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IN LCIA**

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MARINE ECOTOXIC PULSE EFFECTS IN LCIA

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Abstract – Fate modeling for characterization of ecotoxic substances in life-cycle impact assessment (LCIA) is traditionally performed with steady-state multi-compartment models. Instantaneous mixing within compartments is an implicit assumption of the multi-compartment model. Others have shown that steady-state models can account for pulse-exposure if the ecotoxic effect is calculated with a constant effect factor. The potentially affected fraction of species (PAF) has previously been used to derive ecotoxic effect factors. Time and space variant dispersion models (transient models) are used in marine ecological risk assessments for aquatic exposure from intermittent marine discharges. Transient models can implement continuous effect functions in pulse-exposure assessment. In this paper the significance of assuming constant effect factors is quantified by calculation of characterization factors for marine aquatic ecotoxicity with a transient dispersion model. Multi-substance PAF (msPAF) is used as definition of ecotoxic effect. Results show that for characterization factors with msPAF assuming concentration addition only, the deviation between a constant effect factor and a continuous effect function is small. This implies that pulse-effects are well handled with the traditional approach of approximating effect with constant effect factors. For msPAF defined with a combination of response and concentration addition, the deviation can be several orders of magnitude.

Key words – Life cycle impact assessment Ecotoxicity Pulse Transient Fate

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INTRODUCTION

Existing environmental legislation for offshore oil and gas activities in the North Sea is strongly focused on local and regional marine ecotoxic effects. Ecological risk assessments must be performed prior to any activity which may lead to marine discharges. Such assessments include transient simulation of dispersion of substances in the marine sediment and aquatic environment, and take into account currents and wind data, physio-chemical substance properties, degradation rates and threshold levels [1,2].

Offshore drilling operations on the Norwegian Continental Shelf must meet a number of restrictions for handling of their drilling waste. Discharges are permitted in some cases, while for most cases waste must be treated offshore or on shore. The current legislative trend is towards drilling performed as a closed-system, thereby allowing no marine discharges.

Life-cycle assessment (LCA) offers a methodology for environmental product assessment based on a systems life-cycle perspective. LCA addresses a number of environmental issues and represents an expansion of the perspective normally addressed in environmental assessment of offshore drilling technologies. Discharges from offshore drilling operations are intermittent, and while LCA as an assessment tool is applicable for offshore activities, the treatment of ecotoxic effect of pulse-emissions in life-cycle impact assessment (LCIA) is questionable. This specifically relates to ecotoxic effect being estimated with constant effect factors. Quantification of the significance of the assumption of constant ecotoxic effect factors is the objective of this paper.

Ecotoxic effect factors in LCIA are traditionally based on predicted no-effect concentrations (PNEC) [3], or derived from species sensitivity distributions (SSDs) like the potentially affected fraction of species [4,5]. Although a continuous function of concentration, multi-substance potentially affected fraction of species (msPAF) has only been used to derive constant effect factors from the slope of the msPAF curve at given ambient toxicant concentrations [4,5].

An emission to an initial environmental recipient compartment will distribute to other environmental endpoint compartments depending on properties of the substance and the environmental system. Assuming constant effect factors, the effect of a pulse-emission on any of the endpoint compartments is reduced to a problem of assessing the fate of the substance. Fate meaning the distribution between compartments and retention time in each compartment. Fate assessment in LCIA is traditionally performed with steady-state multi-compartment models for both human- and ecotoxic impacts [4-6].

Given the assumption of instantaneous mixing, which is implicit in the multi-compartment model, the increase in concentration in any of the compartments is small compared to PNEC values. The use of constant effect factors therefore seems reasonable. On the other hand, local concentrations may exceed PNEC values depending on mass loading, degradation and toxicity of the substance and the dispersion rate in the environmental compartment. If ecotoxic effect is considered non-proportional to concentration, which is the case when SSDs are used as effect functions, the deviation between the approximated effect with constant effect factors, and the actual effect quantified with the SSD, may be significant.

Two approaches exist for calculation of msPAF, assuming a combination of concentration and response addition when aggregating single-substance PAF into multi-substance PAF [7], or concentration addition only [4].

This paper outlines a procedure to quantify the error of using constant effect factors for the increase of msPAF, i.e. using the slope of the msPAF curve only to derive a constant effect

factor. Dispersion was modeled with spatial and temporal resolution in a marine aquatic dispersion model. The error of assuming constant effect factors was quantified for both msPAF approaches for a number of artificial reference substances. Different mass loadings, degradation rates and ambient toxicity levels were investigated.

