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Comparative risk analysis of waste site toxicants by indices based on concentration distributions, fluxes, environmental fate and critical effects

Timo Walter Assmuth*

Finnish Environment Agency, P.O. Box 140, SF-00251 Helsinki, Finland

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Abstract

The environmental risks associated with toxicants in leachate emissions from 43 Finnish waste sites were analysed and prioritized by site-aggregating procedures using various linear models and indices based on statistics of observed concentration distributions, on available data concerning volatilization and decay, on flux estimates and on toxic values to humans and to aquatic organisms. Considering only concentrations (90% fractiles of distributions) and effect criteria, 1,2-dichloroethane, 2,4,6-trichlorophenol and trichloroethene were the most important toxicants in terms of drinking water standard violation, while PCBs and Cr along with 1,2-dichloroethane displayed the values of carcinogenic risk index, and Cu, PCBs, toluene and endrin ranked highest in terms of aquatic ecotoxicity. The distributions of ecotoxicity indices reached rather consistently more alarming levels than those of health risk indices. When sinks were accounted for, the persistent and nonvolatile dieldrin and lindane emerged as the key toxicants for both human health and aquatic organisms. Considering estimated fluxes (by flow-weighted concentrations), hexachlorobenzene gained the highest values of health risk, Cu topping the list of substance-specific ecotoxic risk fluxes. The procedures for treatment of nondetects and for the estimation of distribution statistics considerably affected the rank orders particularly in the case of ecotoxicity and flux indices and for substances with low detection frequencies and high maxima relative to critical values (e.g., neutral pesticides). The methodological basis and development possibilities of risk indices were critically evaluated.

Keywords: Waste; Landfill; Leachate; Toxic; Risk; Index; Distribution; Field data; Finland

1. Introduction

The environmental risks of waste sites cause considerable concern. In order to assess and manage these risks, improved data and risk analysis methods are required.

* Tel.: +358 0 403000, Fax: +358 0 40300 291. e-mail: 126 086 vyh sf.

An important dimension of the latter is risk identification and prioritization based on measurements of toxicants in waste site emissions.

For measurement-based risk identification and initial risk assessment of toxicants at waste sites, various quantitative and semiquantitative methods have been developed [1–3], some of them proposed for or adopted to use in standardized assessment of investigated sites [2, 3]. Also in other areas of (eco)toxicological risk assessment, principally similar procedures (e.g., ‘quotient methods’) have been increasingly used (for an evaluative review, see [4]). Some of the above procedures have considered concentration distributions, environmental fate properties and effect modes in varying ways. However, all these factors are not routinely treated explicitly and consistently.

In the present study, a procedure accounting for all the above factors was devised for the identification and comparative analysis of human health risks and aquatic ecological risks associated with toxicants at waste sites. The indices were tested on field data to assess the relative importances of the various substances and risk factors, and to evaluate the risk identification methodologies.

2. Study sites and empirical methods

Forty-three Finnish waste sites were studied in the field. They include operating and closed municipal mixed-waste landfills and industrial waste disposal sites, located in various kinds of (boreal) environment. The average length of the period of use at the end of the field studies was 23 yr, and most sites have not been completely guarded; they are thus estimated to contain substantial amounts of wastes which are presently officially designated as hazardous. Almost all sites may be categorized as uncontrolled landfills of low technical standard, implying lack of base compaction, of waste pretreatment and compartmentalization, of top sealing, and of treatment of gas and leachate [5].

Leachate runoff in surface water was sampled from leachate discharge points and downstream points by methods described earlier [5]. Standardized and established analytical methods were used. Considerable attention was paid to the representativity and reliability of methods and materials used in sampling, field and laboratory pretreatment and measurement, and extensive quality assurance procedures were employed, e.g., field and laboratory blanks and replicates. Typical ranges of detection limits in liquid samples were 0.01–1 $\mu\text{g l}^{-1}$ for heavy metals and most organic compounds; the limits were lowest for the most toxic substances.

