

Air Toxics Science Advisory Committee

Meeting minutes

May 20, 2015, meeting #6



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Introduction

The sixth meeting of the 2014/2015 Air Toxics Science Advisory Committee (also referred to as the ATSAC) was held on May 20 from 9 a.m. to noon in Conference Room EQC-A, Oregon Department of Environmental Quality Headquarters, 811 SW Sixth Avenue, Portland, Oregon. Committee attendees included Bill Lambert (ATSAC chair), Kent Norville, Dean Atkinson, David Farrer, Bruce Hope, Max Hueftle, and Dave Stone. DEQ staff in attendance included Sue MacMillan (ATSAC lead), Chris Swab (emissions inventory specialist), Sarah Armitage (air toxics specialist), Phil Allen (air modeling), Kevin Downing, and Anthony Barnack (air quality chemist). Downing and Barnack will give talks during second half of today's meeting.

Committee administrative items

An error in the details of how the toxicity values for tetrachloroethylene were used to identify a revised ambient benchmark concentration (also referred to as an ABC) during the April ATSAC meeting needs to be corrected. Committee will receive the corrected draft April minutes by email, and be asked to edit and approve them via email.

The ATSAC chair person, Bill Lambert, welcomed everyone and noted that this was the sixth meeting of the Air Toxic Science Advisory Committee. He reminded everyone that today's meeting would be largely informational and somewhat of a workshop, and that a variety of expert speakers would be presenting information to the committee as background for discussion of establishing ambient benchmark concentrations for polycyclic aromatic hydrocarbons (also known as PAHs) and diesel particulate matter.

Four speakers will be presenting today: 1.) Staci Simonich, professor at Oregon State University and former ATSAC member, 2.) Kim Anderson, also a professor at Oregon State University and former ATSAC member, 3.) Kevin Downing, DEQ Operations Program, and 4.) Anthony Barnack, DEQ Environmental Solutions Planning Program.

Bruce Hope prepared a few talking-point slides for both PAHs and diesel particulate matter (commonly referred to as DPM) to assist with committee discussions today. He wants to establish a common definition for diesel for use by the committee. Lambert agreed that this was an important task.

In regard to the minutes from the April ATSAC meeting, there were technical concerns related to the documentation of the tetrachloroethylene ABC discussion, which will be revised in those minutes. The committee will plan on approving the April meeting minutes at the June ATSAC meeting, after revised draft April meeting minutes are circulated off-line to the committee.

Presentation: Monitoring PAHs in ambient air – the big picture (Staci Simonich, Oregon State University)

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Simonich has been studying PAHs for the past 20 years, and published her work in technical journals starting in the 1990s. The study of PAHs has become more important over time at Oregon State University (commonly referred to as OSU). OSU has significant expertise in this area. Also, OSU programs were granted funding for a Superfund research program by the National Institute of Environmental Health Sciences that focuses on PAHs in multiple environmental media. Simonich will address some of the topics that DEQ/ATSAC asked for, and then discuss a recent study focused on the Columbia River Gorge Plateau; the results of this study have been submitted to the journal of *Environmental Science and Technology* for publication, which is pending.



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PAHs are a class of organic compounds with two or more fused rings, and so have aromaticity in common. The number of fused rings in a particular PAH has a large effect on its rate of degradation in the atmosphere, and on the toxicity of that PAH. Petrogenic PAHs originate directly from, for example, spills of petroleum that contain PAHs, while pyrogenic PAHs are products of fire or combustion activities. When PAHs in Oregon's atmosphere are being discussed, they're made up primarily of pyrogenic PAHs formed during combustion, and therefore Simonich's talk focused on these pyrogenic PAHs. There is a lot of overlap among individual PAHs in regard to various combustion sources. Even the remote areas of the world have been found to harbor PAHs, such as the Arctic, Beijing, and the tops of mountains. Some PAHs are directly toxic to receptors, and some are indirectly-acting, in that they are mutagens. A mutagen is a physical or chemical agent that alters genetic material (e.g., DNA) of an organism and thus increases the frequency of mutations above the natural background level. Because many mutations cause cancer, mutagens are also likely to be carcinogens.

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At OSU, Simonich and Anderson measure a wide variety of PAHs, not just the typical set of 16 identified by EPA. The 16 PAHs typically assessed by EPA are acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i) perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, pheanthrene, and pyrene. OSU also assesses oxy-PAHs, nitro-PAHs, and the PAHs which have molecular weights near 302, referred to as the "MW 302 PAHs." OSU works on finding and maintaining analytical laboratory standards for each of these atypical PAHs, so that they are able to analyze air samples containing them. In many cases, they have developed their own, new laboratory standards for some of these atypical PAHs. The atypical PAHs can form in the atmosphere or be a product of grilling food, in some cases. Incomplete combustion sources, and natural processes such as volcanic releases and forest fires, can produce these atypical PAHs.

In regard to PAH chemical processes that occur in the atmosphere, studying the partitioning of PAHs between the gas phase and the particle phase is important. Simonich and her team recently published an article in *Environmental Science and Technology* in regard to reactions of PAHs with hydroxyl radicals, ozone, and nitrous oxide species. Simonich has also tracked how the mutagenicity of the related particulate matter changes over time.