The next section outlines the characterization procedure for both the conventional ecotoxic effect approach with the use of constant effect factors, as well as a formalized procedure with continuous effect functions. Methods applied in this paper to quantify the error of using constant effect factors are described in the third section, followed by presentation and discussion of the results in section four.

MATERIALS

Characterization factors in LCIA

The ecotoxic effect of a substance is in LCIA commonly defined as a function of exposure, with exposure in units of concentration. For ecosystem j and substance s , the ecotoxic effect at any location in j exposed to concentration $C_{j,s}$ is

$$Effect_{j,s} = E_{j,s}(C_{j,s}) \quad (1)$$

where $E_{j,s}$ is the effect function for substance s on ecosystem j [6,8]. Although continuous effect functions could be used, the effect is normally calculated with a constant effect factor

$$Effect_{j,s} = E_{j,s} \times C_{j,s} \quad (2)$$

This simplification is common in LCIA [3-5], and represents a first order Taylor approximation of the effect function.

The impact score $q_{j,s}$ for substance s on ecosystem j is defined as the infinite time-integral of the effect,

$$q_{j,s,i} = \int_{t=0}^{\infty} E_{j,s} \times C_{j,s,i} dt = E_{j,s} \times \int_{t=0}^{\infty} C_{j,s,i} dt \quad (3)$$

where $C_{j,s,i}$ is the concentration of substance s in ecosystem j caused by an initial emission to environmental compartment i [8,9].

Multi-compartment steady-state models are normally applied for exposure modeling (also called fate modeling) in LCIA. A multi-compartment steady-state model can be described by a system of first order differential equations [10,11]. For such a model, the infinite time-integral of concentration in each of the environmental compartments can be calculated directly knowing the fluxes into the different compartments [9]. The time-integral of concentration is called the fate factor and commonly denoted F ,

$$F_{j,s,i} = \int_{t=0}^{\infty} C_{j,s,i} dt \quad (4)$$

Assuming a constant effect factor, the impact score $q_{j,s,i}$ simplifies into the product of the effect and fate factors,

$$q_{j,s,i} = E_{j,s} \times F_{j,s,i} \quad (5)$$

If the exposure model consists of several sub-compartments representing geographical scales or regions of the same environmental compartment (marine, freshwater or terrestrial), impact scores are summarized according to area, volume or mass. As an example, the marine aquatic environment can be divided into a continental scale and three climate zones that together cover

the northern hemisphere. The impact scores for the separate marine aquatic ecosystems are then summarized according to the volume of the marine sub-compartments [3]. For an ecosystem j of n sub-compartments, the characterization factor $Q_{j,s,i}$ (sometimes called the damage factor) for emission of substance s to initial recipient i is

$$Q_{j,s,i} = \sum_{k=1}^n [q_{j,s,i,k} \times V_{j,k}] = \sum_{k=1}^n [E_{j,s,k} \times F_{j,s,i,k} \times V_{j,k}] \quad (6)$$

More formally, the characterization factor $Q_{j,s,i}$ is

$$Q_{j,s,i} = \int_{V_j=0}^{V_{j,T}} \int_{t=0}^{\infty} E_{j,s}(C_{j,s,i}) dt dV \quad (7)$$

where V_j is the scaling dimension. In the case of marine aquatic ecotoxicity, $V_{j,T}$ represents the total volume of the marine aquatic compartments. Then, using a first order Taylor approximation for the effect function, the expression for the characterization factor can be simplified into

$$Q_{j,s,i} = E_{j,s} \times \int_{V_j=0}^{V_{j,T}} \int_{t=0}^{\infty} C_{j,s,i} dt dV \quad (8)$$

Replacing the time-integral of concentration with the fate factor from (4), the expression for the characterization factor becomes

$$Q_{j,s,i} = E_{j,s} \times \int_{V_j=0}^{V_{j,T}} F_{j,s,i} dV \quad (9)$$

Given that the fate factor is constant within each of the sub-compartments of $V_{j,T}$, this simplifies to (6).