3. Formulation of risk indices

The baseline substance-specific risk indices for toxicants in surface water emissions were formulated to correspond to previous procedures (see Refs. [1, 2, 6], and also [4]). The baseline indices account only for statistics of toxicant concentrations and for critical measures of toxicity to humans and aquatic organisms. These measures were based on lowest observed adverse effect concentrations, on established health norms

derived in the usual manner from effect or no-effect concentrations by extrapolation using safety factors [6], and on upper-bound estimates of carcinogenicity from extrapolation of rodent tumorigenicity [2]. The indices were defined as follows:

$$HI = c LQG^{-1}, \quad (1)$$

$$CI = cb_1^*, \quad (2)$$

$$TI = c LEC^{-1}, \quad (3)$$

where HI and TI are health norm violation index and toxic risk index for a substance, respectively (dimensionless), CI the human carcinogenic risk index for a substance in surface water use ($\text{kg l}^{-1} \text{d}$), c the statistic of the concentration of a substance in leachate ($\mu\text{g l}^{-1}$), LQG the lowest relevant quality guideline for the concentration of a substance in drinking water ([7, 8], Appendix) ($\mu\text{g l}^{-1}$), b_1^* the carcinogenic potency of a substance in oral exposure, as 95% upper confidence level estimate by the linearized multistage model ([9, 10], Appendix) ($\text{mg kg}^{-1} \text{d}^{-1}$) $^{-1}$ and LEC the lowest LOAEC (lowest observed adverse effect concentration) value for a substance in aquatic environment ([11, 12], Appendix) ($\mu\text{g l}^{-1}$).

The index of ecotoxicity devised in the present work, TI, incorporates data on any reportedly adverse effects on any aquatic organisms. No attempt was made to select data or to modify the model according to the relevance of the end point, of the taxon or of test conditions. The index was based on (usually chronic) LOAEC values, rather than on NOAEC (no observed adverse effect concentration) values or on MATC (maximum allowable toxicant concentration, cf. [4]) or ECL (environmental concern level, cf. [13]) values, because the estimation of NOAECs is principally controversial (e.g., [14]), while MATCs and ECLs depend on partly arbitrary safety factors [4, 13], and since LOAEC values were assumed to suffice for the comparative purposes of initial assessment.

The rationale for the index of carcinogenicity, CI, is the common use in initial assessment of the linear multistage (LMS) model which for many substances is a plausible approximation of tumorigenesis, and the presumed conservativeness of the upper-bound LMS potency estimates [1, 2]. The weight of evidence of the forms of tumorigenic action, of simultaneous genotoxicity and associated dose–response modeling constraints, or of human carcinogenicity were thus not considered at this stage.

Indices were then developed to account for key environmental behavior mechanisms which affect risks. Volatilization and decay (biotic or abiotic) were incorporated because they are relatively separate and function as (nearly) definite sinks from the point of view of the water phase.

$$EHI = c LQG^{-1} H^{-1} t_{1/2}, \quad (4)$$

$$ECI = cb_1^* \cdot H^{-1} t_{1/2}, \quad (5)$$

$$ETI = c LEC^{-1} \cdot H^{-1} t_{1/2}, \quad (6)$$

where, in addition to the symbols explained previously, EHI, ECI, ETI are the effective health, cancer and toxic risk index for a substance, respectively, in surface water, H the coefficient of Henry's law for a substance ([15–17, 10–12], Appendix) ($\text{Pa m}^3 \text{mol}^{-1}$) and $t_{1/2}$ the aquatic half-life under aerobic conditions of a substance ([16, 18, 19, 11, 12], Appendix) (d).

The indices accounting for environmental fate were computed for organic compounds only, since the decomposition of elements is negligible, and their volatilization generally of little importance [16] and is in any case difficult to account for in a consistent manner due to lacking data on the volatilization-related properties (e.g., vapor pressure) of the various speciation forms (including methylmercury, other organometals and volatile arsenic compounds).

