

HEAVY METALS IN EUROPEAN MOSSES: 2010 SURVEY



MONITORING MANUAL

International Cooperative Programme on Effects of
Air Pollution on Natural Vegetation and Crops

<http://icpvegetation.ceh.ac.uk>



**UNITED NATIONS ECONOMIC COMMISSION FOR
EUROPE CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION**

**MONITORING OF ATMOSPHERIC DEPOSITION OF
HEAVY METALS, NITROGEN AND POPs IN EUROPE
USING BRYOPHYTES**

MONITORING MANUAL

2010 SURVEY

ICP Vegetation Coordination Centre

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In collaboration with the participants

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1. INTRODUCTION

The UNECE ICP VEGETATION

In the late 1980's, the International Cooperative Programme on the effects of air pollution on natural vegetation and crops (ICP Vegetation, formally ICP Crops) was established to consider the underlying science for quantifying damage to plants by ozone and other pollutants. Scientists from 35 countries currently participate in the ICP Vegetation. The programme is led by the UK and coordinated by the Centre for Ecology and Hydrology at Bangor.

The programme is part of the activities of the Working Group on Effects (WGE) under the Convention on Long-Range Transboundary Air Pollution (LRTAP), which covers the UNECE (United Nations Economic Commission for Europe) region of Europe and North America. The ICP Vegetation is one of several ICPs and Task Forces investigating effects of pollutants on waters, materials, forests, ecosystems, health, and mapping their effects in the ECE region. International cooperation to control pollution is strengthened by the LRTAP Convention. Its Protocols commit countries to reducing pollutant emissions by specific target years. Results from the ICPs are used in both the development of these Protocols and in monitoring their success in reducing the impacts of air pollutants on health and the environment. For further information on the LRTAP Convention, WGE, and other ICPs, please visit the web-pages listed in Annex 1.

Monitoring long-term and large-scale changes in heavy-metal deposition

Increased and excessive accumulation of heavy metals in the soil, ground water and organisms can cause retarded growth of trees and crops and increased levels of heavy metals in the food chain leading to man.

It is apparent that some heavy metals emitted into the air from sources such as industries and power stations are mainly spread locally around the emission source. The affected area might have a diameter of 10-50 km, depending on wind patterns and height of stacks. Examples of this kind of distribution are chromium and nickel. Other metals are transported longer distances due to the formation of a gaseous phase during combustion, leading to a very small and easily transported particles. This appears to be the case with arsenic, cadmium, lead, mercury and zinc. The LRTAP Convention has negotiated the Heavy Metal Protocol in 1998 in Aarhus (Denmark), committing parties to reducing emissions and consequent long-range transport of heavy metals (Working Group on Effects, 2004). However, further information is needed on the concentrations of heavy metals into environment deposition rates and pathways, and effects on human health and the environment. Data from the 2010 moss survey will add to that of previous European surveys in 1990, 1995, 2000 and 2005 (Harmens et al., 2008a), and thus will provide further information on temporal and spatial trends into concentrations of heavy metals in mosses in Europe at a high spatial resolution.

Mosses as biomonitors of atmospheric deposition of heavy metals

Anyone who wants to measure the fallout of heavy metals from the atmosphere has had access to an alternative that is both simple and inexpensive as compared with the rather arduous methods of analysing precipitation with respect to metal concentrations. The

dense carpets that *Hylocomium splendens*, *Pleurozium schreberi* and other pleurocarpous mosses form on the ground have turned out to be very effective traps of metals in precipitation and airborne particles. This allowed for a dense biomonitoring network to be established across Europe since 1990.

One of the main benefits to be gained from studying heavy-metal fallout through moss analyses is that metals are accumulated by the moss, leading to concentrations which are much higher than in air, rain and snow. The problems of contamination during sampling and analysis are therefore relatively small, and sampling can be carried out using relatively simple methods.

Mosses as biomonitors of atmospheric deposition of nitrogen

In the 2005 European moss survey, the total nitrogen concentration in mosses was determined for the first time. The spatial distribution of nitrogen concentrations in mosses appears to mirror atmospheric nitrogen deposition across Europe to a high degree and is potentially a valuable tool for identifying areas at risk from high atmospheric nitrogen deposition at a high spatial resolution (Harmens et al., 2008b). Determining the total nitrogen concentration in mosses again in the 2010 survey would allow investigation of temporal trends across Europe.

