Invertebrate life cycle responses to PAC exposure

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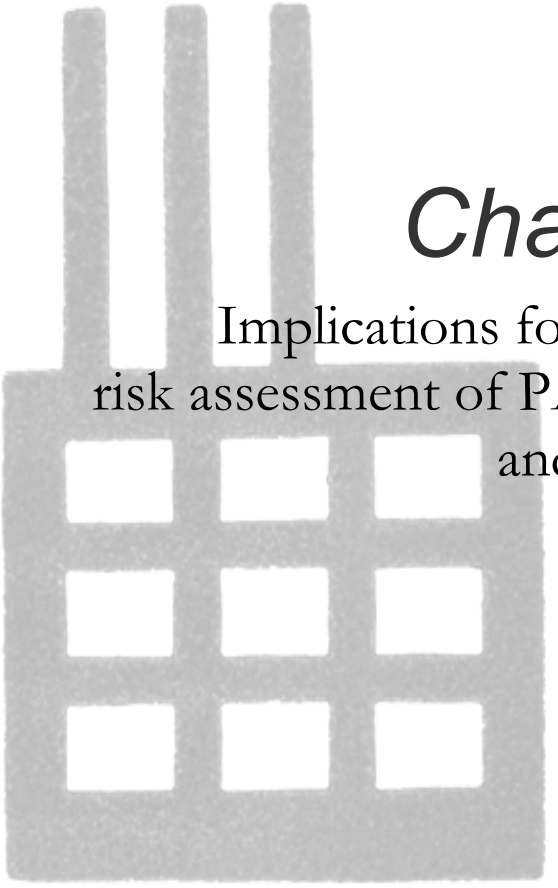

Chapter 7

Implications for ecological risk assessment of PACs in soils and sediments

7.1. Current methodology for PAC risk limit derivation

Following the Technical Guidance for the derivation of risk limits (Van Vlaardingen and Verbruggen, 2007), Maximum Permitted Concentrations (MPC, also called 'risk limit') and Negligible Concentrations (NC, MPC divided by 100) are estimated from single compound toxicity data. It is assumed that at toxicant concentrations above the MPC the risk of adverse effects is high and intolerable; and at concentrations below the NC there is no significant risk of adverse effects for the exposed organisms. In the Netherlands, the ideal risk limit derivation method is based on statistical extrapolation of a 'hazard concentration' from a species sensitivity distribution (SSD). Such an SSD brings together a dataset on the toxicity of a single compound (Posthuma et al., 2001; Van Vlaardingen and Verbruggen, 2007). To create SSDs, No Observed Effect Concentration (NOEC) and/or 10% Effect Concentrations (EC10) are needed for at least eight species belonging to different taxonomic groups. Unfortunately, for the few homocyclic PACs (10 in the Netherlands, Figure 1) for which risk assessment is performed, at the moment too few soil and sediment toxicity data are available to generate SSDs. In such cases, a risk assessment is performed in which the derivation method depends on the availability of PAC toxicity data (Table 1). If some chronic soil/sediment toxicity data are available, the lowest reported effect concentration is used to derive an empirical MPC, which will prevail in the risk assessment. If only acute toxicity data are available, the MPC is also derived using the lowest reported effect concentration, but the next step in the process involves the comparison of the empirical MPC with an Equilibrium Partitioning (EqP) MPC. The EqP MPC is a soil/sediment concentration (mg/kg), estimated from the MPC for the aquatic environment using soil/sediment-water partitioning coefficients. The empirical and EqP MPCs are compared and the lowest value is (usually) set as MPC. If no soil/sediment toxicity data are available, the EqP MPC is used.

The Dutch Ministry of Housing, Spatial Planning and the Environment uses the derived MPC, always expressed as total concentration of the compound in soil or sediment, to set an Environmental Quality Standard (EQS), which is usually the same value (Kalf et al., 1997). It is assumed that if total concentrations of the (group of) toxicants of interest measured at a site are above the EQS, exposed species are at risk, and there is a legal obligation to take measures to reduce contamination. In the Netherlands, the sum of risk quotients for 10 homocyclic Polycyclic Aromatic Hydrocarbons (PAHs, som10 PAK, Figure 1) is used as screening value for PACs in site-specific risk assessment. The risk quotient for the site is obtained dividing each

measured single-PAH concentration by its EQS, and summing up the 10 values. Risk due to exposure to PAHs is present If the risk quotient is higher than 1.