The PAHs which tend to be the mostly routinely measured are the "EPA 16." Combustion sources can also produce oxy-PAHs, and the concentrations of these PAHs can be almost as high as their analogous parent PAH compounds. Oxy-PAHs, then, can

be produced two ways: 1) directly from combustion sources, and 2) parent PAHs react in the atmosphere with ozone or hydroxyl radicals to form oxy-PAHs.

Nitro-PAHs typically come from combustion operations and from the grilling of meat, and certainly from diesel combustion. The concentrations of nitro-PAHs are about 10-fold lower than concentrations of oxy-PAHs, and 100-fold lower than the concentrations of parent PAH compounds that the nitro-PAHs come from. Nitro-PAHs are also produced via atmospheric photochemistry.

Simonich and her team created nitro-PAHs in the lab using nitro oxides, particulate matter collected in Beijing, and a photochemical chamber. In addition, Simonich began measuring MW 302 PAHs about five years ago. She went to Stockholm to meet with only person she knew at the time who was measuring MW 302 PAHs, and brought what she learned back to her lab at OSU.

After that, Simonich began measuring some of the MW 302 PAHs that had high relative potency factors in the analysis of air samples collected from Beijing, and other particulate matter samples from various other Asian locations. A related paper was published in *Environmental Health Perspectives* describing risk assessment work conducted to assess human health risk from chemicals present in air before, during, and after the 2008 Olympics held in Beijing. In urban air, MW 302 PAHs are typically present at low concentrations, and Simonich did not know of any reports of them being present in Portland air. If one were to monitor for MW 302 PAHs in Portland air, a large volume of air would have to be drawn into the monitoring apparatus, and the analyzing laboratory would have to be capable of detecting these PAHs at very low detection limits.

Simonich looked for MW 302 PAHs during an air sampling study conducted on the Confederated Tribe of the Umatilla Indian Reservation in the Columbia River Gorge and Plateau, in part because Simonich and her team suspected the site to be influenced by air emissions from a coal-fired power plant in Boardman, Oregon. They analyzed air samples for MW 302 PAHs, but didn't find any levels above the method detection limits. In general, MW 302 PAHs are not monitored for or analyzed for, and when they are, they are difficult to measure. Coal combustion is thought to be a major source of MW 302 PAHs, but other sources are also likely. A continuum chart of different PAHs was presented, showing where the PAHs fall in relation to whether they're more likely to appear in the gas phase or the particle phase in air. The PAHs with lower molecular weights and a lower number of rings structures tend to appear in the gas phase (e.g., phenanthrene), while PAHs with higher molecular weights, lower vapor pressures, and a larger number of ring structures (e.g., benzo(g,h,i)perylene), tend to bind to particles in air. Benz(a)anthracene, a PAH with a molecular weight that falls somewhere in the middle, appears in the middle of this continuum. About 90 percent of the benzo(a)pyrene present in Portland air/ambient air is bound to particles. The PAHs which bind to PM2.5 particles travel longer distances than other PAHs, or PAHs on larger particles.

Simonich has been studying the trans-Pacific transport of higher-molecular-weight, particle-bound PAHs associated with particles with diameters of 2.5 microns (typically referred to as PM2.5) from Asia to the U.S. West Coast for about 12 years. This information can help determine where the trans-Pacific particles originate and how long it takes them to get to the U.S. West Coast, which in turn helps determine when this pollution might impact populations on the West Coast. In the past, Simonich monitored



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gas-phase compounds and total suspended particulates, but now assesses primarily PM_{2.5}, due to the toxicity now known to be associated with this size of particulate matter.

In order to correctly measure PAHs in air, you must know what you want to measure and sample. The particle-bound PAHs are the ones that tend to have the highest relative potency factors. Simonich published an article in 2011 in *Environmental Health Perspectives* using USEPA relative potency factors to conduct a risk assessment for PAHs. Simonich believes she and her co-authors were probably the first to perform this type of risk assessment, which assessed potential health impacts related to air exposure in Beijing before, during, and after the 2008 Olympics. Note that oxy-PAHs and nitro-PAHs generally have the same or lower vapor pressure than the corresponding PAH parent, and so will tend to be more particle-bound than the corresponding PAH parent.

In order to study the inter-continental transport of PAHs from Asia to the Pacific northwest, Simonich and her lab have monitored the air over the past 14 years at a number of different locations at various elevations, including Mt. Bachelor, Oregon at 2,700 meters; Mary's Peak, in the Oregon coast range at 1,250 meters; Cheeka Peak Observatory at the tip of the Olympic peninsula in Washington, at 500 meters; Okinawa, Japan at 60 meters; and Beijing, China at 45 meters. In the spring of each year, Simonich notes a greater movement of trans-Pacific air masses, which, depending on meteorology, will show up at higher-elevation locations such as Mt. Bachelor, more so than at Mary's Peak or the Cheeka Peak Observatory locations.

