

NPRI - Polycyclic Aromatic Hydrocarbons Subgroup

ENGO Position Paper February 2007

Prepared by Anna Tilman

1. Background

i) Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) constitute a class of chemical products made up of carbon and hydrogen atoms grouped into rings containing five or six carbon atoms. They include about 100 individual compounds that are formed during the incomplete burning of coal, oil and gas, wood, garbage, or other organic substances¹.

PAHs have been declared CEPA toxic and are listed as a group on Schedule I of CEPA 1999. Many individual PAHs meet criteria for persistence, bioaccumulation and toxicity, as defined by various international bodies². Some PAHs, such as benzo [a] pyrene, have been classified as probably carcinogenic to humans by the International Agency for Research on Cancer (IARC), while others such as benzo [j] fluoranthene are classified as possible human carcinogens. PAHs are introduced to the environment either in the gaseous phase or bound to particles, most commonly soot. PAHs are also usually found concentrated near specific point sources and their concentration tends to decrease rapidly with distance from their source.

PAHs are usually found as a mixture containing many compounds in materials such as soot or creosote and are emitted from natural and anthropogenic sources. Anthropogenic sources of PAHs include: aluminum smelters, residential wood heating, agricultural burning, wood waste incineration, creosote-treated products, oil spills, metallurgical plants, coking plants, and atmospheric fallout. The majority of anthropogenic sources are point sources that regularly release PAHs, either on a continuous or intermittent basis (e.g., foundries, coking plants, metallurgical plants), or non-point sources that release PAHs at a very specific time and place (e.g., urban sources, such as vehicle emissions or wood combustion), resulting in chronic exposure for living organisms.

In Canada, alumina & aluminum production and processing and iron & steel mills and ferro-alloy manufacturing account for approximately 94 % of all PAHs reported in Canada to the NPRI in 2003 (approximately 430 tonnes).

¹ http://www.hc-sc.gc.ca/hecs-sesc/exsd/pdf/polycyclic_aromatic_hydrocarbons.pdf

² PAHs as a group have been assigned Track 2 status under the Toxic Substances Management Policy (TSMP) because many sources are natural rather than resulting from human activity. They are listed on the UN/ECE POP Protocol as a toxic with the potential for long-range transport through the atmosphere.

While forest fires, which release about 2,000 tonnes of PAHs per year, are the single most important natural source of PAHs in Canada (Environment Canada, 1989), these releases are generally widely separated in time and space across the country and do not result in continuous exposure in any specific area.

ii) **Proposal for PAH additions to the NPRI**

In 2005, Environment Canada (EC) proposed the addition of 12 new Polycyclic Aromatic Hydrocarbons (PAH) to the National Pollutants Release Inventory (NPRI). At that time, 17 PAHs were listed on the NPRI (Part 2) (refer to Appendix for this list of PAHs on the NPRI). Reporting was triggered when the total PAHs emitted was 50 kg.

These additional PAHs included:

- Three PAHs from the Ontario Ministry of Environment (MOE) Ontario Regulation 127: acenaphtene (CAS No. 83-32-9), acenaphtylene (CAS No. 208-96-8), and fluorene (CAS No. 86-73-7); and
- Nine PAHs from the United States Toxic Release Inventory (TRI): 3-Methylcholanthrene (CAS No. 56-49-5), 5-Methylchrysene (CAS No. 3697-24-3), 1-Nitropyrene (CAS No. 5522-43-0), 7,12-Dimethylbenz(a)anthracene (CAS No. 57-97-6), Dibenzo(a,h)acridine (CAS No. 226-36-8), Dibenzo(a,e)fluoranthene (CAS No. 5385-75-1), Dibenzo(a,h)pyrene (CAS No. 189-64-0), Dibenzo(a,e)pyrene (CAS No. 192-65-4) and Dibenzo(a,l)pyrene (CAS No. 191-30-0).

At that time, ENGOs offered a two-phased approach regarding the addition of these PAHs:

Phase 1: 2006 Reporting Year

- 1) The 3 PAHs be added to the NPRI at the 5 kg threshold to harmonize with current Ontario requirements for the 2006 Reporting Year. The addition of these PAH to the NPRI offered several advantages including removal from the O. Reg.127/01 list to avoid duplicative reporting; to identify priorities for action and to support targeted regulatory initiatives.
- 2) The reporting for the 17 PAHs currently on the NPRI (Part 2) remain as is - that is, report each PAH if the sum total of the PAHs released on site or disposed of is 50 kg. (*No de minimus for individual PAHs*).