Additionally, quantitative indices of (waterborne) risks were produced from estimates of toxicant fluxes and toxicity (for simplicity, carcinogenicity was not considered but was assumed to be accounted for by the health norms). Due to infrequent sampling and flow measurements, flux estimates are approximate. The estimates of risk flux indices and of effective risk indices were computed both from statistics of truncated distributions (where nondetects were substituted by missing values) and from substitution by half detection levels or by zero (cf. [20]). The measures of risk flux were defined as follows:

$$\text{HRF} = F \text{LQG}^{-1}, \quad (7)$$

$$\text{TRF} = F \text{LEC}^{-1}, \quad (8)$$

where, in addition to symbols defined previously, HRF is the health risk flux of a substance ($\text{m}^3 \text{d}^{-1}$), F the flux of a substance in surface runoff, as calculated by arithmetic means (for a sampling point, subsequently for a site, and finally for all study sites) of the products of instantaneous flows and concentrations (mg d^{-1}), and TRF is the toxic risk flux of a substance ($\text{m}^3 \text{d}^{-1}$).

4. Results and discussion

4.1. Empirical data

The key concentration statistics of main toxicants in runoff from sampling points downstream of the study sites along with the respective numbers of observation and with the detection frequencies have been presented in Table 1. The detection frequencies are based on substitution of non-detects by half detection limits (cf. [21]). For elements only such data were included where medians exceeded detection limits by a factor of ca. 5 (with the exception of Hg), because the inclusion of data with higher detection limits and associated strongly truncated distributions would have caused difficulty in the estimation of concentration distribution statistics to be used in the computation of risk indices, e.g. unrealistically high concentration estimates.

Several organic compounds in particular were detected only infrequently, and the probability distributions of the toxicants were usually skewed. The most frequent

Table 1
Concentration statistics of toxicants in leachate runoff points downgradient of waste sites^a

Toxicant (abbreviation)	n	f _{D_{etn}} ^b (%)	Concentration (µg l ⁻¹)			
			f ₅₀ ^c	\bar{x} ^d	f ₉₀ ^e	Max
<i>Elements</i>						
Arsenic (As)	103	72	4.0	15	16	760
Cadmium (Cd)	101	59	0.25	0.56	0.80	12
Cobalt (Co)	47	100	30	39	80	260
Chromium (Cr)	128	98	8	110	24	65
Copper (Cu)	106	99	6.1	13	28	170
Mercury (Hg)	35	31	0.025	0.038	0.050	0.30
Nickel (Ni)	98	100	12	18	43	83
Lead (Pb)	102	85	1.0	2.2	7.2	15
Zinc (Zn)	217	94	90	1500	1600	34 000
<i>Organic compounds</i>						
Dichloromethane (DCM)	68	57	3.6	130	140	4800
Chloroform	65	18	0.025	2.0	5.0	68
Carbon tetrachloride (CCl ₄)	77	7.8	0.025	0.36	1.7	81
1,2-dichloroethane (12-DCE _a)	78	47	1.5	32	110	670
1,1,2-trichloroethane (112-TCE _a)	67	18	0.025	1.0	5.0	8.5
1,1,2,2-tetrachloroethane (1122-TeCE _a)	99	4.0	0.025	0.27	1.3	2.5
trans-1,2-dichloroethene (t12-DCE _e)	98	10	0.025	17	12	430
Trichloroethene (TCE _e)	14	21	2.5	14	63	88
Tetrachloroethene (TeCE _e)	34	59	0.23	3.9	1.4	110
Benzene	15	27	0.5	0.67	1.2	1.9
Toluene	81	72	0.8	56	70	1500
Ethylbenzene (EthBz)	89	36	0.14	48	62	980
1,3/1,4-xylene (13/14-xylene)	89	40	0.25	79	190	2000
1,2-xylene (12-xylene)	87	26	0.05	18	27	430
Di-n-octylphthalate (DOP)	23	78	0.4	4.8	1.0	100
Monochlorobenzene (MCBz)	88	5.7	0.05	0.18	0.50	2.6
1,2-dichlorobenzene (12-DCBz)	77	29	0.05	1.2	2.0	58
Hexachlorobenzene (HCBz)	71	13	0.025	0.13	0.10	2.7
2-cresol	61	20	0.25	3.8	8.8	67
3-cresol	61	41	0.25	9.6	29	94
4-cresol	61	39	0.25	44	140	810
2,4,5-trichlorophenol (245-TCP)	35	37	0.0025	0.76	3.4	8.6
2,4,6-trichlorophenol (246-TCP)	37	62	0.11	0.64	1.8	6.0
3,4,5-trichlorophenol (345-TCP)	30	53	0.043	0.25	0.85	1.6
2,3,4,6-tetrachlorophenol (2346-TeCP)	52	77	0.074	0.55	1.5	5.6
Pentachlorophenol (PeCP)	52	88	0.057	0.20	0.50	3.0
Aldrin	54	7.4	0.025	0.030	0.028	0.35
Dieldrin	54	9.3	0.05	0.059	0.061	1.1
Endrin	51	9.8	0.0125	0.23	0.25	7.5
44'-DDT	54	5.6	0.025	0.022	0.025	0.23
44'-DDD	52	27	0.025	0.13	0.27	2.2
24'-DDE	53	15	0.025	0.091	0.10	2.1
Lindane	52	29	0.025	0.41	0.40	15
α-HCH	70	13	0.025	0.096	0.075	1.4
PCBs	50	44	0.025	0.63	1.5	7.6