Simonich discussed some work that she had presented at the Oregon Modeling Steering Committee meeting held in Portland, Oregon about a month earlier. Through funding provided to Simonich by the National Institute of Environmental Health Sciences via the Superfund Basic Research Program, Simonich conducted air sampling for PAHs at a location designated as the Cabbage Hill site on the Confederated Tribes of the Umatilla Indian Reservation, because the source of PAHs in air was a concern there. Simonich also collected air samples from the Mount Bachelor location (higher elevation where mostly skiers and hikers are active) at approximately the same time in order to compare and assess how trans-Pacific air masses influence PAH concentrations at the lower elevations where people live (i.e., the Cabbage Hill site).

When Simonich looked at the data from Cabbage Hill and a couple of other nearby sites, she found a statistically significant difference in the mean concentrations of the sums of PAHs and PAH derivatives in air at these sites between 2010 and 2011, with 2011 concentrations being significantly lower. This was a confusing result, as a similar pattern was not observed in air collected from the Mount Bachelor location. As a result, Simonich and her team began to try to figure out why the concentrations had decreased from 2010 to 2011, including trying to identify sources of the PAHs and PAH derivatives. To do this, Simonich used a comparison of the *ratios* of the concentrations of various PAH isomers among the different potential sources. With atmospheric PAHs, if the air samples of interest are analyzed fairly quickly, the results are expected to be representative of what's being emitted from a *nearby* source.

The results indicated that the 2010 PAH data likely came from a grass, wood, and/or coal combustion source, while the 2011 PAH data appeared to have originated from a mixed petroleum source. At this point, Simonich began to look at influences from sources in and



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around Boardman, Oregon, because the coal-fired power plant at Boardman was a known source of particulate matter for the Columbia River Gorge. She looked at locations, wind direction, air mass back-trajectories, etc. She also wanted to answer the question of whether concentrations detected at her study locations had anything to do with changes in emissions coming from the Boardman coal-fired plant. The resulting data indicated that the Boardman power plant was the major source of PAHs and PM2.5 to that area. Simonich found out from plant employees that emission control technologies had been implemented at the plant in the spring of 2011, which would account for the lower concentrations that appeared during sampling conducted by Simonich in 2011. It also helps to explain why, in 2010, the Cabbage Hill site PAHs were predominantly from grass, wood, and coal combustion. At times when the Boardman plant was shut down, the Cabbage Hill site PAHs were predominantly originating from mixed-diesel sources, which are likely attributable to the nearby Highway 1-84 traffic. The plant upgrades appeared not to have made as much of a difference with nitro-PAH concentrations as they did with oxy-PAH and parent PAH concentrations. It is likely that currently, Interstate I-84 is a more predominant source of the nitro-PAHs. Note that PAH source apportionment techniques tend to be more accurate in a setting where there are only one or two major point sources; not as accurate in an urban setting that has lots of different sources.

Simonich, Lambert, and Hope then discussed the fact that PAHs -- due to activities like wood combustion (wood smoke) -- aren't as well-studied as PAHs coming from diesel sources. Similar air assessment work in the valley near Simonich's Cabbage Hill site indicated that PM2.5 coming from wood smoke can be very high in that area. Same is true in southern Oregon/Klamath Falls area, and in Eugene.

A committee member asked if the committee can get a copy of today's presentation by Simonich. MacMillan responded by saying that she would forward the presentation to the committee as soon as she receives a revised version of today's slides from Simonich. All of today's presentations will be posted on the ATSAC website, as well.

Presentation: Challenges of PAH analysis (Kim Anderson, Oregon State University)

Anderson discussed the challenges of PAH analysis and the availability of laboratory analytical standards. Anderson reviewed and used as a starting point the table created by Bruce Hope, which shows a list of 38 PAHs used for regulatory purposes by a number of different state and federal agencies. On this list, the PAHs presented in red font are not part of the 32 PAHs originally used by Oregon to identify the current ABC for PAHs, which was established in 2006. Anderson added two columns to the table (see Slide 4, the last two columns entitled "62 PAHs" and "Accu-Standard"), to depict the PAH analysis that her lab is currently conducting. Anderson noted that she included only typical PAHs and occluded PAHs in this table, and chose to leave out the oxy-PAHs and nitro-PAHs, which were discussed by Simonich. She also noted that in the column entitled "Accu-Standard", analytical standards are available for all but three of those listed. However, these "missing" standards are available for purchasing, if needed.

On Slide 5, Anderson pointed out that the row listing "Benz(j) and (e)aceanthrylene" indicates that the analytical standard for these two chemicals is a mixture, and so these two chemicals cannot be differentiated from each other analytically. In Anderson's lab, however, there is a chemist who can speciate these two compounds.



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Anderson conducts primarily vapor-phase analysis, and does not work much with particulates. Multiple publications have indicated that vapor-phase PAHs can account for 35 percent to 86 percent of the cancer risks associated with PAHs. She cautioned that although researchers tend to focus on PAHs bound to particulate matter in air, the vapor phase PAHs have a significant amount of risk associated with them, and should not be ignored, or there will be a danger of underestimating the total risk by as much as a third. Note that in the case of DEQ, there is an ABC value for naphthalene which is separate from the ABC for total PAHs. The ABC for total PAHs does not include naphthalene in the assumed mixture of PAHs that are assessed using the ABC for total PAHs. In addition to cancer effects, vapor-phase PAHs are the biggest trigger of asthma, which is another important reason not to ignore vapor-phase PAHs.