Mosses as biomonitors of atmospheric deposition of persistent organic pollutants (POPs)

In a pilot study, selected POPs will be determined in mosses for the first time within the framework of the European moss survey. Mosses have been applied in the past as biomonitors of POPs, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in particular, at the local or national scale (e.g. Lead et al., 1996; Zechmeister et al., 2003a). In this pilot study we will focus on PAHs, PCBs, polybromodiphenylethers (PBDEs; Mariussen et al., 2008), dioxins (Carballeira et al., 2006) and perfluorooctane sulfonic acid and its salts (PFOS), but other POPs could also be included if there is a national interest.

2. AIMS AND OBJECTIVES

The aims of the 2010 survey are to:

- characterise qualitatively (and quantitatively where possible) the regional atmospheric deposition of heavy metals, nitrogen and POPs in Europe.
- indicate the location of important heavy metal, nitrogen and POPs emission sources and the extent of particularly polluted areas.
- produce maps of the deposition patterns of heavy metals and nitrogen (and possibly for selected POPs) for Europe.
- help to understand the extent of long-range transboundary pollution.
- analyse temporal trends to establish the effectiveness of air pollution abatement policies within Europe.

3. SAMPLING PROGRAMME

Number of sampling sites

Similar to previous surveys each country should aim to collect at least 1.5 moss samples/1000 km². If this is not feasible, a sampling density of at least 2 moss samples per EMEP¹ grid (50 km x 50 km) is recommended. It is recommended to make an even and objective distribution of the samples whenever possible, and to have a more dense sampling regime in areas where steep gradients in the deposition of heavy metals can be foreseen. To aid the analysis of temporal trends in the concentration of heavy metals in mosses, it is recommended to collect samples from the same sites as in the previous surveys. Regarding the pilot study for POPs, a lower sampling density is anticipated, depending on national resources available.

Moss species

Only pleurocarpous mosses should be sampled. As in earlier investigations two pleurocarpous moss species are favoured: *Pleurozium schreberi* and *Hylocomium splendens*. However, in some countries it might be necessary to use other pleurocarpous species. In that case, the first choice would be *Hypnum cupressiforme*, followed by *Pseudoscleropodium purum* (Harmens et al., 2008a). The use of bryophytes other than *Hylocomium* or *Pleurozium* must be preceded by a comparison and calibration of their uptake of heavy metals relative to the main preferred species. For the correct nomenclature of moss species we refer to Hill et al. (2006). The POPs pilot study should be conducted with *Pleurozium schreberi* and *Hylocomium splendens* only (and possibly *Hypnum cupressiforme* as an alternative).

Field sampling

Sampling in the field should be done according to the following principles:

1. Each sampling point should be situated at least 3 m away from the nearest projected tree canopy: in forests or plantations primarily in small gaps, without pronounced influence from canopy drip from trees, preferably on the ground or on the level surface of decaying stumps.
2. In habitats such as open heathland, grassland or peatland, sampling below a canopy of shrubs or large-leafed herbs should be avoided, as well as areas with running water on slopes.
3. The sampling points should be located at sites representative of non-urban areas of the respective countries. In remote areas the sampling points should be at least 300 m from main roads (highways), villages and industries and at least 100 m away from smaller roads and houses.

¹ Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe. <http://www.emep.int/>

4. In mountainous areas such as the Alps the sampling points should be below the timberline in order to eliminate confounding influences of altitude on the heavy metal concentration in mosses (Zechmeister, 1995).
5. In order to enable comparison of the data from this survey with previous surveys, it is suggested to collect moss samples from the same (or nearby, i.e. no more than 2 km away but with the same biotope conditions) sampling points as used in previous surveys (at least the same sampling points as used in the 2000 and 2005 survey). In addition, sampling of mosses near (long-term) monitoring stations of atmospheric heavy metal, nitrogen or POPs deposition is recommended in order to directly compare their concentration in mosses with the accumulated atmospheric deposition.
6. It is recommended to make one composite sample from each sampling point, consisting of five to ten (ten for POPs) subsamples, if possible, collected within an area of about 50 x 50 m.