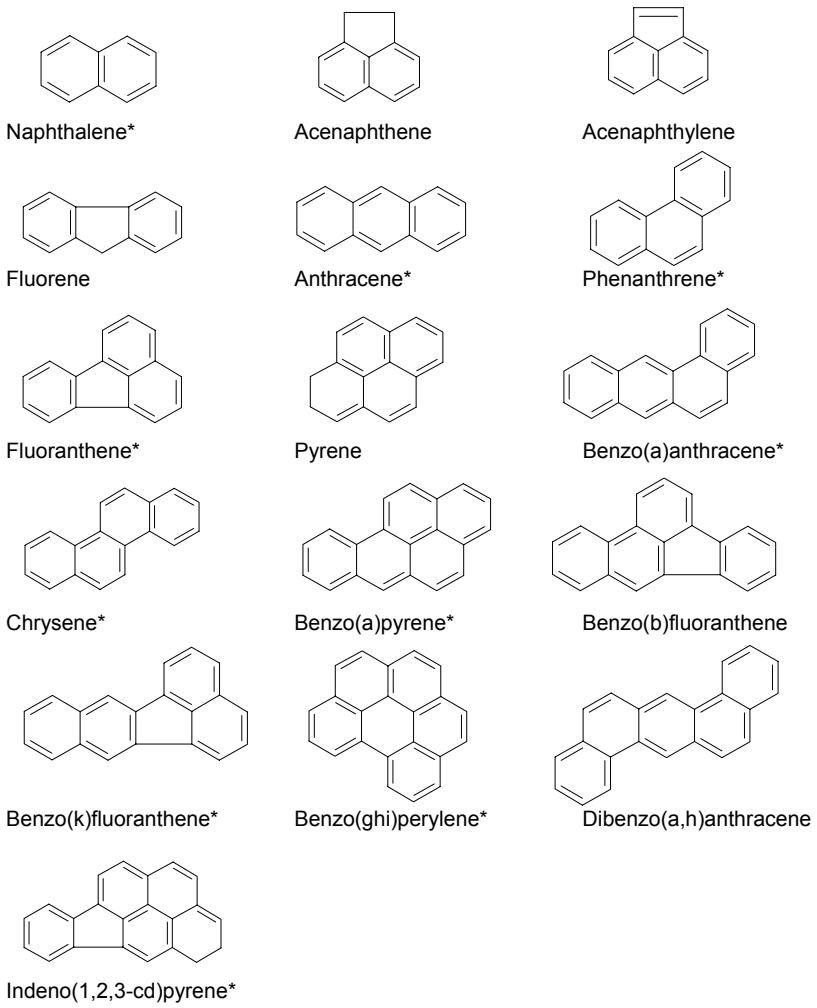

Figure 1. Polycyclic Aromatic Hydrocarbons (PAHs) included in the risk assessment performed by the Dutch and US Environmental Protection Agencies (respectively RIVM and US EPA). All PAHs are used by the US EPA, RIVM PAHs are marked with an asterisk (*).

Table 1. Risk limit derivation method and assessment factors applied according to effect data availability in the derivation of soil and sediment risk limits (van Vlaardingen and Verbruggen, 2007). LC/EC: Lethal Concentration/Effect Concentration; NOEC: No Observed Effect Concentration; EqP: Equilibrium Partitioning; MPC: Maximum Permitted Concentration; SSD: Species Sensitivity Distribution; NC: Negligible Concentration; PNEC: Predicted No Effect Concentration.

procedure	effect data	derivation method	assessment factors	risk limits
preliminary risk assessment	none	EqP	from aquatic MPC (1-1000)	**MPC, NC** **PNEC**
	acute LC/EC	empirical, comparison with EqP MPC	1000	
	chronic NOEC (<8)	empirical	10-100	
refined risk assessment	chronic NOEC (>8)	SSD	expert judgement	
	mesocosm	-	expert judgement	