Historically, liquid chromatography or gas chromatography methods have been used to analyze PAH's. Anderson uses gas chromatography/mass spectrometer analysis, which is commonly referred to as GC/MS. There are challenges in regard to the use of mass spectrometry for PAH analysis. Because PAH isomers have the same chemical formula and mass, and share significant underlying structural similarities, GC/MS products from isomers often share ion fragments with identical mass-to-charge ratio. Thus, accurate identification of isomers requires chromatographic separation prior to MS detection, and confirmation with appropriate analytical standards. Anderson went on to describe in great detail the other kinds of problems that can occur with PAH analysis as related to laboratory equipment, how the sampled PAHs are treated prior to and during analysis, and other cautions.

When analyzing for a large number of PAHs, the high boiling points of the larger-size PAHs lead to a marked tendency during analysis toward desublimation and deposition of material within the laboratory instrument, which limits things like the sensitivity of detection, reproducibility, analytical precision, and other concerns. Several published analytical methods provide accurate PAH determination, but are limited to relatively small sets of analytes. The take-home message is: be aware of all available types of analytical options for the set of PAHs you're interested in analyzing, and be aware of the differing potential problems related to analyzing a large suite of PAHs versus a small subset of PAHs. Anderson also discussed the details and potential problems related to analyzing for PAHs with molecular weights greater than 300.

Currently, Anderson and her team are able to accurately analyze for 62 different PAHs, and their precision is good. In addition, her lab's linear dynamic range for all 62 PAHs is a minimum of four orders of magnitude. The reason this information is important is because Anderson's lab can run numerous PAH samples day after day, week after week, without having to recalibrate or do extra maintenance on the analytical equipment. The large linear dynamic range mentioned earlier means that her lab can avoid having to dilute samples in order to bring the concentrations within a range that the machine can read. In addition, this allows Anderson's lab to be much more accurate in estimating the masses and concentrations of individual PAHs, without causing analytical overlap of PAHs which are very similar, which would result in less-credible analytical results.

Chairperson Lambert thanked Anderson for her presentation, as one of the committee's concerns has been the actual measurability of the various PAHs.



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Before the break began, Hope and Stone offered some talking points about PAHs and the issues they've pondered, so that the full committee can consider their information. Hope went through the slides that he and Stone had prepared. Benzo(a)pyrene serves as a kind of surrogate, or index PAH, for the other carcinogenic PAHs, and is recognized to have a certain carcinogenic potency, to which the other carcinogenic PAHs can be compared and converted, using potency equivalency factors published in the literature. The converted PAH concentrations are then summed, and the sum of total PAHs is used as an equivalent toxicity value for benzo(a)pyrene. The ABC set for total PAHs in 2006 was based on a California Office of Environmental Health Hazard Assessment (OEHHA) unit risk estimate for benzo(a)pyrene of 1.0E-04 per microgram per cubic meter, which converts to an ABC value of 0.0009 micrograms per cubic meter (commonly referred to as ug/m3). In 2014, EPA updated their toxicity information for benzo(a)pyrene to recommend a new unit risk estimate for benzo(a)pyrene of 6.0E-04 per ug/m3, which converts to a concentration of 0.002 ug/m3. This value is not radically different from the toxicity value used to set the 2006 ABC for PAHs.

In addition, the 2006 ABC was based on assessment of 32 PAHs, all of which were incorporated into the ABC for (total) PAHs. An important question posed by Hope is whether the ATSAC wants to continue to use 32 PAHs to estimate a concentration for total PAHs. For example, the Minnesota Department of Health has published guidance that focuses on 19 PAHs as being adequate to assess health issues.

Hope pointed out that a goal of the committee is to protect people from exposure to PAHs regardless of source. Therefore, we may want to revise the list of 32 PAHs on which the current ABC is based, to reflect a broader range of potential sources. So the committee could assess 32 PAHs, or some other number of PAHs, but it needs to be discussed. Hope pointed out that a goal of the committee is to protect people from exposure to PAHs, regardless of source. What sources do the PAHs that the committee will pick, relate to? Can we measure the PAHs we choose to assess? Today's presentations answered that question pretty well. Furthermore, are any new PAHs we add to the list actually relatable in terms of toxic potency to benzo(a)pyrene? In other words, is there a way to convert concentrations of each PAH we choose to the toxic potency of benzo(a)pyrene? The committee also needs to consider including enough PAHs to potentially provide fingerprinting protocols for source attribution; but perhaps fingerprinting concerns should be considered on a case-specific basis. Also, if the Minnesota approach is one that the committee would like to look at in more detail, we can do that. Their program did consult with Oregon State University about 18 years ago in regard to funding the research program, and so it's likely that we could get Minnesota's main toxicologist to call in to one of the ATSAC meetings and explain how they made their decisions.