Potentially affected fraction of species

The endpoint considered in LCIA for ecotoxicity should be on ecosystem level. A method to achieve this is offered by the concept of species sensitivity distributions (SSDs). “A SSD is a statistical distribution describing the variation among a set of species in toxicity of a certain compound or mixture” [12]. Using an SSD based on no-effect concentrations (NOECs), the adverse effect considered is the probability that “a species chosen randomly out of a large assemblage is exposed to an environmental concentration greater than its no-effect level” [13]. Assuming a log-normal SSD for the inter-species distribution of NOECs for substance s in ecosystem j , the cumulative density function for species exposed above their respective NOEC at a concentration level of $C_{j,s}$ is

$$PAF_{j,s}(C_{j,s}) = \frac{1}{1 + \exp\left\{\frac{-[\log_{10}(C_{j,s}) - \alpha_{j,s}]}{\beta_{j,s}}\right\}} \quad (10)$$

where PAF is the Potentially Affected Fraction of species, $\alpha_{j,s}$ is the geometric mean of NOECs, while $\beta_{j,s}$ is the shape factor for the PAF curve

$$\beta_{j,s} = \frac{\sqrt{3}}{\pi} \times \sigma_{j,s} \quad (11)$$

and $\sigma_{j,s}$ is the standard deviation for the set of $\log_{10}(\text{NOEC})$ [14]. The PAF function is commonly defined with chronic NOECs, although the SSD concept is applicable to acute sensitivities as well [12].

The intention in LCA normally is to find the marginal environmental effect. In most ecosystems, toxicants are present before any new emissions and LCIA should take this into account. Hamers et al. proposed to use a combination of concentration and response addition for the combined effect of toxicants [7]. The result of this approach is a multi-substance PAF, $msPAF_j$, for ecosystem j

$$msPAF_j = 1 - \left(1 - PAF_{\sum_{j,narc}}\right) \prod_s (1 - PAF_{j,s}) \quad (12)$$

where concentration addition is used to calculate $PAF_{\sum_{j,narc}}$ for hydrophobic, chemically inert substances (i.e. narcotics), while for all other substances response addition is used. Further, it is assumed that there are no antagonistic or synergistic effects.

With Hamers et al.'s definition of msPAF, it is required to create PAF curves for a number of toxic substances in order to find the ambient msPAF. When Goedkoop and Spriensma applied the concept of PAF in LCIA they assumed a general concentration addition rule [4]. In this approach, a single msPAF curve is used, based on an average β_j and the sum of toxic units, TU_j , present in the ecosystem

$$TU_j = \sum_s \left(\frac{C_{j,s}}{10^{\alpha_{j,s}}} \right) \quad (13)$$

The $msPAF_j$ is then calculated from TU_j

$$msPAF_j(TU_j) = \frac{1}{1 + \exp\left[\frac{-\log_{10}(TU_j)}{\beta_j}\right]} \quad (14)$$

msPAF and ecotoxic effect factors

Goedkoop and Spriensma use the slope of the msPAF-curve at $msPAF_{j,0}$, the ambient msPAF concentration in ecosystem j , as ecotoxic effect factor [4],

$$E_{j,s}^{GS} = \left. \frac{\partial msPAF_j^{GS}}{\partial C_{j,s}} \right|_{msPAF_{j,0}} = \left(\frac{\partial msPAF_j^{G\&S}}{\partial TU_j} \times \frac{\partial TU_j}{\partial C_{j,s}} \right) \Bigg|_{msPAF_{j,0}} \quad (15)$$

Substitution with (13) and (14) gives

$$E_{j,s}^{GS} = \frac{msPAF_{j,0}^{GS} \times (1 - msPAF_{j,0}^{GS})}{\beta_j \times \ln(10) \times TU_{j,0}} \times \frac{1}{10^{\alpha_{j,s}}} \quad (16)$$

where $msPAF_{j,0}$ is the ambient msPAF and $TU_{j,0}$ is the ambient concentration of toxicants.

Likewise, with Hamers et al.'s definition of msPAF the effect factor is

$$E_{j,s}^H = \left(\frac{\partial msPAF_j^H}{\partial PAF_{j,s}} \times \frac{\partial PAF_{j,s}}{\partial C_{j,s}} \right) \Bigg|_{msPAF_{j,0}} \quad (17)$$

Substitution with (10) and (12) gives

$$E_{j,s}^H = (1 - msPAF_{j,rest,0}) \times \frac{(1 - PAF_{j,s,0}) \times PAF_{j,s,0}}{\beta_{j,s} \times \ln(10) \times C_{j,s}} \quad (18)$$

where $msPAF_{j,0}$ is the ambient msPAF from substances other than s . From (12) we get

$$msPAF_{j,rest,0} = \frac{msPAF_{j,0} - PAF_{j,s,0}}{1 - PAF_{j,s,0}} \quad (19)$$

Further research is needed to validate the ecological relevance of either of the two approaches [5].