^a Only those data on element concentrations have been used which result in median values > 5 times the lowest detection limits; nondetects have been substituted by 0.5 × detection limits; ^b Frequency of detection; ^c Median value; ^d Arithmetic mean; ^e 90% fractile.

Table 2

Comparative analysis of the risks caused by selected toxicants observed in landfill leachate runoff by indices based on statistics of observed concentration distributions^a and on published toxicity values and water quality guidelines^b. Only high-ranked and frequently analyzed toxicants^c are included

Toxicant ^d	Health norm viol. index			Cancer risk index			Toxic risk index		
	HI ₅₀	HI ₉₀	Rank order ^e	CI ₅₀	CI ₉₀	Rank order ^e	TI ₅₀	TI ₉₀	Rank order ^e
<i>Elements</i>									
As	0.10	0.40		0.060	0.24		0.0076	0.03	
Cd	0.035	0.16		0.003	0.004		3.0	4.2	
Co	0.030	0.080					3.0	8.0	
Cr	0.16	0.47		0.41	2.3	3./3.	0.088	0.26	
Cu	0.12	0.56					850	3900	1./4.
Hg	0.013	0.025					0.0098	0.020	
Ni	0.25	0.86	6./11.	0.015	0.046		1.0	3.6	
Pb	0.10	0.72					2.5	18	
Zn	0.09	1.6					3.0	53	
<i>Organic compounds</i>									
DCM				0.027	1.1	11./6.	0.036	1.4	
12-DCE _a	0.30	21	4./1.	0.14	9.7	6./2.	26	1800	9./6.
TCE _c	0.50	13	3./3.	0.028	0.69		0.14	3.5	
TeCE _e	0.0077	0.047		0.012	0.071		0.046	0.28	
Toluene	0.057	5.0	15./6.				150	13 000	6./2.
12-DCBz	0.17	6.7	7./5.				0.065	2.6	
HCBz	2.5	10	1./4.	0.043	0.17		1.6	6.3	
246-TCP	1.1	18	2./2.	0.0022	0.035		1.1	18	
PeCP	0.0057	0.050					2.3	20	
Aldrin	0.0003	0.00028		0.29	0.32	4./10.	530	580	2./7.
Dieldrin	0.25	0.50	5./14.	0.75	1.5	2./4.	28	55	
Endrine	0.13	2.5					210	4200	4./3.
44'-DDD				0.15	1.3	5./5.	39	420	
Lindane	0.0083	0.13		0.033	0.52		150	2400	5./5.
PCBs	0.05	3.0		5.9	350	4./1.	250	15 000	3./1.