Presentation: Diesel engines and air quality (Kevin Downing, DEQ)

Downing presented a short video clip of a truck with the engine running, to provide some overall context. It was obviously emitting a certain amount of diesel particulates, a lot of different human receptors were nearby: truck operators, spectators, kids at a nearby picnic table, all being exposed to high concentrations of the truck's emissions. It is very important to be aware of the fact that diesel exhaust is a complex mixture of gases and particles, including the various chemicals associated with those gases and particles.



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Diesel engines are still the most efficient internal combustion engines available. Historically, there has been more concern focused on the particulate side of diesel emissions, and less on the gaseous phase. In 1999, diesel was identified by the California Air Resources Board as a known human carcinogen. Eventually, it was generally thought that diesel particulate matter was the known carcinogenic entity, and so it became the focus of that program. EPA did a public health assessment in 2002 where they concluded that the data indicated that diesel particulate matter was a probable human carcinogen, and it became the focus at that point. Our current Oregon ABC, which was established in 2006, is based on these assumptions.

In 2012, the International Agency for Research on Cancer concluded that whole diesel exhaust was a known rather than a probable carcinogen, based on data available at that time. Downing described details from a number of studies on diesel particulate matter.

Downing noted that he has been pushing for the past 14 years, as a DEQ representative, to clean up diesel engines. Through various funding mechanisms, DEQ has been able to provide technical and financial assistance for people to change out older, traditional diesel engines to reduce the impact from diesel emissions originating from traditional diesel engines. All of this work has made headway, but it is still inadequate in terms of protecting people from exposure to diesel particulate emissions.

Downing then did a search for studies that looks at the toxicity of diesel particulates, and elemental carbon or black carbon, and compiled the information in a paper he wrote, and has provided to the committee. He focused on primary particulates and associated health effects. The data are clear on the cancer risks and heart disease associated with exposure to diesel emissions, and indicates effects on the overall cardiovascular system and nervous system as well, with possible connections to autism and the development of brain tumors. It's been found that the children of parents who were exposed to diesel at their jobs (occupational settings), have an increased incidence of brain tumors. Interestingly, it appears that the fathers who were exposed through their occupational settings have the most to do with passing on the effects of diesel exposure to their children, which might mean that the time of conception is actually more important in terms of toxic effects than the long gestational contact the fetuses have with the mother. This may be primarily a reflection of impacts to the immune system, or via immunogenicity, which led to a higher risk for brain tumors in the child nine months later, or within several months after birth.

Downing described the types of diesel exhaust control mechanisms that are available, and exactly how they work. In some cases that Downing described, the control mechanisms actually produced emitted air that was cleaner than the air pulled from the laboratory where the testing was conducted; so the control mechanisms are extremely effective at controlling the toxic diesel emissions being generated by the engine.

People living within approximately 500 meters of a roadway are suffering high exposures to diesel emissions. Furthermore, there are a huge number of people who travel *on* the roadway, and are exposed to even higher concentrations of diesel emissions, particularly during rush hours. A substantial portion of a person's exposure to diesel particulate occurs during his/her commute time; so, although that person is spending a relatively small part of their day commuting, they are getting hit with high doses of diesel emissions during that time. So it's important to understand that the new technology diesel



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engines produce significantly lower emissions of diesel particulates – in some cases, up to 99 percent lower emissions. Studies have shown that there’s also a 96 to 99 percent reduction in elemental carbon and organic carbon. Also, and thus, the emission technology on the new engines materially changes the pollutants that come out of the engine, as compared to those that are generated by older, traditional diesel engines. This will impact decisions we make on which chemicals to monitor for and how to determine impacts from this altered set of chemicals in the emissions from new technology diesel engines.

Heavy-duty diesel engines make up only 6 percent of the vehicles used in Oregon, but contribute 70 percent of the particulate matter and 35 percent of the nitrogen oxides, also referred to as “NO_x.” Note that heavy-duty trucks weight more than 26,000 pounds. In terms of fleets of diesel-engine trucks, there is a mix of pre- and post-2007 engines (i.e., traditional diesel engines versus new technology diesel engines). But we don’t know what this mix is, or how quickly it is changing. In regard to the Oregon truck fleet, heavy-duty trucks (weight greater than 26,000 pounds) are required to register in any state that they operate in. So, a person could choose to register a truck for operation in Oregon, or could choose to register in other states where the truck will operate, as well. Multi-state trucks and Oregon-based trucks are commonly discussed.

Companies tend to buy new diesel-engine trucks, drive them 100,000 to 120,000 miles per year for five to six years, and then sell them. So the purchasers continue to use old, more broken-down trucks, including here in Oregon, among other places. About one third of the multi-state trucks still have traditional diesel engines (320,000 trucks total); Oregon-based trucks make up about 53,000 of the 320,000 traditional diesel engines being used in the region. Downing doesn’t yet have good data to figure out what the migration rate of traditional diesel engines from California is. Trains and ships are more locally impactful; people nearby are potentially highly impacted (e.g., Brooklyn Yards area in Portland). Regionally, these train- and ship-based diesel emissions are a small piece of the total diesel emissions pie. More importantly, older trucks from outside of Oregon, with older engines that emit high levels of diesel particulates, are still being used in Oregon to a significant degree.