METHODS

This section describes the application of the effect function for calculation of characterization factors, and outlines the procedure used to quantify the error implied by a constant effect factor for the case of a single closed marine aquatic compartment. Both the combined response and concentration addition rule (H: Hamers et al.), and the concentration addition only rule (GS: Goedkoop and Spriensma), were investigated with transient dispersion modeling.

The transient dispersion model

Dispersion of toxicant in the marine environment was modeled with a transient dispersion model. The marine ecosystem was considered closed and of finite volume in order to account for all mass loadings. Adsorption and evaporation processes were not included and substances were assumed fully water soluble. This setup illustrates upper bounds for the error in using constant effect factors.

Dispersion of toxic substances in the marine compartment follows the general diffusion equation:

$$\frac{\partial C_{\mathbf{x},s}}{\partial t} = \nabla \cdot (D \times \nabla C_{\mathbf{x},s}) - k_s \times C_{\mathbf{x},s} \quad (20)$$

where $C_{\mathbf{x},s}$ is the concentration of the substance s at location \mathbf{x} , and k_s is the effective degradation rate of s . D is the tensor of dispersion coefficients. The term dispersion is used for the combined action of advection and diffusion [15]. Advective transport was assumed constant and therefore removed from (20) by using Lagrangian coordinates. Radial symmetry was assumed, $\mathbf{x} = (r, z)$, and so the only components of D are in the radial and vertical direction.

The dimensions of the model are given in Table 1. The Appendix gives further descriptions of the transient dispersion model and discusses the methods for solving (20).

Table 1. Dimensions of the fate model

Name	Description	Value
r	Radius	4×10^5 m
z	Depth	200 m
\mathbf{x}_0	Discharge point	$(r_0, z_0) = (0, -30)$

Turbulent dispersion coefficients

The radial (horizontal) dispersion coefficient was assumed as

$$D_r = \begin{cases} 0.0233 \times (t \times 8.64 \times 10^4)^{1.34} & ; t < 29 \text{ days} \\ 8.64 \times 10^6 & ; t > 29 \text{ days} \end{cases} \quad (21)$$

with D_r in units of m^2/day and t in days. The expression for D_r was reported from studies of oceanic turbulent dye dispersion from point sources [16]. As the size of the dye patch increases, larger eddies take part in the dispersion of the patch. The dispersion of the patch therefore increases with time. At some point in time the patch reaches a size comparable to the size of the largest eddies contributing to the dispersion, and the rate of dispersion stabilizes [15]. This point was assumed at 29 days [17].

The vertical dispersion D_z was assumed constant at $43.2 \text{ m}^2/\text{day}$. This is in the low range of $43.2\text{-}864 \text{ m}^2/\text{day}$ indicated by Bowden [15]. Kullenberg reported $26 \text{ m}^2/\text{day}$ for tritium fallouts in Norwegian Seas [17].

msPAF effect functions

For simplicity, the notation for endpoint ecosystem j and initial recipient i will from now on no longer be used since a single closed marine compartment is assumed.

The msPAF at any location $\mathbf{x} = (r, z)$ and time t is denoted $msPAF_{\mathbf{x},t}$

$$msPAF_{\mathbf{x},t} = f(\mathbf{x}, t) \quad (22)$$

The msPAF at \mathbf{x} and t after a discharge of substance s at time t_0 is denoted $msPAF_{\mathbf{x},t,s}$. In the GS-approach, the increase of msPAF caused by the discharge of substance s is

$$\Delta msPAF_{\mathbf{x},t,s}^{GS} = msPAF_{\mathbf{x},t,s}^{GS} - msPAF_0^{GS} \quad (23)$$

$msPAF_{\mathbf{x},t,s}$ is calculated from (14) using the relation

$$TU_{\mathbf{x},t,s} = TU_0 + \left(\frac{C_{\mathbf{x},t,s}}{10^{\alpha_s}} \right) \quad (24)$$

with ambient TU, TU_0 , calculated from $msPAF_0$. Equation (14) gives

$$TU_0 = 10^{\left[-\beta \times \ln \left(\frac{1 - msPAF_0}{msPAF_0} \right) \right]} \quad (25)$$

In the H-approach, the effect function is

$$\Delta msPAF_{\mathbf{x},t,s}^H = msPAF_{\mathbf{x},t,s}^H - msPAF_0^H \quad (26)$$

were

$$msPAF_{\mathbf{x},t,s} = 1 - \left[(1 - msPAF_{rest,0}^H) \times (1 - PAF_{\mathbf{x},t,s}) \right] \quad (27)$$

and $PAF_{\mathbf{x},t,s}$ is the single substance PAF for substance s at location \mathbf{x} and time t after a discharge of substance s at time t_0 . $PAF_{\mathbf{x},t,s}$ is calculated from (10). $msPAF_{rest,0}$ is the contribution to $msPAF_0$ from substances other than s .