Mosses: In the composite sample only one moss species should be represented. The sub-samples should be placed side by side or on top of each other in large paper or plastic bags (POPs: polythene bags or glass jars), tightly closed to prevent contamination during transportation. The amount of moss needed is about one litre (or two litres when POPs analysis will be conducted as well). As some POPs are susceptible to volatilization and photochemical breakdown, samples for POPs analysis should be kept cool and in the dark at all times. Note: The latter is less important when analysing only the seven PAHs recommended by the EU (see annex 4).

7. Smoking is forbidden during sampling and further handling of samples, and disposable plastic, non-talcum gloves should be used when picking up the mosses. Do not use vinyl examination gloves if they are powdered with talcum as this will contaminate the samples.
8. Samples should preferably be collected during the period April - October. In arid regions of Europe it is advised to collect the samples during the wet season. Although the heavy metal concentration in *Hylocomium splendens* and *Pleurozium schreberi* appear not to vary with season (Thöni et al., 1996, Berg and Steinnes, 1997), this might not be true for other moss species (e.g. Couto et al., 2003; Zechmeister et al., 2003b) and all climates in Europe. Therefore, it is suggested to sample the mosses in the shortest time window possible.
9. Each locality must be given co-ordinates, preferably longitude and latitude (Greenwich co-ordinates, 360° system), suitable for common data processing.
10. In order to determine the overall variability associated with the entire procedure (sampling + analysis), multiple moss samples (at least 3 samples per site) must be collected from at least two sites with different levels of overall contamination (one expected to have a high level of contamination and one expected to have a low level of contamination based on the results of the 2005 survey). These multiple moss samples must be collected, processed and analysed individually in order to characterise the overall variability of the data.

4. ANALYTICAL PROGRAMME

Utmost care should be taken in order to avoid contamination from smoke and laboratory tables. The material should therefore be handled on clean laboratory paper, glass shields or clean polythene. Non-talcum, disposable plastic gloves should be worn and no metal tools should be used.

Cleaning and storing of moss samples

If the samples cannot be cleaned straight after sampling, they should be put into paper bags and dried and stored at room temperature (20-25°C) until further treatment. Alternatively, samples can be deep-frozen. For POPs analysis, samples should be stored at 4°C and in the dark (see Field sampling – point 6).

The samples should be carefully cleaned from all dead material and attached litter, so that just the green and green-brown shoots from the last three years growth are included. Brown parts should not be included, even if the green parts only represent the last two to three years of growth. Sampling of *Hylocomium splendens* in 2010 would include the fully developed segments from 2007, 2008 and 2009; any segments developed from the 2010 growing season should be discarded, unless sampled at the end of a full growing season in 2010.

If other moss species are collected, shoots corresponding to three years of growth are recommended for the analyses.

Drying of moss samples before determination of heavy metals and nitrogen

The samples should be dried to constant weight at 40°C, which is used as a reference for the calculations. It is recommended to record the drying loss at 40°C (compared to room temperature) for future reference. The rest of the dried material not used in analyses should be stored in an environment specimen bank for future investigations.

For mercury, analysis should be conducted on fresh material or material dried at a lower temperature than 40°C and the determination of drying loss at 40°C on a separate aliquot is recommended.

Drying of moss samples before determination of POPs

Preparations of the moss samples for the determination of POPs will depend on the compounds analysed and the analytical technique applied in the laboratory. For example, drying of moss samples for the determination of PAHs might be best done by freeze-drying (lyophilisation). However, laboratories need to check for losses of POPs in the various steps leading up to the analysis.

Determination of heavy metals

Digestion

Wet ashing of a homogeneous sub-sample is recommended for the decomposition of organic material. Dry ashing is not acceptable. The preferred method of digestion is microwave digestion. Wet ashing, using nitric acid, has been used in most countries in

the past and has proven to give reproducible results. If excess acid is evaporated, samples should not be allowed to become completely dry. **Note:** wet ashing should not be applied when INAA (Instrumental Neutron Activation Analysis) is used as analytical technique; a homogenous, dried sub-sample should be analysed without further pre-treatment.