The lack of chronic toxicity data is a recognized problem which hampers an accurate derivation of PAC EQSs. For anthracene and phenanthrene no sediment and soil toxicity data were available when the Dutch MPCs were derived in 1995 (Kalf et al., 1997), while these compounds are nearly always measured in PAC contaminated sites, so quality standards were required (Khodadoust et al., 2005; Kitazawa et al., 2006; Liu et al., 2004; Prevedouros et al., 2004; Srogi, 2007; Wild and Jones, 1995). Therefore, EqP MPCs were derived from aquatic toxicity data using high assessment factors (Kalf et al., 1997), and were consequently highly uncertain. In 2005, sediment MPCs for anthracene and other PACs (fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene and indeno(1,2,3-cd) pyrene) were derived in the context of the 'priority substances list' for the European Water Framework Directive (European Commission, 2005a; 2005b). The MPCs for anthracene and the five higher molecular weight PACs included in the list were again derived from effect concentrations for aquatic organisms, as reliable sediment toxicity data were still lacking (European Commission, 2005a; 2005b).

Parallel to the derivation of MPCs for single compounds in the context of the Water Framework Directive, environmental risk assessments (ERAs) are being performed at the European level to evaluate environmental risks due to industrial emissions of existing substances. When available, these risk assessments use chronic toxicity data to calculate soil and sediment Predicted No Effect Concentrations (PNECs). An example is the draft of the European risk assessment for high temperature coal-tar pitch (published in May 2008, (European Commission, 2008)),

which is coordinated by the Netherlands. Coal-tar pitch is a mixture of substances obtained from destructive distillation of coal at high temperatures (higher than 700°C), and is included in the European 'existing priority substances' list (production volume over 10 tonnes/year). PACs are the main contaminants present in coal-tar pitch, but the composition of the mixture varies depending on the coal used for the distillation. Soil and sediment PNECs have been derived for the traditional 16 EPA PAHs (Figure 1) based on literature data, which for the majority of these compounds have become available in the last few years. Chronic soil toxicity data for anthracene and phenanthrene from chapter 2 of this thesis were included in the derivation process (European Commission, 2008). It has to be kept in mind that contrary to EQSs, which are included in environmental legislation, PNECs only have an advisory status. However, the derivation method for PNECs and MPCs is the same (Table 1), implying that usually their values will be the same.

7.2. Derivation of empirical MPCs

Using the current Dutch guidance for derivation of risk limits (Van Vlaardingen and Verbruggen, 2007) we derived empirical MPCs for the six homo- and heterocyclic test compounds selected in this thesis (Table 2), by selecting the lowest reported EC10s from the available literature (Table 3). To derive these soil and sediment MPCs we recalculated the effect concentrations to standard soil, containing 2% organic carbon (European Commission, 2008), and standard sediment, containing 5.8% organic carbon. Different assessment factors were applied according to the data availability for the selected compounds (Table 3). For the homocyclic compounds, we compared the MPCs and PNECs with the current dutch EqP EQSs. For the two azaarenes and the two azaarene transformation products, which are currently not included in the risk assessment, we derived empirical MPCs based only on our data (Table 3). This allowed us to compare the empirical MPCs for homo- and heterocycles, and evaluate the possible inclusion of PAC heterocycles in the current PAC risk assessment.

7. 2. 1. Risk limits for homocyclic PACs

As mentioned before, soil toxicity data for the two homocycles (chapter 2) were already included in the coal-tar pitch risk assessment for the EU (European Commission, 2008), resulting in equal values for soil PNECs and soil MPCs of this thesis (Table 2). Therefore, we did not derive the MPCs again, but compared soil coal-tar pitch PNECs to actual Dutch soil EQSs instead. Sediment MPCs for the

homocyclic compounds could be compared to current Dutch EQSs and sediment coal-tar pitch PNECs.

Table 2. Dutch soil and sediment Environmental Quality Standards (EQS), Predicted No Effect Concentrations (PNECs) for coal-tar pitch risk assessment (European Commission, 2008) and Maximum Permitted Concentrations (MPCs) for selected homocyclic and heterocyclic aromatic compounds derived from data from this thesis (all in mg/kg DW standard soil/sediment). Grey cells: compounds not included in current PAC risk assessment. n.t.: not toxic; ANT: anthracene, PHT: phenanthrene, ACR: acridine, PHI: phenanthridine, ACO: acridone, PHO: phenanthridone. EqP: Equilibrium partitioning; emp.: empirical. * values include data from this thesis.