^a Based on nondetects substituted by half detection limits.

^b Sources: [2, 7–12].

^c Detection frequency > 20%.

^d For explanation of the abbreviations, see Table 1.

^e Based on 50% and 90% fractiles of the index, respectively.

toxicants were generally among those found frequently also in foreign studies (cf. [5]), with the exception of chlorophenols which were more frequently detected in high concentrations in the present work, probably due to their common use as wood preservatives.

4.2. Baseline risk indices based on concentration statistics and critical effects

Median and 90% fractile values of the baseline indices displayed noticeable differences between the various toxicants (Table 2). The discrepancy between their order

according to health norm violations and to carcinogenicity reflects that other norm setting criteria have played a role. The most prominent toxicants included 1,2-dichloroethane (by all indices), toluene and endrin (by ecotoxicity), 2,4,6-trichlorophenol (by violation of norms largely based on tumorigenicity) and PCBs (by tumorigenicity and ecotoxicity). Elements were not among the high-ranked toxicants, with the exception of Cu which scored high due to a more isolated report of chronic sublethal toxicity [11].

The choice of distribution statistics affected the values of risk indices. The relation of the median values of the indices, which may be considered plausible estimates, to 90% fractiles, which represent conservative estimates, was more than two orders of magnitude for many toxicants (Table 2). The incorporation of detection frequencies in the models (cf. [3]) was excluded because the detection levels are variable (even for a single substance) and thus constitute arbitrary ranking factors.

The proposed aggregate risk indices resemble the hazard indices (HI) promulgated by US EPA [2], i.e. the quotient of observed concentration and a reference concentration, or the quotient of observed (or estimated) dose and reference dose (RfD) corresponding to background risk. However, such HIs are used in risk identification with little consideration of factors such as environmental fate. In this respect, the relationship between estimated and acceptable doses [2, 6] is more comparable to the present indices.

Values of $HI > 1$ imply violation of health norms, and the absolute values of these indices display the magnitude of violation [2]. Median values exceeding 1 were observed with HCBz and 2,4,6-TCP only, while violations of health norms by the top 10% of the distribution were found with ten substances, all except toluene belonging to chlorinated organic compounds (Table 2). These levels of violation indicate the degree of dilution required to achieve safe levels (with respect to the analysed substances). By contrast, ecotoxicological effect levels were exceeded by much more substances, particularly elements and organochlorinated pesticides, and to much greater extent (up to 10 000 times for the top 10% of the distributions). It is to be noted that no safety factors were included in this LOAEC-based analysis, which further emphasizes the relative importance of ecotoxicological risks as compared with health risks. On the other hand, these index values were based on pooled data including some effects on exceptionally sensitive receptor systems.

The interpretation of CI values is more complex. Assuming that (a) observed concentration in the recipient equals exposure concentration (a conservative assumption in most cases) and (b) the dose–response function of (oral) animal tumorigenesis may be extrapolated to humans and estimated by the upper-bound levels from the LMS model, as commonly done in a first conservative approximation [2, 12], CI values may be converted to rough estimates of lifetime excess cancer risks by multiplication with intake (e.g., of potable water) and by division with body weight after interspecies dose scaling. However, the level of confidence in such estimates varies, since many of them are based on limited and variable animal data [2, 9, 10, 12], and exposure factors are neglected. No attempt was made in the present work to account for the weight of evidence for carcinogenesis (e.g., ranking differently known and suspected human carcinogens or nongenotoxic and genotoxic carcinogens).