Transient characterization factors

The characterization factor $Q_{T,s}$ for substance s with transient modeling of a continuous effect function was found by integration of $\Delta msPAF_{\mathbf{x},t,s}$ over time and volume, in accordance with (7),

$$Q_{T,s} = \int_{V=0}^{V_T} \int_{t=0}^{\infty} \Delta msPAF_{x,t,s} dt dV \quad (28)$$

Since numerical integration can only be computed for finite time, the time-integral was divided into a transient period and a non-transient period,

$$Q_{T,s} = \int_{t=0}^{t_p} \int_{V=0}^{V_T} \Delta msPAF_{x,t,s} dt dV + \int_{t_p}^{\infty} \int_{V=0}^{V_T} \Delta msPAF_{x,t,s} dt dV \quad (29)$$

where t_p was determined from values of k_s . Settings for t_p , and procedures for integration, are further described in the Appendix. The non-transient integral is estimated with a constant effect factor, so that

$$\int_{t_p}^{\infty} \int_{V=0}^{V_T} \Delta msPAF_{x,t,s} dt dV \approx E_s \times \int_{t_p}^{\infty} \int_{V=0}^{V_T} C_{x,t,s} dV dt = E_s \times \int_{t_p}^{\infty} m_{t,s} dt \quad (30)$$

The time integral of mass was solved analytically. Effect factors E_s are described in (16) for the GS-approach, and in (18) for the H-approach.

Error in constant effect factors

Characterization factors were calculated using both constant effect factors; see (8), and continuous effect functions; see (7). Characterization factors found with constant effect factors are named Q_s . Effect factors are described in (16) (GS-approach) and (18) (H-approach). Characterization factors calculated with transient modeling of a continuous effect function are named $Q_{T,s}$. Effect functions are described in (23) (GS-approach) and (26) (H-approach). The procedure outlined in (29)-(30) was used for $Q_{T,s}$ for both approaches. The error in assuming constant effect factors was quantified with the ratio

$$W = \frac{Q_{T,s}}{Q_s} \quad (31)$$

W is a function of different parameters depending on the definition of msPAF. In the GS-approach, α_s , β and $msPAF_0$ describe the ecotoxic effect, m_0 is the mass loading from the point source and k_s is the degradation rate of substance s . In the H-approach, an additional parameter $PAF_{s,0}$ must be introduced for the ambient single substance PAF for substance s .

RESULTS AND DISCUSSION

For the interpretation and discussion of the results it is beneficial to illustrate the difference between using effect functions and approximating effect with constant effect factors. Figure 1 shows $\Delta msPAF$ for both methods. Note that as the continuous effect function converges toward $1-msPAF_0$ for high concentrations, this is not the case when effect factors are used. The difference in result between the two methods increases with increasing concentration. The error in replacing the effect function with a factor approximation is quantified in Figure 2 for both the concentration addition only assumption for msPAF (GS-approach) and the combined concentration and response addition assumption (H-approach). Table 2 lists variables used in calculation of plots in Figure 2. Only one msPAF curve is illustrated for the GS-approach, but the general conclusion is that the concentration increase of the substance investigated must be the same order of magnitude as α_s for the error to be significant. The conclusion for the assumption

of combined concentration and response addition is different. If the ambient concentration of the substance (or toxic mode of action) investigated is low, even small increases in concentration result in significant deviation between the effect function and the effect factor approximation for $\Delta msPAF$. The deviation might result in errors in the characterization factors calculated with transient exposure modeling if sufficient concentration levels are present for a longer period of time (with regards to the half life of the substance).