		EQS NL	PNEC ERA coal-tar pitch	MPC this thesis
	method	**EqP**	**emp.**	**emp.**
soil (mg/kg dw)	**ANT**	**0.1**	**0.1***	**0.1**
	PHT	**0.5**	**1.8***	**1.8**
	ACR			**3.2**
	PHI			**1.1**
	ACO			**n.t.**
	PHO			**n.t.**
sediment (mg/kg dw)	**ANT**	**0.1**	**0.1**	**0.2**
	PHT	**0.5**	**5.0**	**2.4**
	ACR			**0.5**
	PHI			**0.1**
	ACO			**0.4**
	PHO			**0.7**

Table 3. Summary of lowest reported effect concentrations and assessment factors used to derive MPC values for soil and sediment.

Comp.	organism	test	Endp.	EC	value	unit	derivation method	mg/kg dw st. soil/sed	ass. fact.	MPC/ PNEC mg/kg	reference
MPC soil											
MPC / PNEC ERA coal-tar pitch = MPC this thesis											
ANT	*F. fimetaria*	chronic	reprod.	EC10	5	mg/kg	empirical	6.3	50	**0.1**	Sverdrup et al. 2001
PHT	*F. fimetaria*	chronic	reprod.	EC10	9.4	mg/kg	empirical	18	10	**1.8**	Sverdrup et al. 2001
MPC this thesis											
ACR	*F. fimetaria*	chronic	reprod.	EC10	891	umol/kg	empirical	160	50	**3.2**	Droge et al. 2006
PHI	*E. crypticus*	chronic	reprod.	EC10	297	umol/kg	empirical	53	50	**1.1**	Droge et al. 2006

Table 3 (continued).

MPC sediment

MPC / PNEC ERA coal-tar pitch											
ANT	*C. riparius*	chronic	reprod.	LC10	-	mg/kg	empirical	14	100	**0.1**	Bleeker et al. 2003
PHT	*H azteca*	chronic	growth	NOEC	-	mg/kg	empirical	50	10	**5.0**	Verrhiest et al. 2001
MPC this thesis											
ANT	*L. variegatus*	chronic	reprod.	EC10	17	umol/kg	empirical	2	10	**0.2**	León Paumen et al. 2008b
PHT	*L. variegatus*	chronic	reprod.	EC10	187	umol/kg	empirical	24	10	**2.4**	León Paumen et al. 2008b
ACR	*L. variegatus*	chronic	reprod.	EC10	197	umol/kg	empirical	25	50	**0.5**	León Paumen et al. 2008b
PHI	*L. variegatus*	chronic	reprod.	EC10	37	umol/kg	empirical	5	50	**0.1**	León Paumen et al. 2008b
ACO	*L. variegatus*	chronic	reprod.	EC10	138	umol/kg	empirical	19	50	**0.4**	León Paumen et al. 2008b
PHO	*C. riparius*	chronic	reprod.	LOEC	506	umol/kg	empirical	71	50	**0.7**	León Paumen et al. 2008a

Sediment PNECs for the two homocycles were similar to sediment MPCs derived from our data: for anthracene, our MPCsed was 0.2 mg/kg dw and the PNECsed was 0.1 mg/kg dw; for phenanthrene, our MPCsed was 2.4 mg/kg dw and the PNECsed was 5.0 mg/kg dw. For the two homocyclic isomers, comparison of the soil and sediment PNECs / MPCs from this thesis with the Dutch EQSs showed that risk limits for anthracene were identical using either chronic toxicity data or the EqP derivation method. Consequently, the actual Dutch EQS is protective enough for chronic anthracene exposure in soils and sediments. For phenanthrene, in contrast, the empirical soil and sediment PNECs and our sediment MPC were about one order of magnitude higher than the current Dutch EQS. Thus, the current Dutch EQS for phenanthrene may be overprotective for chronic toxicity in soil and sediment.

Our risk limit derivation shows that the use of chronic toxicity data to derive MPCs is a robust method, that clearly diminishes the uncertainties associated to the derivation of MPCs using equilibrium partitioning. Similar to our findings, previous studies comparing EqP and empirical risk limits (Van Beelen et al., 2003) have shown that the use of chronic effect concentrations to derive environmental risk limits is a step forward to reduce uncertainties in PAC risk assessment.