Phase 2: 2007 Reporting Year

- 1) The 9 PAHs on the TRI list should be added to the NPRI. Environment Canada should consider reviewing PAH reporting in general in terms of examining the possibility of harmonizing with the US TRI for better comparability.

The NPRI Working Group (WG) agreed to the addition of three MOE PAHs. Subsequently, EC added these PAHs to Part 2 of the NPRI beginning with the 2006 reporting year.

At the same time, the WG recognized there were issues related to the reporting of minimum amounts of PAH, including determining what may be an appropriate *de minimus* reporting threshold. Other issues identified included health and environmental questions, the prevalence of these PAHs in Canada and availability of detection techniques. EC created an *ad hoc* group to examine these issues. A summary of the findings of the ad hoc group is in the Appendix to this paper.

2. ENGO Position

ENGOS had supported the addition of the 3 MOE PAHs to the NPRI at the 5 kg threshold for the 2006 Reporting Year. In addition, ENGOS supported the addition of the TRI PAHs to the NPRI in that the lack of specific health and environmental considerations on these PAHs should not deter from the addition of these substances to the NPRI as the class of PAH substances as a whole are toxic. ENGOS were willing to consider a *de minimus* level for triggering reporting individual PAHs under the same conditions that currently exist for PAHs, that is, a 50 kg total PAH trigger.

Furthermore, while industry felt that these substances are emitted in “small amounts” and measurement and detection were difficult, ENGOS pointed to instrumentation that was available to detect such levels and that should present no barrier to reporting. In fact, all of the 9 PAHs can be detected using Gas Chromatography (GC) methodology.

4. Summary

The *NPRI Ad Hoc PAH Sub-group* agreed to the following recommendations:

- Add the 9 TRI PAHs to Part 2 of the NPRI for the 2006 reporting year for 3 to 5 years to assess the information collected by facilities
- Retain a 50 kg reporting threshold for Total PAH
- Add a 5 kg *de minimus* for each individual PAH (17 NPRI PAHs, 3 MOE PAHs and 9 TRI PAHs)

EC accepted this recommendation and proceeded to make the necessary changes. On the whole, ENGOS were satisfied with the outcome of this work and expect that EC will do further review on PAHs in terms of the value of information collected, the *de minimus*, and harmonization, where feasible with the U.S. TRI.

Appendix

A. The 17 PAHs on NPRI Part 2 (2005)

Name	CAS No.
Benzo(a)anthracene	56-55-3
Benzo(a)phenanthrene	218-01-9
Benzo(a)pyrene	50-32-8
Benzo(b)fluoranthene	205-99-2
Benzo(e)pyrene	192-97-2
Benzo(g,h,i)perylene	191-24-2
Benzo(j)fluoranthene	205-82-3
Benzo(k)fluoranthene	207-08-9
Dibenz(a,j)acridine	224-42-0
Dibenzo(a,h)anthracene	53-70-3
Dibenzo(a,i)pyrene	189-55-9
7H-Dibenzo(c,g)carbazole	194-59-2
Fluoranthene	206-44-0
Indeno(1,2,3-c,d)pyrene	193-39-5
Perylene	198-55-0
Phenanthrene	85-01-8
Pyrene	129-00-0

B. TRI Polycyclic Aromatic Hydrocarbons

B.1 Human Health

It was noted that reliable health-based and environmental information exists on only a few of the TRI PAHs under discussion and the potential health effects of the other less well-studied PAH are inferred from information on other PAHs.