Table 3

Statistics and rank orders of effective risk indices of high-ranked organic toxicants in surface water runoff from waste sites accounting for concentrations and sinks^a. The values of the indices are given as logarithms due to the high maxima. The ranges correspond to distributions obtained by truncation at detection levels (DL) and by substitution of nondetects by $0.5 \times DL$

Toxicant ^b	Effective health risk		Effective cancer risk		Effective toxic risk	
	log EHI ₉₀ ^c	Rank order	log ECI ₉₀ ^c	Rank order	log ETI ₉₀ ^c	Rank order
Chloroform			–2.48– –2.43		–1.64– –1.70	
CCl ₄	–2.37– –1.92		–3.25– –2.80		–2.51– –2.96	
12-DCE _a	0.63–0.85	5.	0.29–0.52	5.	2.56–2.79	
TeCE _c	–1.04– –1.85		–1.68– –0.85		–1.08– –0.26	
Benzene	–2.74– –2.55		–3.34– –3.14		–0.24– –0.04	
Toluene	–1.44– –1.08				1.97–2.34	
12-DCBz	0.14–0.29				–0.27– –0.12	
HCBz	–0.20–1.2		–1.96– –0.54		–0.40–1.03	
246-TCP	2.12–2.27	3.	–0.59– –0.43	6.	2.12–2.27	
PeCP	0.47–0.49	6.			3.08–3.10	5–6.
Aldrin	–0.92–0.17		2.13–3.23	3.	5.39–6.50	3–4.
Dieldrin	5.87–7.13	1.	6.35–7.61	1.	7.91–9.17	1–2.
44'-DDT	1.36–2.33	4.	0.95–1.92	4.	4.81–5.77	3–4.
Lindane	3.57–4.23	2.	4.16–4.82	2.	7.82–8.47	1–2.
PCBs	–0.75–0.35				2.94–3.35	5–6.

^a Sources: [10–12, 15–19].

^b For explanation of the abbreviations, see Table 1.

^c The ranges correspond to distributions truncated at detection levels or to those obtained by substituting nondetects with half detection limits.

Carcinogenic risks have been incorporated in other comparative assessments of waste site toxicants in the risk identification stage [2, 1], but not addressing concentration distributions and environmental fate. Kerndorff et al. [3] included these properties in their standardized assessment model but accounted for carcinogenicity only qualitatively.

4.3. Risk indices incorporating information on environmental fate

When volatilization and decay were included in the models, the relative risks of toxicants changed considerably. Particularly nonvolatile and lipophilic organic compounds (e.g., dieldrin and lindane) emerged among the most significant toxicants (Table 3). Some of them also exhibited high relative values of cancer risk. These indices are not commensurable for both elements and organic compounds because of the difficulty in defining values of H and $t_{1/2}$ for the former [16].

Environmental fate factors which vary by several orders of magnitude, such as biotic and abiotic decay, strongly affect effective risk indices. Also the availability and

precision of data may be crucial [17]. For instance, the reported lower persistence of some of the analysed Arochlor mixtures (see Appendix) reduced the overall ranking of PCBs.

Sedimentation after sorption or precipitation was not included in the indices since it does not imply permanent removal from the aquatic system but constitutes a mobilizable pool. Bioaccumulation was not explicitly considered; it is conceptually ambiguous since it decreases risks mediated by one exposure route (drinking water) and increases those by another (biota). Bioconcentration in laboratory tests (or estimated from K_{ow}) is also a bad predictor of actual environmental bioaccumulation [12]. Moreover, the inclusion of bioaccumulation was not deemed necessary in the present models because it correlates with persistence (and, for many compounds, inversely with volatility, cf. [17]).

4.4. Risk indices based on toxicant fluxes

The most important toxicants on the basis of flux estimates (serving as a form of flow-weighting of concentrations) and of ecotoxicity included primarily heavy metals, while those based on fluxes and drinking water norms were chloroaromatic and other organic compounds, especially when nondetects were substituted by missing values (Table 4). These rankings differ substantially from those based on concentrations and critical effect only, as well as from those index values (for organics) obtained by considering environmental fate factors (Table 3).

