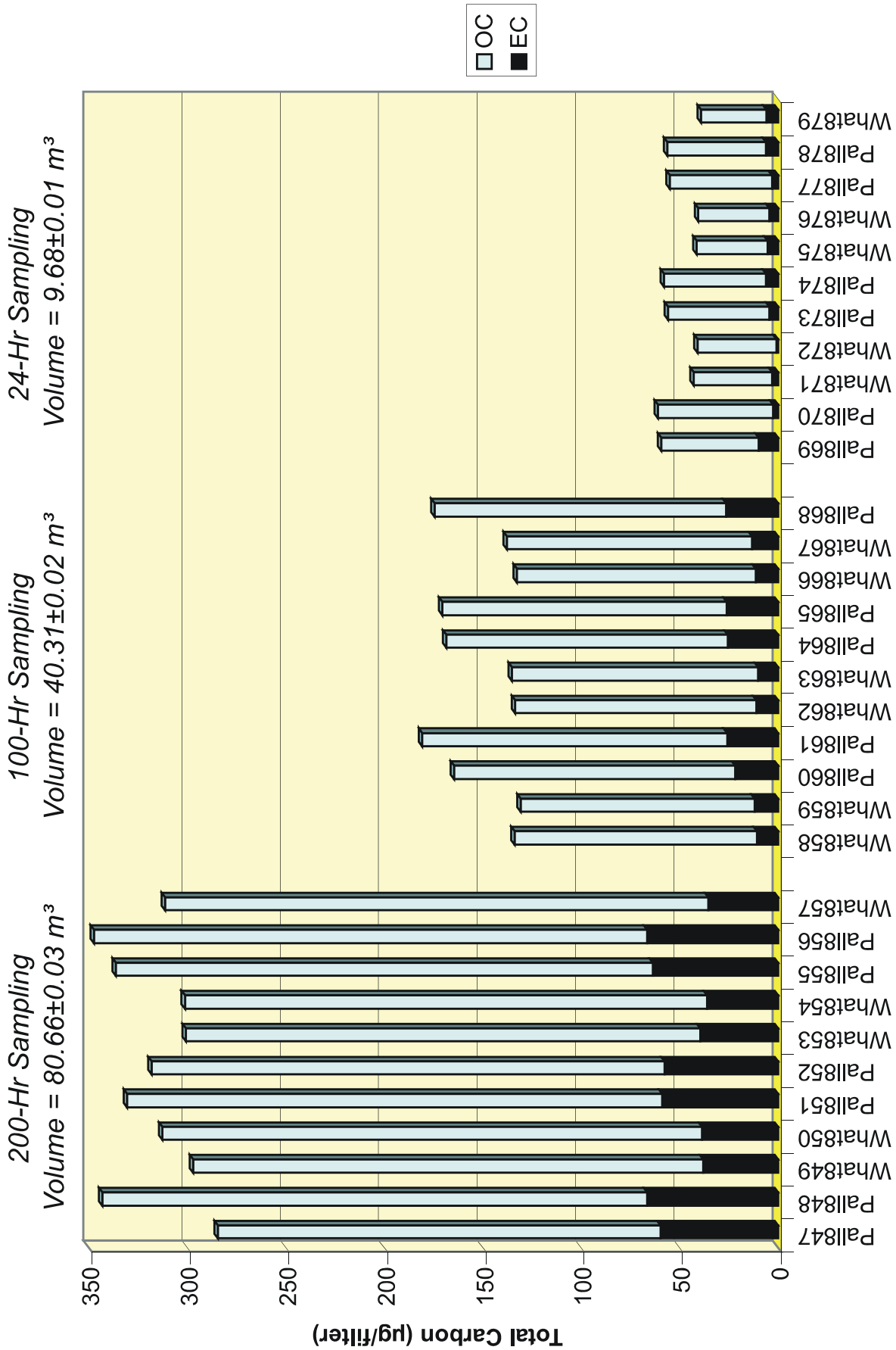

Figure 3. IMPROVE-A/TOR Analysis Results–OC and EC

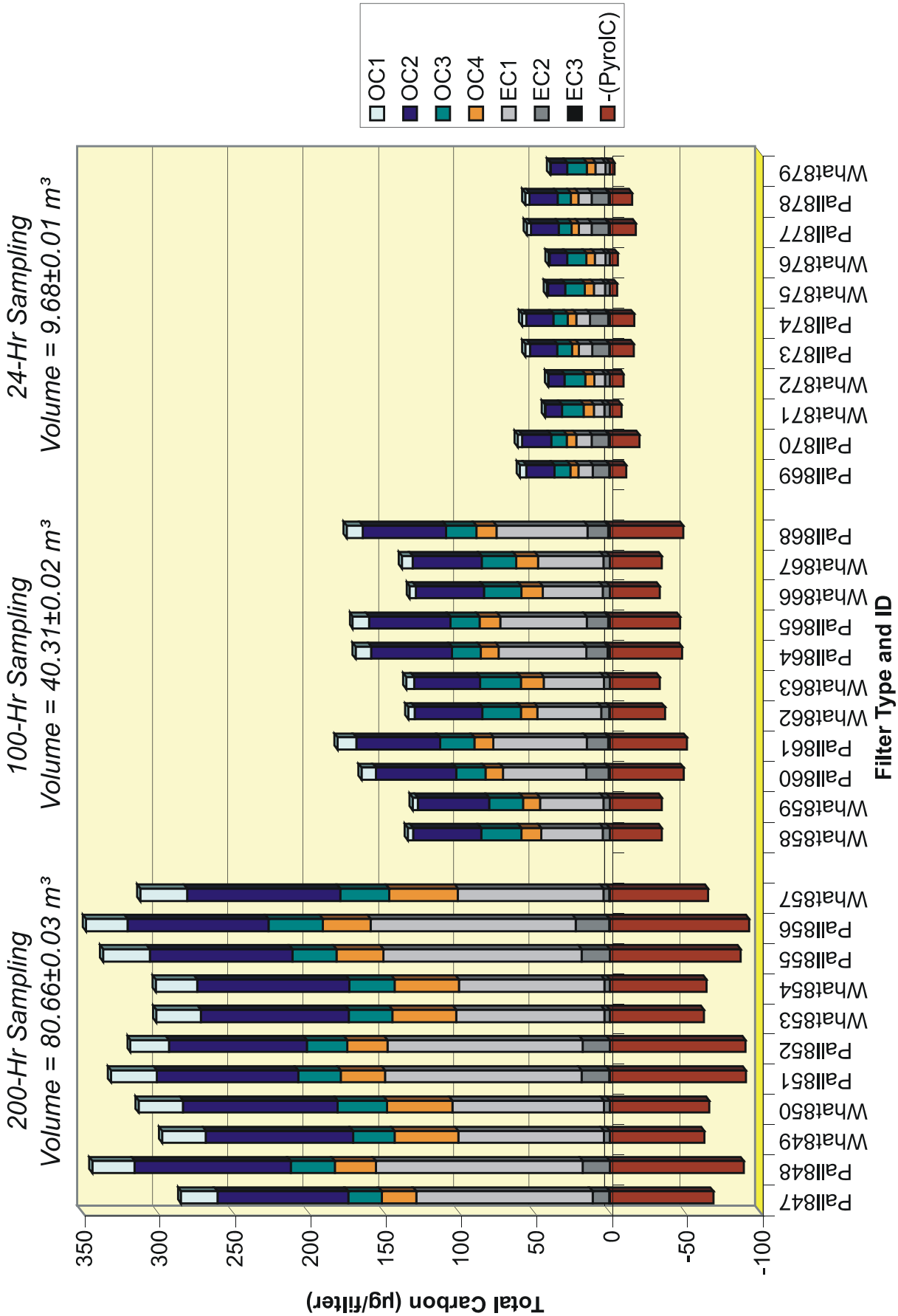

Figure 4. IMPROVE-A/TOR Analysis Results–Peaks and Pyrolyzed Carbon

Figure 4 gives the seven IMPROVE-A carbon peaks and PyrolC for the same IMPROVE-A/TOR analyses. The seven IMPROVE-A carbon peaks (OC1, OC2, OC3, OC4, EC1, EC2, and EC3) are measured without regard to the OC/EC split. PyrolC is plotted as negative values on the figure because carbon reported as PyrolC is also reported in the data for the seven carbon peaks. Again the much larger values of PyrolC for the Pall filters is evident in the figure.