A number of technical papers, including Jansenn et al., suggest the use of elemental carbon or even black carbon as analytical markers that could present diesel emissions. Jansenn himself may even be available to the committee by phone, although he is located in the Netherlands. Jansenn’s work indicates that there are strong correlations between black carbon and long-term and short-term mortality, morbidity, and health effects, which may mean that black carbon is a better indicator than particulate matter of potential harm from emissions coming from combustion sources. But Jansenn also suggests that black carbon may not be a major toxin in itself, but rather a carrier for the compounds that are responsible for the harmful health effects that you see expressed.

Hope pointed out that this discussion is now using the terms “elemental carbon” and “black carbon” interchangeably, which is likely incorrect and definitely confusing. Downing agreed that these two terms need to be specifically defined and differentiated. Hope then asked if the EPA has a good, detailed description of black carbon versus elemental carbon and how they’re analyzed, and where they fit on a continuum of potentially related effects. Downing suggested that Antony Barnack, who will give the next presentation, may be better able to answer this question. A committee member



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clarified that he thought Downing was suggesting that an ABC for diesel particulate matter not be eliminated, but rather than an additional ABC for black carbon be identified to use as a marker in conjunction with diesel particulate matter monitoring and analysis.

MacMillan pointed out that a couple of the technical papers provided to the committee do differentiate between elemental carbon and black carbon, but that more papers than not seem to use the terms interchangeably, which is confusing.

Lambert mentioned that that the committee probably does not have adequate information to choose a compound, such as elemental carbon, to serve as an absolute substitute for diesel particulate matter. Use of something like elemental carbon as an additional piece of information in the assessment of diesel particulate matter might be a consideration. It should be noted that there is no way to measure diesel particulate matter directly.

Downing brought up other points about older trucks being moved out of California into other states, including Oregon and even Vancouver, British Columbia, without very much informative documentation of that fact. Because of the registration protocols, it's possible for companies that have purchased new trucks and used them for 5 or 6 years to move equipment out of state, and not have it show up in any kind of records database. For example, the film industry is doing a lot of filming in Vancouver due to lower costs, and they're bringing up old equipment, including trucks, and operating it in Vancouver to support the filming efforts. So it's clear that people are making this wide-ranging business decision to simply move their old equipment out of state, rather than retrofitting the old engines with control technology. But we don't have the data to quantifiably track this trend.

A committee member asked if Downing could talk more about the diesel emissions coming from Brooklyn Yard in Portland. Downing explained that, in regard to Brooklyn Yard, diesel emissions coming from trains and ships in that area make up a relatively small piece of the pie of total diesel emissions regionally, but are almost certainly impacting the people who live near Brooklyn Yard to a much higher degree. For about 14,000 people or so that are located near Brooklyn Yard, they experience an increased risk for cancer that is specific to the operations in the yard, aside from any potential exposure impacts due to garbage trucks, transit buses, and other trucks that are operating in the area. The health impacts from Brooklyn Yard could be substantial for the nearby population.

A committee member asked Downing if he was aware of other standards or regulatory approaches that have used something other than elemental carbon or black carbon as a marker for diesel emissions, because it seems like using a combination of more than one indicator to ascertain diesel emissions toxicity would be very difficult to use as an enforcement tool. Downing clarified that in terms of health effects, he had seen more technical study information on elemental carbon than he had on black carbon. He also acknowledged that combining the use of elemental carbon as an assessment tool with diesel particulate matter benchmarks would be difficult.

Swab, as a point of clarification, advised the committee that the 2011 Emissions Inventory data, upon which much of the committee's discussion regarding current air quality information will rest, will list diesel particulate matter as a compound along with its air emission information. But because EPA hasn't recognized diesel particulate matter



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as a known human carcinogen, EPA won't use it to assess risk in the National Air Toxics Assessment (NATA) report. Therefore, although diesel particulate matter will be reported in the Emissions Inventory, it won't show up as part of the upcoming NATA report for risk assessment.

Presentation: Diesel talking points (Bruce Hope, ATSAC member)

Hope will send the committee an EPA report appendix that provides good definitions of each of the carbon types, because we have to be careful not to equate black carbon with elemental carbon. One paper proposed the monitoring and analysis of black carbon as well as diesel particulate matter, to serve as an additional marker, rather than as a replacement for diesel particulate matter.

In terms of how diesel engines operate, air, diesel fuel, and lubricating oils are part of the mix. An incomplete combustion process occurs, and which generates gaseous emissions, oxides, monoxides, for which we have protective standards. Heavy-molecular-weight hydrocarbons, which are also generated during the incomplete combustion process, appear as vapors and liquid droplets. Soot is also generated, which conglomerates on particles that are about 0.1 micron in diameter. Particles of this size are typically referred to as ultrafine particles, and are a unique characteristic of this type of emission. Other parts mix with fly ash and heavy hydrocarbons to form what are called wet particles. So we're really dealing with gaseous components, vapor, aerosol components and soot and dry soot. But a lot of the focus is on this wet particle because it's a conglomeration.