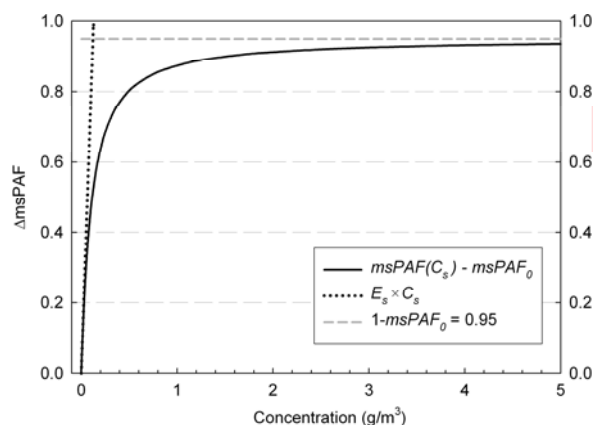


Figure 1. The increase of $msPAF$ calculated with effect factor and effect function. $msPAF_0$ is assumed as 0.05. Note that concentration is on linear scale.

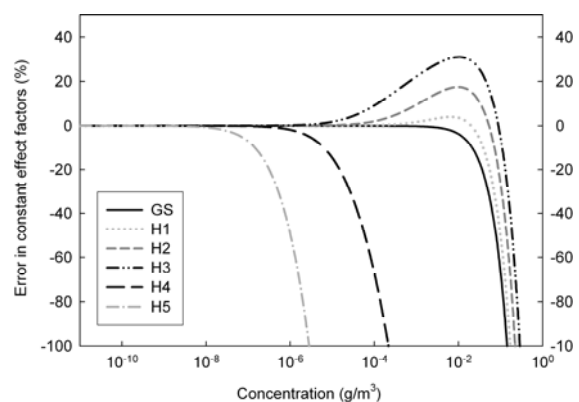


Figure 2. Deviation between effect calculated with continuous effect function and effect approximated with effect factor, plotted as function of concentration. The error is quantified as $HOT/\Delta msPAF$ in percent, with HOT as the higher order terms for the first order Taylor approximation of the continuous effect function, while $\Delta msPAF$ is calculated with the continuous function. Legends are described in Table 2.

Table 2. $msPAF$ parameters for Figure 2.

	GS	H1	H2	H3	H4	H5
α_s	-1	-1	-1	-1	-1	-1
$\beta_{(s)}$	0.4	0.4	0.4	0.4	0.6	0.8
$msPAF_0$	0.05	0.05	0.05	0.05	0.05	0.05
$PAF_{s,0}$	n.a.	0.01	0.001	0.0001	0.001	0.001
$C_{(s),0}$	6.64×10^{-3}	1.45×10^{-3}	1.73×10^{-4}	2.07×10^{-5}	7.18×10^{-6}	2.98×10^{-7}

For the calculation of characterization factors, results for the GS-approach are discussed first. A base set of values for parameters describing mass loading, substance properties and ambient $msPAF$ level according to the GS-approach was defined. Results for W_{GS} were calculated using the base set and changing one parameter at a time. The base set is given in Table 3. Parameters investigated are listed in the table with indicators A-C. Results are presented in Figure 3. Overall, the values for W_{GS} are close to one. This implies that calculation of the increase of $msPAF$ with constant effect factors is a good approximation for the GS-approach. The deviation between effect factor and function results decreases as α_s decreases. This is expected since the significance of the discharge of substance s on the overall $msPAF$ level increases the more toxic the substance is. α_s of -3 is equivalent to $\log_{10}(\text{NOEC})$ average of 1 mg/m^3 . A brief review of literature data for α_s shows that few substances have values of less than 1 mg/m^3 for aquatic species [4,5,18]. The shape factor β is investigated for values up to 0.8. This is twice the value originally proposed by

Goedkoop and Spruiensma [4]. Van de Meent [18] lists average β values for a number of toxic modes, with the highest being 0.71 (not including standard deviations). Relevant ambient marine msPAF levels were assumed to be within $0.05 < \text{msPAF} < 0.5$. This interval has been reported for freshwater ambient levels of msPAF for surface waters in the Netherlands [19]. In Figure 3, the deviation increases with increasing mass loadings. It can be assumed that pulse emissions will not to exceed 100 tonnes, and emissions of 1 tonnes are more realistic. The lower bound is therefore calculated with a point source pulse emission of 1 tonnes. Combining the values which give the highest deviation for W_{GS} into an expected “*lower bound*” case resulted in a W_{GS} still in the scale of one.