There were considerable differences in many cases between the relative importance of the toxicants on the basis of truncated distributions and of distributions which included estimates of concentrations for nondetects (Table 4); the same holds for the other indices. This difference was particularly pronounced for median values and for substances which had low detection frequencies and thus displayed greater estimates of median fluxes when nondetects were omitted. In several cases (e.g., for many neutral organochlorine pesticides), the statistics of the indices of risk flux could not be estimated with reasonable generalizability since the frequency of detection was so low for these compounds.

4.5. General methodological evaluations and lines of development

No single risk index, model or analysis approach is universally applicable, or wholly sufficient for analysing even a single application. The present risk indices, conceptually extending the previous standardized assessment models of similar kinds, serve as screening tools e.g., for the selection of toxicants subjected to in-depth analyses in site assessments. Also site-specific values of the indices may be computed for such assessments [2] or for site comparisons, after correction for flows, dilution or other site-specific risk factors. Sum indices may be produced simply by addition of the values of substance-specific indices.

Risk indices of the kind used in this study are comparative or (strictly defined) semiquantitative. They are not necessarily proportional to actual risks posed by the substances on a site-specific basis, because exposure factors, e.g. dilution prior to point

Table 4
Medians and rank orders of indices of risk fluxes from the studied waste sites^a

Toxicant ^b	Health risk flux index HRF (m ³ d ⁻¹)				Toxic risk flux index TRF (m ³ d ⁻¹)			
	<DL ^c = 0.5 × DL		<DL = missing		<DL = 0.5 × DL		<DL = missing	
	<i>f</i> ₅₀	Rank order	<i>f</i> ₅₀	Rank order	<i>f</i> ₅₀	Rank order	<i>f</i> ₅₀	Rank order
As	12		26		0.90		2.0	
Cd	4.4		4.4		130	5.	130	
Co	2.4		2.9		240	3.	290	5.
Cr	14		14		8.0		8.0	
Cu	17	6.	17		74 000	1.	120 000	1.
Ni	21	5.	20		89	6.	82	
Pb	11		11		280	4.	420	4.
Zn	10		13		340	2.	450	3.
12-DCE _a	47	4.	490	3.	4.0		42	
TeCE _e	0.99		800	2.	0.0060		0.0096	
Toluene	6.9		25		18		60	
12-DCBz	2.1		71		0.0081		0.28	
HCBz	430	1.	3700	1.	0.27		2.3	
246-TCP	140	2.	420	5.	0.14		0.42	
PeCP	0.7		1.0		0.28		0.41	
Lindane	71	3.	480	4.	21		140	6.
PCBs	14		240	6.	68		1200	2.

^a Only toxicants with >10 values above DL have been included.

^b For abbreviations, see Table 1.

^c DL = detection limit.

of exposure, are not wholly considered. However, in the pooled data the possibilities for comparison of the indices are better. The risk flux indices account for some of the variation in exposure factors by incorporation of data on flows. In absolute terms, the indices represent approximations of worst-case risks, assuming no dilution. This assumption may be justified particularly for comparing risks to other organisms than humans by the use of TI values, because they integrate information on various species, some of which may be plausibly assumed to be present at sampling points.

The risk analysis procedures involve substantial uncertainty in measurements (both with respect to site data and to empirical or estimated chemical properties) and in the models, which were kept simple on purpose. The large ranges of various fractiles of the indices display considerable uncertainties associated with measurement and estimation. Also uncertainty due to the representativity and comparability of measurements is present, particularly without account for dilution or flow. As for model uncertainties, the definitions and weighing of the different kinds of indices and of factors combined in them is open to discussion [4]. For instance, normalized scales (e.g., to 0–1) and nonlinear (e.g., logarithmic) scales may be used, in part to cope with the large

ranges of effective risk indices, instead of using logarithms of final values of the indices as in the present work.