7. 2. 2. Risk limits for heterocyclic PACs

Despite of their lower lipophilicity, soil MPCs for the two azaarenes were in the same range (3.2 and 1.1 mg/kg dw for acridine and phenanthridine, respectively) as the PNEC for the homocyclic phenanthrene (1.8 mg/kg dw). This means that the tested azaarenes exert toxic effects at similar concentrations in soil as one of the homocycles, and should therefore not be neglected. Empirical sediment MPCs for the azaarenes (0.5 mg/kg dw for acridine, 0.1 mg/kg dw for phenanthridine) and the transformation products (0.4 mg/kg dw for acridone and 0.7 mg/kg dw for phenanthridone) were one order of magnitude lower than soil MPCs, and similar to the lowest sediment MPC for the homocyclic analogues (0.2 mg/kg dw for anthracene). Remarkably, sediment MPCs for the transformation products were in the same range as MPCs for their azaarene parent compounds, whereas transformation products were not toxic at all for the soil test organisms and consequently no MPCs could be derived. The reason for the high toxicity of azaarenes and transformation products in benthic systems remains unclear, as discussed in chapter 5. Based on our results, we can conclude that heterocyclic PACs could and should be incorporated in PAC risk assessment. However, it has to be kept in mind that estimated azaarene concentrations in the field are usually one order of magnitude lower than concentrations of the homocycles (Neilson, 1998), and their contribution to the overall toxicity of PAC mixtures in the field may vary greatly from site to site

(Blotevogel et al., 2007; Lundstedt et al., 2007). At the moment, the lack of azaarene field measurements hampers an accurate estimation of the risk associated to this group of toxicants, and should obviously be addressed.

7. 3. Prospective PAC risk assessment

The European risk assessment for coal-tar pitch (European Commission, 2008), in which our soil data were included, shows the actual state of the art regarding PAC risk assessment, and identifies its shortcomings. However, it is also emphasized that the scientific underpinning of PAC risk assessment is limited and sometimes ambiguous. Knowledge gaps hamper in many cases the inclusion of aspects like availability, bioaccumulation and degradation; and force the choice for merely homocyclic PACs in the risk assessment procedures. In this thesis, some of these shortcomings were experimentally addressed. In the next paragraphs, possible applications and consequences of our findings and their implications for PAC risk assessment will be discussed.

- PAC availability:

PAC availability is known to be lower in aged soils and sediments compared to freshly spiked substrates (Kreitinger et al., 2007; Landrum et al., 1992; Northcott and Jones, 2001; Sverdrup et al., 2002c). Results from chapter 4 showed that available PAC concentrations in pore water decreased more than total concentrations in the sediment, even during the relatively short time span of a four-week chronic toxicity test. At the moment, risk limits are calculated using total concentrations and neglect bioavailability, although this is one of the major factors affecting PAC exposure in soils and sediments. In chapter 4 of this thesis we showed that with the available methodologies it is possible to calculate effect concentrations taking into account the real exposure scenario occurring in sediment. The use of effect concentrations based on the available fraction of the compound would undoubtedly reduce some uncertainties in risk limit derivation, but the methodological shortcomings associated to a relatively new method limit its direct application (Jensen and Mesman, 2006). Nevertheless, including a correction for PAC availability in site assessments may reduce to some extent risk overestimation due to the use of total PAC concentrations (Ghosh, 2007). Some efforts are already being made to incorporate PAC availability into site-specific risk assessment. The US EPA sediment benchmarks for homocyclic PAC mixtures (Driscoll and Burgess, 2007), for example, incorporate site-specific adsorption of PACs to black carbon; and thanks to the European project Liberation, a decision support system is now available allowing corrections, not only for historical

contamination, but also for background PAC concentrations in soils (Jensen and Mesman, 2006). This approach encourages the use of mild extraction methods or passive samplers, as we did in chapter 4, to quantify the toxic potential of historical PAC contamination, what is undoubtedly a step forward. The Liberation project shows that PAC contamination in soil has received some attention during the last years due to obvious implications for land use (e.g. agriculture, building sites). PAC contamination in sediment, however, is still frequently neglected, while it is especially important in deltaic countries like the Netherlands, where deposition of organic contaminants transported by the large rivers is widespread (Lahr et al., 2003; Peeters et al., 2001). Moreover, dredging and land disposal of contaminated sediment also increases the (sometimes highly available) toxicant concentrations in arable soils (Peijnenburg et al., 2005). Our empirical risk limits for the tested heterocycles (using total PAC concentrations) showed that benthic species may be at risk in more cases than soil species. The relatively low sensitivity of soil species has been documented previously (Kapustka, 2004a; Kapustka, 2004b), but more research is needed to explain the underlying mechanisms (e.g. metabolism, exposure route) that cause the differences in sensitivity of soil and sediment inhabiting species.