Relevant parameters for investigation with the H-approach were selected with the purpose of quantifying error bounds. Only emissions of with a mass loading of 1 tonnes were investigated. Two degradation rates were simulated, with half-lives of seven ($k_s = 0.1 \text{ day}^{-1}$) and 70 days ($k_s = 0.01 \text{ day}^{-1}$). Table 4 summarizes the base set of parameters and parameter variations investigated for the H-approach. Results for W_H are presented in Figure 4. As can be seen from the figure, the error implied by the constant effect factor is much higher for the H-approach than for the GS-approach. The main reason for this lies in the concentration addition assumption in the GS-approach. Any contribution to msPAF_{GS} by the discharge of substance s comes on top of the background concentration of toxic units, which in any case is relatively high for relevant msPAFs (> 0.05).

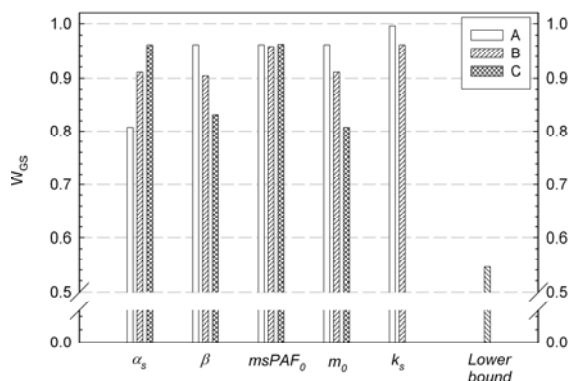


Figure 3. W_{GS} for different parameters settings. W_{GS} is calculated with the base set of parameters listed in Table 2 and changing one parameter at a time. Legends A-C are described in Table 3. An additional set up is defined to illustrate a lower bound of W_{GS} . The W_{GS} for the *Lower bound* case is calculated with $(\alpha_s, \beta, \text{msPAF}_0, m_0, k_s) = (-3, 0.71, 0.05, 10^3, 0.1)$ and units from Table 3.

Table 3. Investigated values (GS-approach)

Parameter	Base set	A	B	C
α_s	-1	-3	-2	-1
$[\log_{10}(\text{g}/\text{m}^3)]$				
β	0.4	0.4	0.6	0.8
msPAF_0	0.05	0.05	0.24	0.5
m_0 [kg]	10^3	10^3	10^4	10^5
k_s [day^{-1}]	0.1	0.01	0.1	

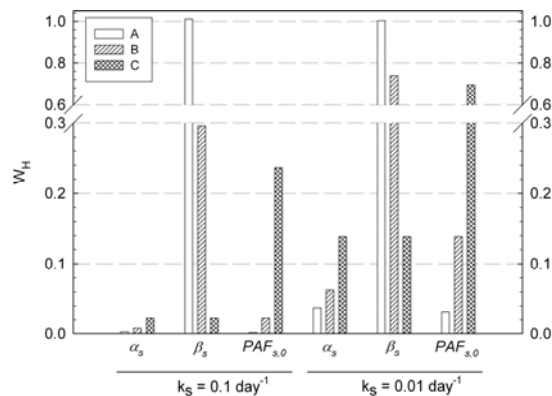


Figure 4. W_H for different parameters settings. W_H is calculated with the base set of parameters listed in Table 3 and changing one parameter at a time. Legends A-C are described in Table 4. Two values for k_s are investigated for all combinations.

Table 4. Investigated values (H-approach)

Parameter	Base set	A	B	C
α_s	-1	-3	-2	-1
β_s	1.2	0.4	0.8	1.2
$\text{PAF}_{s,0}$	10^{-3}	10^{-4}	10^{-3}	10^{-2}
msPAF_0	0.05			

Figure 5 shows pooled results for W from Figures 3 and 4 plotted as functions of initial concentration. The plot illustrates that in the H-approach, background concentration of substance s can be low independent of $msPAF_0$. The approximation of effect with constant effect factors is less robust for higher concentrations in the H-approach than in the GS-approach, as shown also in Figure 2. The error in the effect factor approximation causes significant deviations between the effect function and effect factor characterization factors calculated with transient dispersion modeling for the H-approach.