Table 4 gives the results of the T-Test run on each carbon fraction for each OC/EC analysis method and each group of replicate filter samples. All T-Tests were run on air concentration data (mass of carbon per filter shown in Figures 1 through 4 divided by the volume of air sampled from Table 2). Using air concentration data for the statistical tests eliminated any between-replicate differences in loading measurements due to slight differences in volume of air sampled through each filter.

The T-Test results clearly indicate substantial differences in OC/EC analysis results with the two types of filters. For the STN/TOT method, air concentration measurements for eight carbon fractions were tested across the three filter loadings, and 18 of the 24 T-Tests indicated that the two filters give statistically different results at the 5% level of significance. For the IMPROVE-A/TOR method, air concentration measurements for eleven carbon fractions were tested across the same three filter loadings, and 26 of the 33 T-Tests indicated that the two filters give statistically different results at the 5% level of significance.

Figure 5 gives the OC Peaks and EC data for STN/TOT analysis results for laboratory blanks and filter samples from the fourth sampling event. TC measurements for laboratory blanks, back filters, and no-flow filters were very similar across both filter types, but the OC peaks data were quite different. Pall front filters had larger OC (and TC) loadings than Whatman front filters. STN/TOT EC measurements were again similar across filter types.

CONCLUSIONS

The earlier evolution of high-temperature organic carbon from Whatman QMA filters was not a surprise. Fortunately, using transmission to set the OC/EC split correctly adjusts for the formation of less organic char and provides EC measurements that are consistent across both filter types. The consistency of EC measurements is significant because it indicates that the two filter types are equally efficient at collecting and holding non-volatile particulate matter.

The adsorption of additional OC during sampling with Pall TissueQuartz filters was a surprise. The results of this study indicate that Pall filters collect or retain significant amounts of vapor phase organics that get assigned to OC by the STN/TOT method and mostly to EC by the IMPROVE-A/TOR method. Whatman filters appear to cause earlier evolution of OC components during analysis but retain less vapor phase organic compounds; and Pall filters cause later evolution of OC components during analysis but retain significant quantities of vapor phase organic carbon compounds. Regardless of the filter type or heating profile, using transmittance to set the OC/EC split is essential to prevent assigning unwanted vapor phase organics to EC rather than OC.

Results of the stacked-filter experiment indicated that the difference in adsorption of vapor-phase OC only occurs when the Pall filter is the front filter. Back-filter and no-flow filter TC measurements were very similar across both filter types.

Table 4. Summary of T-Test Results

Collection Time	Number of Replicate Samples (Pall:What)	Summary of T-Test Results at the 5% Level of Significance for STN/TOT Results*							
		OC	EC	TC	OC1	OC2	OC3	OC4	PyroIC
24-hr	6:5	Different	Not Different	Different	Different	Different	Different	Different	Different
100-hr	5:6	Different	Not Different	Different	Different	Different	Different	Different	Different
200-hr	6:5	Not Different	Different	Not Different	Not Different	Different	Not Different	Different	Different

*STN/TOT analyses were run on NAREL's Sunset Laboratory TOT Carbon Aerosol Analyzer.

Collection Time	Number of Replicate Samples (Pall:What)	Summary of T-Test Results at the 5% Level of Significance for IMPROVE-A/TOR Results**										
		OC	EC	TC	OC1	OC2	OC3	OC4	EC1	EC2	EC3	PyroIC
24-hr	6:5	Different	Not Different	Different	Different	Different	Different	Different	Different	Different	Different	Different
100-hr	5:6	Different	Different	Different	Different	Different	Different	Not Different	Different	Different	Different	Different
200-hr	6:5	Not Different	Different	Not Different	Not Different	Different	Not Different	Different	Different	Different	Not Different	Different