Analytical technique

The metal determinations can be performed using various analytical techniques. Earlier studies have shown that both AAS (atomic absorption spectroscopy) and ICP-ES/MS (plasma emission spectroscopy) are suitable methods. INAA (instrumental neutron activation analysis) tends to give higher metal concentrations as it determines the total heavy metal concentration (Steinnes et al., 1993). Therefore, it is recommended to compare the results for INAA with other techniques such as ICP-MS using the same moss samples and include standard moss reference material to further compare the performance of these techniques (see below).

An intercalibration of the analytical procedure took place in 1995 and 2005, and will be repeated in 2010. For quality assurance purposes, participants must include the moss standards M2 and M3 that were used in the 1995 and 2005 survey (Steinnes et al., 1997; Harmens et al., 2008a). The moss standards must be analysed at the same time as the collected moss samples. The moss standards will be supplied at a reduced cost by Mr Eero Kubin, Finnish Forest Research Institute, Muhos Research Station, and the distribution of the standards will be coordinated by Juha Piispanen (Juha.Piispanen@metla.fi). Although no recommended values are available for POPs, M2 and M3 should also be included as standards in POPs analyses, to investigate whether recommended values can be established for several POPs. The following certified reference material of organic contamination has to be included for POPs: IAEA-140/OC Fucus (35g) from Analab (seaweed material containing organochlorine compounds (pesticides and PCBs) and petroleum hydrocarbons (aliphatic hydrocarbons and PAHs)).

For quality assurance and cross-border calibration purposes, participants are encouraged to exchange ca. six to ten moss samples (clean and three years growth selected) from selected sites near the border of the country with neighbouring countries.

The following elements with mainly anthropogenic and atmospheric origin should be determined: As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn. In addition, Al and Sb should be determined to indicate contamination of the samples by soil/the contribution of wind-blown dust and to indicate anthropogenic origin respectively. Other elements of national concern or local importance (e.g. Bi, Mo, S, Ti, Se) may also be studied. Including as many elements as possible will aid the identification of the sources of heavy metals by applying multivariate analysis.

Determination of nitrogen

The ICP Vegetation encourages participants also to determine the total nitrogen concentration in mosses and hopes to increase the spatial coverage of Europe in comparison to the 2005 survey (Harmens et al., 2008b). To directly compare the nitrogen concentration in mosses with atmospheric nitrogen deposition, it is recommended to include sites near monitoring stations of atmospheric nitrogen

deposition. Suggested methods for nitrogen analysis are Kjeldahl (wet digestion) and elemental analysis (Dumas method). For quality assurance purposes the nitrogen concentration in the moss standards M2 and M3 must be determined (in addition to any certified standards for nitrogen) along with the moss samples (see above). Recommended values for M2 and M3 for nitrogen were reported previously (Harmens et al., 2008a).

Determination of POPs

The ICP Vegetation encourages participants also to take part in the pilot study of POPs. Annex 4 provides a list of POPs recommended to be included. No specific analytical techniques are recommended at this stage due to the diverse nature of POPs.

5. FURTHER SITE-SPECIFIC DATA

To determine which site-specific parameters affect the heavy metal and nitrogen concentration in mosses, participants are encouraged to provide further site-specific data via Web MossMet. This will allow detailed geostatistical analysis of factors influencing element concentrations in mosses (Schröder et al., 2008). For further details, please contact Mr Winfried Schröder (wschroeder@iuw.uni-vechta.de) or Mr Roland Pesch (roland.pesch@uni-vechta.de).

6. DATA PROCESSING, REPORTING AND PUBLICATION

The Programme Coordination Centre for the ICP Vegetation (Bangor, UK) will be responsible for common data processing, the construction of maps and the final report. In collaboration with the ICP Vegetation Coordination Centre:

- Data regarding the moss standards will be processed further by Mr Eero Kubin (Finland) and Mr Eiliv Steinnes (Norway).
- Detailed geostatistical analysis of data provided to MossMet will be conducted by Mr Winfried Schröder and colleagues (Germany) in collaboration with the participants.