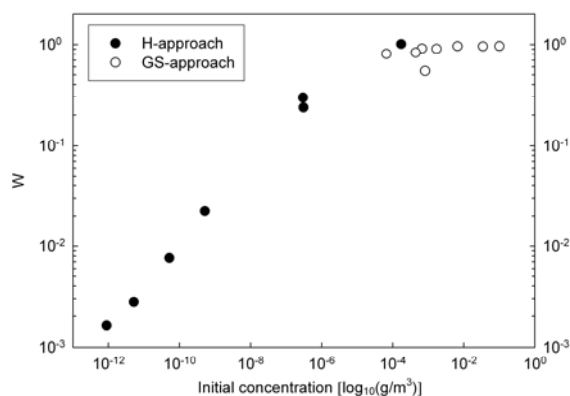


Figure 5. W for both GS and H-approach plotted as function of initial concentration. Initial concentration of toxic units is normalized into units of C_s for the GS-approach. Only scenarios with $k_s = 0.1 \text{ day}^{-1}$ and $m_0 = 10^3 \text{ kg}$ are plotted.

CONCLUSION

Characterization factors have been calculated for marine aquatic ecotoxicity from point source discharges. A number of artificial reference substances have been investigated, assuming different mass loadings and ambient toxicity levels. Two effect functions have been applied, based on msPAF with concentration addition only [4] and combined concentration and response addition [7]. Dispersion has been modeled with a transient fate model. Factors have also been calculated for the corresponding traditional approach, i.e. with constant effect factors. Results show that the deviation between characterization factors calculated with constant effect factors based on msPAF, and calculated with a continuous msPAF function, are small for the concentration addition only msPAF. This implies that ecotoxic pulse effects from marine point source discharges are well handled with the traditional effect factor approach if concentration addition only is assumed for msPAF. If the combined concentration and response addition assumption is made, the conclusion is different. The constant effect factor may lead to an overestimation of ecotoxic effect of several orders of magnitude.

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APPENDIX

Transient dispersion model setup

The transport equation (20) was solved using the finite element method (FEM). Commercial software, FemLab [20], was used to perform the calculations. The model was solved as a closed system ($\nabla C = 0$ at the boundaries). Since the boundaries are located far from the discharge point, the concentration at the boundary is negligible and hence the boundaries do not affect the solution. The discharge was modeled as a point source,

$$C(\mathbf{x}, t_0) = m_0 \delta(\mathbf{x}) \quad (\text{A.1})$$

where m_0 is the mass discharged and δ is the Dirac delta function. Calculations show that the method closely agrees with the analytical solution of (20), see [15], with a point source and constant D .

The FEM grid used was more refined near the discharge point, but coarser towards the boundary where concentration gradients are smaller. The volume was scaled with a factor 5 in the z-direction prior to FEM grid generation in order to increase number of elements in the vertical direction. Approximately 1000 elements were used.

Transient integral period

The time integral for effect modeled with effect function was divided into a transient and a non-transient period; see Equation (29). The time t_p was set as 70 days for $k_s = 0.1 \text{ day}^{-1}$, and as 365 days for $k_s = 0.01 \text{ day}^{-1}$. Simulations show that the integral of $\Delta msPAF_{x,t,s}$ over volume converges to the integral of $E_s C_{x,t,s}$ over volume for $t > t_p$. This is expected since $\Delta msPAF_{x,t,s}$ converges to $E_s C_{x,t,s}$ for small $C_{x,t,s}$.

Discrete time integration

The software FemLab [20] allows for volume integration of defined functions at specified times. Time-integration was approximated using

$$Q_{T,s} = \int_{t=0}^{t_p} \int_{V=0}^{V_T} \Delta msPAF_{x,t,s} dV dt = \sum_{i=1}^n \left(\Delta t_i \times \int_{V=0}^{V_T} \Delta msPAF_{x,t_i,s} dV \right) \quad (\text{A.2})$$

The time-step Δt_i was not set constant, but increased with time. This is justified since the integrand flattens with time. Simulations show this is a reasonable approach. Volume-integrals were recorded at

$$t_i (k_s = 0.1 \text{ day}^{-1}) = \{0.1, 0.2, 0.6, 1.0, +\Delta t_i = 1 \text{ for } t_i \in \langle 1, 30 \rangle, +\Delta t_i = 5 \text{ for } t_i \in \langle 30, 70 \rangle\}$$

$$t_i (k_s = 0.01 \text{ day}^{-1}) = \left\{ \begin{array}{l} 0.1, 0.2, 0.6, 1.0, \Delta t_i = 1 \text{ for } t_i \in \langle 1, 20 \rangle, \Delta t_i = 5 \text{ for } t_i \in \langle 20, 50 \rangle, \\ \Delta t_i = 10 \text{ for } t_i \in \langle 50, 130 \rangle, \Delta t_i = 20 \text{ for } t_i \in \langle 130, 240 \rangle, 290, 340, 365 \end{array} \right\}$$

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