An illustration of a typical particle of this type was shown on a slide. The particle is made up of an elemental carbon core; then it's layered with organic carbon compounds which include PAHs, and sulfates. The particle is primarily made up of carbon, but it also contains 20 percent to 40 percent by mass of dense or adsorbed compounds, and these adsorbed compounds are available to be released into the body when the particle is inhaled into the lungs. The particle diameter is such that it can penetrate very deeply into the lung, which results in greater health impacts. The PAHs make up a fairly low portion of these ultrafine particles, but they are present. So, once again, the core of this ultrafine particle is composed of elemental carbon, but it's surrounded by adsorbed organic material which is available to be released from the particle once it's taken into the body.

One of the issues with trying to assess the toxicity of diesel particulate matter – which is a complex mix of other compounds – is to determine where protective benchmarks are available for these compounds, which include high-molecular-weight hydrocarbons, the lighter-molecular-weight hydrocarbons, the related gases, NOx gasses, and PAHs. Benchmarks are available for many of these components, with the exception of ultrafine particles, for which benchmarks are currently unavailable. EPA has announced that they may assign a benchmark to ultrafine particles in 2017, but a lot of technical review and other work will have to be accomplished first.

Vermeulen's paper presents a risk estimate based on elemental carbon as a surrogate for whole engine diesel exhaust. Hope went on to discuss the facts behind why it cannot be assumed that elemental carbon is only associated with diesel emissions; things like wood smoke also contribute significant amounts. Residential wood smoke, not just diesel emissions, need to be considered when assessing the potential impacts of elemental carbon, particularly in our urban areas here. In addition, if our fundamental health goal is proposed to be health protection from exposure to elemental carbon, then maybe we need



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to look at the bigger picture of related potential toxins. As we've discussed, a diesel particulate contains a carbon core that is surrounded by other compounds, some or all of which may or do have their own toxic effects.

Presentation: PAH and black carbon monitoring and analysis (Anthony Barnack, DEQ)

DEQ uses EPA Method TO-13a to analyze for PAHs, which are collected on PUF/XAD module systems from air ("PUF" stands for polyurethane foam; XAD is the name of a trademarked resin compound). Anthony can talk further with the staff at the DEQ laboratory to determine what other compounds can be assessed, and can also work with Anderson's and Simonich's people at OSU to obtain various laboratory standards and discuss other types of available analytical methods. DEQ doesn't have the time or money to develop its own analytical methods, so DEQ depends on help from the university. A committee member asked Barnack if the DEQ lab has problems with obtaining adequate reproducibility in regard to PAH lab standards, which is an issue that Anderson had just discussed. Barnack will need to talk to a couple of DEQ lab people to answer this question.

A committee member pointed out that the DEQ laboratory is actually extracting the organic layers off of diesel particles. Barnack responded by saying that diesel particulate matter is the only compound that is defined based on its source; and the sources of diesel particulate matter are multiple, so it's very hard to pin down diesel particulate matter. Currently, no analytical method specific to diesel particulate matter is available; instead, black carbon is analyzed and used as a surrogate for diesel particulate matter, in tandem with EPA conversion factors.

The DEQ uses aethalometers to measure particulates with a diameter of 2.5 microns, also referred to as PM_{2.5}. An aethalometer is an instrument that measures the concentration of optically-absorbing ('black') suspended particulates in a gas colloid stream. Although this method collects black carbon, it does not provide a way to determine where the black carbon originated: in other words, it cannot reveal where the source(s) of black carbon in that sample come from. Also, as the collected black carbon is converted to diesel particulate matter concentrations, we need to be aware that there are a lot of assumptions that go into this modeling effort -- including assumptions about diurnal patterns of air compounds, meteorology, and other parameters -- in the effort to identify the sources of the emissions. For example, more organic carbon is present in air in the evenings, which is probably due to the use of woodstoves. Note that particulates of 0.1 micron or less in diameter are typically referred to as "ultrafine particulates," or PM_{0.1}. This smaller particulate fraction is collected as a part of the mix of larger particulates, such as PM_{2.5}.

Barnack is the Ambient Monitoring Coordinator for DEQ, and also coordinates the monitoring that DEQ conducts at sites around the state, with an emphasis on monitoring in the Portland area. DEQ also works with the Lane Regional Air Protection Agency in regard to air toxics monitoring in Lane County. Barnack will discuss what DEQ does in regard to air assessment, how DEQ monitors air compounds and how DEQ does their laboratory analysis.

Currently DEQ has a monitoring site in North Portland, one at Swan Island, and one in La Grande, and one planned for installation in Fall 2015 in Gresham. Currently, there are two air monitoring stations in Eugene, as well. In the past, DEQ has operated sites in



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Hillsboro, northwest Portland, Salem, Medford, and Klamath Falls. One of the challenges that DEQ faces over this next year is choosing five new locations. DEQ will choose these as part of 2015 the five-year monitoring plan that identifies new locations where the agency would like to place air monitoring stations.