All data should be sent to Mr Harry Harmens, ICP Vegetation Coordination Centre (see front page for details). Please submit the data by e-mail as an Excel spreadsheet to hh@ceh.ac.uk

THE SPREADSHEET SHOULD CONTAIN THE FOLLOWING INFORMATION
(see Annex 2):

Country

Name, address, telephone no., fax no. and e-mail address for all participants

Analytical procedure used for each metal, nitrogen and POP, including sample preparation, digestion method and analytical technique.

Data in rows, with one row for each site sampled. The column headings should read:

Site name

Coordinates

Date sampled

Altitude (m above sea level)

Land cover (according to CORINE classification label level 3; see Annex 3)

Topography (plain or slope)

Any further details regarding the site or climate are optional

Moss species (see Hill et al., 2006)

For each metal, nitrogen and POP, the name and units of concentration. For each metal, nitrogen and POP the quantification limit of the applied analytical technique must be provided.

Data must also include the individual values (metals, N and POPs) for each moss standard, such that the mean value and standard deviations per moss standard can be determined for each participating laboratory. In addition, data for cross-border calibration should be clearly labelled.

A report will be prepared in 2013 that will contain European maps of heavy metal and nitrogen concentrations in mosses and wherever possible, an indication of temporal trends.

7. TIME SCHEDULE

The main sampling period will be April to October 2010 (or 2011, depending on available funding). Data should be submitted to the Coordination Centre as soon as possible, but no later than 1 September 2011 (or 1 April 2012 if survey conducted in 2011). It is envisaged that preliminary maps will be produced by September 2012, and a final report will be prepared early 2013.

8. FUNDING

Sampling and analyses must be paid for by each country separately. Coordination and collating data by the ICP Vegetation Programme Coordination Centre will be funded by the Department for Environment, Food and Rural Affairs (Defra), UK.

9. REFERENCES

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Annex 1

WWW LINKS

ICP Vegetation <http://icpvegetation.ceh.ac.uk>

UNECE <http://www.unece.org>

LRTAP Convention <http://www.unece.org/env/lrtap/welcome.html>

Working Group on Effects

<http://www.unece.org/env/lrtap/WorkingGroups/wge/welcome.html>

This web-page contains links to the other ICPs and the Task Force on Health.

EMEP <http://www.emep.int>

With links to MSC-West and MSC-East.

Stockholm Convention on persistent organic pollutants (POPs) - <http://chm.pops.int>

Annex 2

Template data sheet

Country																						
For all participants:																						
Name																						
Address																						
Tel.																						
Fax																						
e-mail																						
Full description of analytical procedure for each metal, N and POP, including sample storage and preparation, digestion method and analytical technique																						
Site name	Longitude	Latitude	Sample date	Altitude (m)	Land cover	Topography	Further details	Moss species	Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	V	Zn	N	Each POP
	xx°xx'xx" or in decimals	xx°xx'xx" or in decimals	dd/mm/yr		See annex 3	Plain or slope	Site or climate		(ug/g)	(ug/g)	(ug/g)	(mg/g)	(unit)									
Quantification limit for each metal																						
Also include:																						
Values for all moss standard runs (M2 & M3)																						
Data to determine overall variability (see Monitoring Manual, field sampling bullet point 10)																						
Also include cross-border calibration data (if done any)																						