- Toxicity of homo- and heterocyclic PAC mixtures:

As discussed in chapter 5, effect prediction for the tested azaarenes and transformation products was subjected to larger uncertainties than predictions for their homocyclic analogues. Results from chapter 5 also showed that in many cases (mainly in soil) toxicity of heterocycles was governed by the same properties as toxicity of their homocyclic analogues, and therefore heterocyclic PACs might be easily incorporated into current PAC risk assessment. Still, the use of individual risk limits for the ecological risk assessment of complex PAC mixtures is clearly not effective and should be improved. The Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE) of the EU has already stated that a group approach to tackle PAC toxicity would be necessary in order to make risk assessment more realistic, but the SCTEE also argues that such an approach is not possible with the current scientific knowledge, and risk limits for single compounds still have to be used (European Commission, 2005a). This means that at the moment, PAC risk assessment can only be improved by increasing the number of compounds for which individual risk limits are derived. A USEPA guideline has been developed to derive sediment benchmarks for mixtures of up to 34 PACs using a toxic unit approach based on critical body burdens for chemicals acting by narcosis (Di Toro and McGrath, 2000; Di Toro et al., 2000; Hawthorne et al., 2006). In this guideline, corrections for uncertainties in field measurements due to incomplete datasets have been included,

because concentrations of the 34 PAHs are not always available in assessment datasets. Other studies have also used a toxic unit approach to calculate risk limits for specific homocyclic PAC mixtures in Danish soils (Jensen and Sverdrup, 2003b). These examples show that risk assessment is moving towards a more mixture driven approach, but still based on the use of toxicity data for single homocyclic compounds. As an alternative, a chemical fractionation-based approach (with lipophilicity as steering property) could be applied to quantify the toxic potential of the main fractions (homocyclic and heterocyclic) present in PAC mixtures. This is already being done in effect fractionation studies (Lundstedt et al., 2007; McGrath et al., 2005), which quantify the toxicity of the different fractions present in a mixture of chemicals. A similar approach has been applied by the Dutch Institute for Public Health and the Environment (RIVM) to calculate the risk associated to the different homocyclic chemical fractions present in mineral oil, making use also of critical body burdens for narcosis as standardized effect concentrations (Verbruggen, 2004). In this approach, availability could be incorporated by using passive samplers to quantify the toxicity of the available fraction in a PAC mixture (Leslie et al., 2002; Parkerton et al., 2000). Still, it should be kept in mind that deviations from narcosis like the ones observed in this thesis for the tested heterocycles in sediment could hamper the use of narcosis-based models to accurately predict risks associated to PAC contamination.

- Multi-generation effects

Nowadays, multi-generation effects are terra incognita in risk assessment. The few reported multi-generation experiments quantify effects during exposure for several generations and compare them to single-generation effect concentrations (as we did in chapter 6). Information obtained from these comparisons could be used to refine the choice of proper assessment factors in the derivation of risk limits, but at the moment too few studies are available to allow any generalization according to, for example, mode of toxic action of the test compound. Results from chapter 6 confirmed the existence of large uncertainties associated to multi-generation exposure to a ubiquitous homocyclic PAC (phenanthrene). The existence of a threshold concentration below which effects did not occur after several generations of exposure challenges the use of concentration-response relationships as is common practice in ecotoxicology. The fact that this threshold concentration was close to the one-generation EC50 is a clearly disturbing new insight for the traditional risk assessment, based on single generation effect concentrations. This threshold for multi-generation effects should be further investigated, yet our findings emphasize the importance of understanding the mechanisms behind observed effects of toxicants. By expanding the knowledge on molecular and physiological mechanisms, individual and even

population effects could be better understood, and a more comprehensive view on the consequences of multi-generation exposure might be achieved. This kind of research is currently receiving increasing attention, and experiments trying to link molecular and population effects are being performed for several 'model' test organisms (Connon et al., 2008; Heckmann et al., 2008; Roelofs et al., 2008). Hopefully, the knowledge gained in the laboratory will be used in the future to model the risk of long-term population effects in a more well-founded way.