Placement of new air monitoring stations depends on things like population density in the area, whether or not the area is one that has been previously monitored by DEQ, where sources of air pollution are located, and similar considerations. The Swan Island site only has funding for one year for source monitoring, and so the DEQ is asking legislature to provide additional funds in order to continue use of that monitoring station. Currently, the air monitoring station at Swan Island is located on the bluff by the University of Portland to monitor Swan Island. If the agency does get additional funding, then DEQ can identify other areas of the state for potential air monitoring which may be impacted by sources near buildings and communities, where higher concentrations of air chemicals may exist. To clarify, the community sites which are located near sources and which are being considered for monitoring may not actually have impacts from high concentrations, but the results should tell us what people living there are actually being exposed to.

The DEQ analyzes PAHs using the EPA TO-13a method, and based on the list of PAHs that EPA requests from us. EPA stipulates to DEQ the type of analytical extraction that should be performed, the type of analytical method, and the type of analytical matrix to use. The laboratory has found that the polyurethane foam used for PAH sample collection is not adequate for certain chemicals, especially naphthalene, so EPA has updated the method to include XAD to address this problem.

Once the lab puts the sampling equipment together, they install it on a sampler which runs at 230 liters per minute, which is equivalent to 331,200 liters per sample, during a 24-hour time period. Typically, they let the system run from midnight to midnight. Then they pick the sample up with 48 hours, transport it to the lab, and store it at 4 degrees Celsius until it's analyzed.

Because EPA is paying for two of Oregon sites that are national air ambient air toxics trend sites, they tell DEQ what to monitor for. However, throughout the state, the problem that they face with this method is that most of the PAH concentrations that are obtained are below analytical laboratory detection limits. The lab detection limit is 0.6 nanograms per cubic meter. As a result, the lab only gets quantifiable detections for a subset of the chemicals we're assessing, due to the fact that many results are below the analytical detection limit; in fact, about 35 percent of the lab values are above detection limits.

Hope asked Barnack if DEQ is basically analyzing for the 16 PAHs that EPA requires. Barnack responded yes, along with some other PAHs. Hope then said that if the AT SAC recommends the use of additional PAHs, then the DEQ lab will not be obtaining results for all the PAHs needed. Barnack responded that the DEQ lab can, if needed, analyze for more PAHs than just the 16 that are required by EPA, but that so far no one has made a request like this. Barnack said he can check with the DEQ lab staff and see how many of the suggested additional PAHs can be analyzed for. The DEQ lab could probably also get some help from Anderson's group at PSU, if needed.



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Atkinson asked Barnack if the DEQ lab had experienced the same problems with reproducibility of the PAH standards that Anderson's group has had. Barnack responded that he was not the right person to ask, but believes that the DEQ lab also has problems with their analytical standards. Atkinson then asked some detailed questions about exactly what was done with the sampling equipment in preparation for extraction and analysis. Atkinson told Barnack that it appears that the method would allow DEQ lab staff to measure the PAHs directly associated with diesel emission. Barnack responded that this was correct, along with whatever else is present, and went on to say that it's really difficult to say that we can measure diesel particulate matter, because all the related particles, and/or black carbon, come from a lot of different sources. Also, the only method that Barnack was aware of to measure diesel particulate matter is to analyze for black carbon, and then provide some modeled calculations for the related diesel particulate matter. Elemental carbon is another type of compounds that is discussed as it's related to the assessment of diesel particulate matter, but the definition of elemental carbon itself is controversial. Because one of the methods is used to identify both black and elemental carbon based on a temperature cut-point, and because the cut-point is sometimes defined differently by different laboratories, there is quite a bit of confusion in regard to identifying amount of elemental carbon analytically. However, currently EPA has dealt with this issue by stating that the IMPROVE analytical method is the correct one to use when analyzing for elemental carbon.

So, DEQ has to take all of the black carbon data collected and, to try to figure out the sources from which it came, as well as assess multiple parameters (weather patterns, traffic patterns, seasonal variation, etc.) in order to make an educated estimate the source of the black carbon.

Barnack then asked Hope if he agreed that the diameter of diesel particulates is about one micron. Bruce responded that the diameter is much less than one micron. Barnack stated that aethalometers typically collect PM_{2.5} via a filter, so the smaller particles end up also being collected, but are not specifically identified as smaller particles during analysis.

During the analysis of air samples, the lab analytically looks at black carbon using two different types of wavelengths: called BC and ultraviolet. BC measures black carbon only, while ultraviolet measures both black carbon and organic carbon. These kinds of methods have indicated that in the evenings, organic carbon levels are a bit higher, which points to the source being wood stoves used for residential wood combustion activities. During morning rush hours, the lab sees a lot more black carbon, which indicates that the pollution is coming from traffic. Those are examples of the kinds of things DEQ has to consider when trying to ascertain the sources of black carbon in the air.

Concluding items

Lambert thanked the speakers for their presentations and for all of the information provided to the committee. Lambert then asked the audience for questions or comments, and reminded the audience that policy dictates that questions and comments first be written down on comment sheets and given to him.

There were no questions, so Lambert stated that the committee would again be discussing PAHs and diesel particulate matter at the upcoming June 2015 ATSAC meeting. MacMillan announced that the next meeting would be held on June 17, in the same conference room and at the usual time of 9 a.m. to noon.



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