Annex 3

Corine Land Cover 2000 classes

Code Level 3	Label Level 1	Label Level 2	Label Level 3
111	Artificial surfaces	Urban fabric	Continuous urban fabric
112	Artificial surfaces	Urban fabric	Discontinuous urban fabric
121	Artificial surfaces	Industrial, commercial and transport units	Industrial or commercial units
122	Artificial surfaces	Industrial, commercial and transport units	Road and rail networks and associated land
123	Artificial surfaces	Industrial, commercial and transport units	Port areas
124	Artificial surfaces	Industrial, commercial and transport units	Airports
131	Artificial surfaces	Mine, dump and construction sites	Mineral extraction sites
132	Artificial surfaces	Mine, dump and construction sites	Dump sites
133	Artificial surfaces	Mine, dump and construction sites	Construction sites
141	Artificial surfaces	Artificial, non-agricultural vegetated areas	Green urban areas
142	Artificial surfaces	Artificial, non-agricultural vegetated areas	Sport and leisure facilities
211	Agricultural areas	Arable land	Non-irrigated arable land
212	Agricultural areas	Arable land	Permanently irrigated land
213	Agricultural areas	Arable land	Rice fields
221	Agricultural areas	Permanent crops	Vineyards
222	Agricultural areas	Permanent crops	Fruit trees and berry plantations
223	Agricultural areas	Permanent crops	Olive groves
231	Agricultural areas	Pastures	Pastures
241	Agricultural areas	Heterogeneous agricultural areas	Annual crops associated with permanent crops
242	Agricultural areas	Heterogeneous agricultural areas	Complex cultivation patterns
243	Agricultural areas	Heterogeneous agricultural areas	Land principally occupied by agriculture, with significant areas of natural vegetation
244	Agricultural areas	Heterogeneous agricultural areas	Agro-forestry areas
311	Forest and semi natural areas	Forests	Broad-leaved forest
312	Forest and semi natural areas	Forests	Coniferous forest
313	Forest and semi natural areas	Forests	Mixed forest
321	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Natural grasslands
322	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Moors and heathland
323	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Sclerophyllous vegetation
324	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Transitional woodland-shrub
331	Forest and semi natural areas	Open spaces with little or no vegetation	Beaches, dunes, sands
332	Forest and semi natural areas	Open spaces with little or no vegetation	Bare rocks
333	Forest and semi natural areas	Open spaces with little or no vegetation	Sparsely vegetated areas
334	Forest and semi natural areas	Open spaces with little or no vegetation	Burnt areas
335	Forest and semi natural areas	Open spaces with little or no vegetation	Glaciers and perpetual snow
411	Wetlands	Inland wetlands	Inland marshes
412	Wetlands	Inland wetlands	Peat bogs
421	Wetlands	Maritime wetlands	Salt marshes
422	Wetlands	Maritime wetlands	Salines
423	Wetlands	Maritime wetlands	Intertidal flats
511	Water bodies	Inland waters	Water courses
512	Water bodies	Inland waters	Water bodies
521	Water bodies	Marine waters	Coastal lagoons
522	Water bodies	Marine waters	Estuaries
523	Water bodies	Marine waters	Sea and ocean

Annex 4

Recommended list of persistent organic pollutants (POPs)

Name/Synonym	Group	EMEP modelled	POPs	Stockholm	Notes
			Protocol	Convention	
PCB	Polychlorinated biphenyls		x	x	Dielectric fluids in transformers, capacitors, coolants
BDE-x	Polybromodiphenylether	BDE-28, 47, 99, 153		2009	Flame retardants
HBB	Polybrominated biphenyls			2009	Flame retardants, see polybromodiphenylether
HxCDD	Polychlorinated dibenzo-p-dioxins (PCDD) (Dioxins)	x	x	x	PVC production, industrial bleaching, incineration
PFOS	Perfluorooctane sulfonic acid and its salts			2009	(Fluoro)Surfactant
	PAHs				
Benzo(a)anthracene	EU, US EPA				Seven EU PAHs are non-volatile and the most toxic
Benzo(j)fluoranthene	EU				
Benzo(b)fluoranthene	EU, POPs Protocol indicator, US EPA				
Benzo(k)fluoranthene	EU, POPs Protocol indicator, US EPA				
Benzo(a)pyrene	EU, POPs Protocol indicator, US EPA	x	x		
Dibenzo(a,h)anthracene	EU				
Indeno(1,2,3-cd)pyrene	EU, POPs Protocol indicator, US EPA				
Naphthalene	US EPA				
Acenaphthylene	US EPA				
Acenaphthene	US EPA				
Fluorene	US EPA				
Phenanthrene	US EPA				
Anthracene	US EPA				
Fluoranthene	US EPA				
Pyrene	US EPA				
Chrysene	US EPA				
Dibenzo(a,h,)anthracen	US EPA				
Benzo(g,h,i)perylene	US EPA				