**IMPROVE-A/TOR analyses were run on NAREL's Sunset Laboratory Dual-Mode Carbon Aerosol Analyzer.

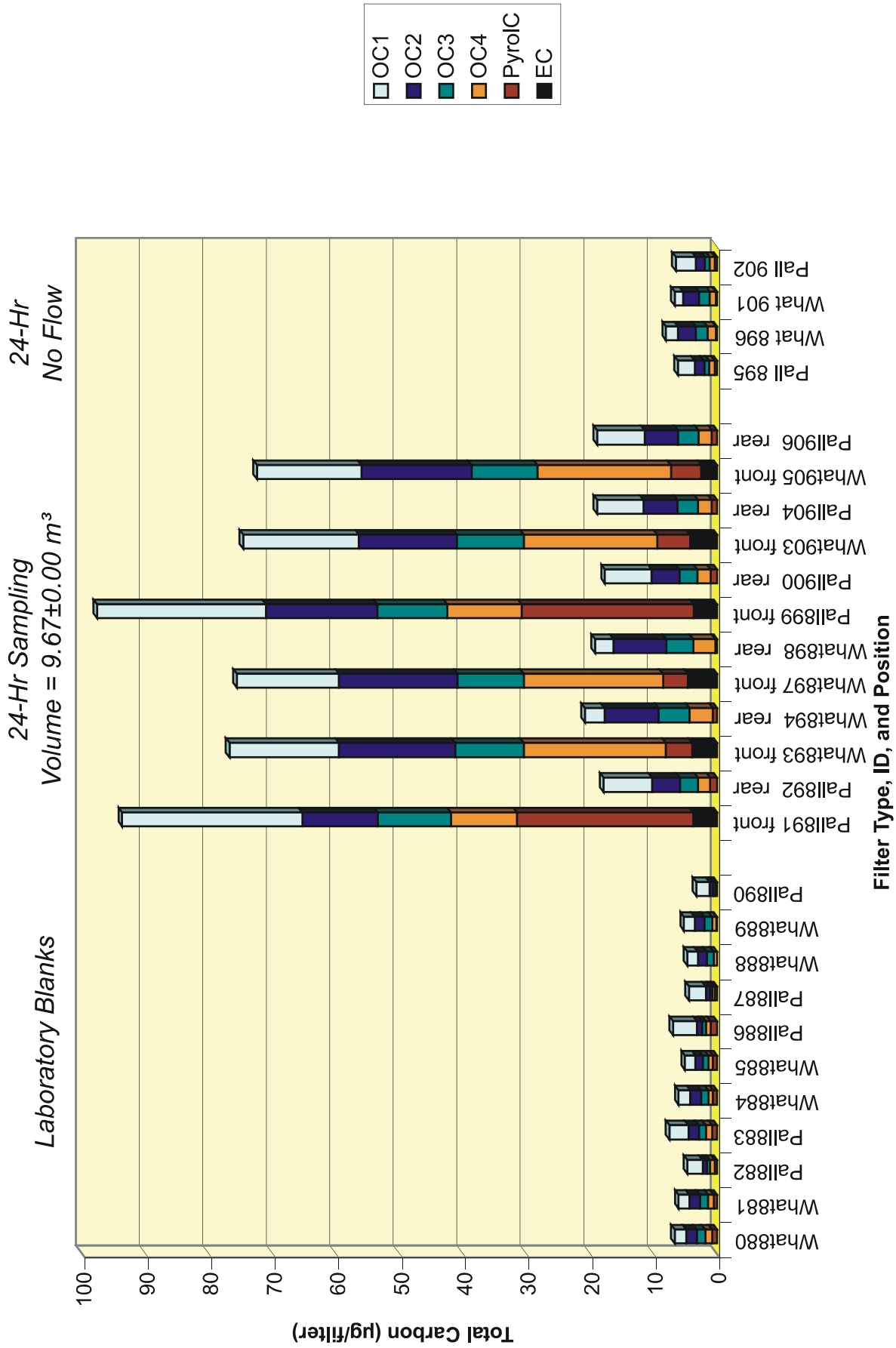

Figure 5. Lab Blanks, Stacked Filters, and No-Flow Filters--STN/TOT OC Peaks and Pyrolyzed Carbon