- In numerous studies in laboratory animals, various PAHs have induced tumours following principally dermal exposure [see, for example, ATSDR (1990 (a;b), IARC (1983)]. Data are quite limited, however, on induction of tumours following exposure by routes by which the general population are principally exposed (i.e., inhalation and ingestion).
- Epidemiological studies have shown increased mortality due to lung cancer in humans exposed to coke oven emissions, roofing-tar emissions and cigarette smoke. Each of these mixtures contains potentially carcinogenic PAH and other carcinogenic and potentially carcinogenic chemicals, tumour promoters, initiators, and co-carcinogens (DHHS/ATSDR 1995).
- Though there have been increases in lung and skin tumour incidence in populations occupationally exposed to complex mixtures containing principally PAH, these data have been considered inadequate as a basis for assessment of the weight of evidence of carcinogenicity in humans (IARC, 1983; 1987). Moreover, it is not possible on the basis of these data to assess effects of individual PAH. The composition of mixtures to which these workers (principally those in coke production, roofing, oil refining, or coal gasification) are exposed may vary considerably from those in the general environment.
- Observed health effects may be due to confounding by concomitant exposure to other substances. Therefore, available epidemiological data are considered inadequate to assess the health risks (including carcinogenicity) of PAH in humans (Government of Canada, 1994).

B.2 Environmental Considerations

- In air, soil, and water, PAHs are mostly adsorbed to particulate matter, on which they are transported and can be degraded slowly. Since degradation is very slow in sediments, this medium is the major environmental sink for PAH.
- PAHs have been measured in water from railway and utility ditches at concentrations higher than those recognized to cause harmful effects to biota under laboratory conditions. Concentrations of PAHs in surface waters elsewhere in the country are orders of magnitude lower, and are below concentrations that cause harmful effects to aquatic biota.
- At several sites in Canada, including the tidal flats of Muggagh Creek in the vicinity of the tar ponds in Sydney Harbour, Nova Scotia, and near a former oil gasification plant at Kettle Creek, Port Stanley, Ontario, populations of aquatic organisms have been adversely affected by contamination by PAH. Moreover, PAHs in sediments from Hamilton Harbour, Ontario, have been associated with mortality of sensitive aquatic invertebrates under laboratory conditions.

- Under laboratory conditions, neoplastic effects such as liver tumours in aquatic organisms have been associated with exposure to PAH. Field evidence also supports this association. In Vancouver harbour, neoplastic liver lesions were observed in up to 75% of the English sole caught in areas where sediments are highly contaminated by PAHs.
- PAHs in the atmosphere are not considered to contribute significantly to stratospheric ozone depletion, global warming, or ground-level ozone formation.

B.3 Analytical Considerations (from G. Prill, personal communication)

All of the 9 PAHs can be detected using Gas Chromatography (GC) methodology. The sampling technique employed is referred to as MM5, and is designed to collect PAH components as well as other streams such as dioxins, furans, PCBs, and chlorophenols. Detection limits (ng/m³) are of course controlled by the total volume of sample collected. Instrumentally, approximately ~10 ng per analyte is required to enable detection using GC/MS SIM technology.

Adding these components to the standard mixture of PAHs components screened for does not affect the sampling protocol required. It is a minimal amount of extra effort on the analytical side. Analysis time is not increased. Primarily, just the standards and calibration effort is expanded.

B.4 References

1. ATSDR (Agency for Toxic Substances and Disease Registry), "Toxicological Profile for Benzo(a)pyrene", ATSDR/TP-88-05 (1990a).
2. ATSDR "Toxicological Profile for Polycyclic Aromatic Hydrocarbons", ATSDR/TP-90-20 (1990b).
3. DHHS/ATSDR; "Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)" p.22-3 (1995).
4. Government of Canada (Health Canada, Environment Canada), Polycyclic Aromatic Hydrocarbons", *Canadian Environmental Protection Act. Priority Substances List Assessment Report*. Ottawa, Canada (1994).
5. Government of Canada (Environment Canada). First Priority Substances List
6. (PSL 1). Ottawa, Canada (1989).
7. IARC (International Agency for Research on Cancer), "Polynuclear Aromatic Compounds, Part 1, Chemical, Environmental and Experimental Data", *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*, Vol. 32, Lyon, France, pp. 33-91(1983).
8. IARC "Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42", *IARC Monographs on the Evaluation of Carcinogenic Risk to Humans*, Suppl. 7, Lyon, France (1987).
9. Miller, Catherine. 2006. Hampshire Research.
10. Nathan, Tom. 2006. Research Director. National Environmental Trust.
11. Prill, Grant. 2006. ARC Labs.