The indices strongly depend on quantitative and qualitative definitions of critical effects which rely on evolving and diverse toxicity data as well as on evaluations of reasonable prudence e.g., in connection with safety factors (with HI and CI). Some end points are thus not reflected well in LEC (or LQG) values. LQGs for toxicant concentrations are still developing, inconsistent and uncertain.

Structural lines of development could thus include the incorporation of new types of data, new variables and models, and specification of the indices for new cases (e.g., other transport routes). Explicit consideration of environmental fate seems important also in initial comparative risk analyses. For instance, bioaccumulation could in principle be accounted for in other indices addressing secondary poisoning, e.g. by the use of measured or estimated bioconcentration factors ([21], see also [13]). However, attention would have to be paid to deficiencies in data and estimation models, as well as to the conceptual differences of risks mediated in soluble phase or in biota [17, 19]. Also reformulation of the present fate factors may be feasible to more realistically reflect the underlying mechanisms. The indices may also be combined; for instance, flux indices accounting for sinks could be devised.

The probability distributions of concentrations (and, potentially, of other risk factors and variables in the models underlying indices) are crucial in the above prioritizing procedures. The treatment of empirical distributions constitutes an important source of variation and uncertainty (Table 4, cf. [3, 20]). Due to the common skewness of the distributions and to low detection frequencies, many substances which were important on the basis of isolated maxima did not have high (or even estimable) median values. However, the exclusion of nondetects would result in unrealistically high estimates of indices for some substances, as well as in loss of data. An analysis of data obtained both by truncation and by substitution of nondetects by default values (e.g., 0, 0.5 or 1 times the detection levels) is thus justified. The straightforward inclusion of detection frequencies in substance-ranking indices [3] is methodologically questionable because of the variation, also due to external factors, in detection levels. A better way to deal with these kinds of truncated data would seem to be to consider more explicitly concentration distributions and the frequency of exceeding critical levels, which was already to some degree done in the present work by the analysis of the various distribution statistics of the indices.

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Appendix

Physicochemical, environmental and biological properties^a and environmental and health criteria of analyzed toxicants and mixtures

Name, symbol, abbreviation or formula ^b	Volatility ^c log <i>H</i> (Pa m ³ mol ⁻¹)	Persist. ^d (acr.), log <i>t</i> _{1/2} (d)	Aquat. chronic toxic. ^e log LEC ⁻¹ (ppm ⁻¹)	Carcinog. ^f log <i>b</i> _{1,01} [*] ppm ⁻¹ (d)	Drink. water norms, ^g log LQG (ppm)
<i>Elements</i>					
As(III/V)		≈ 10	0.28	1.19	-1.40
Cd(II)	-	≈ 10	3.77	0.79	-2.30
Co(II)	-	≈ 10	2.00	-	0.00
Cr(III)	-	≈ 10	1.05	-	-1.30
Cr(VI)	-	≈ 10	0.72	1.61	-
Cu(II)	-	≈ 10	5.15	-	-1.30
Hg(II)	3.05	≈ 10	2.59	-	-2.70
Ni(II)	-	≈ 10	1.92	0.06	-1.30
Pb(II)	-	≈ 10	3.40	-	-1.40
Zn(II)	-	≈ 10	1.52	-	0.00
<i>Chlorinated aliphatic compounds</i>					
DCM	2.44	-	-2.00	-3.20	-
Chloroform	2.69	1.23	-0.31	-1.15	-
CCl ₄	3.37	0.60	-0.60	-0.89	-3.00
12-DCE _a	2.02	-	1.23	-1.04	-1.60
111-TCE _a	3.11	-	-1.72	-	-0.70
112-TCE _a	2.08	-	-1.26	-1.24	-1.52
1112-TeCE _a	2.38	-	-1.30	-2.24	-
1122-TeCE _a	1.67	-	-0.97	-0.70	-2.00
t-12-DCE _c	2.83	-	-	-	-
TCE _c	3.00	0.85	-1.26	-1.96	-2.30
TeCE _c	3.07	2.54	-0.70	-1.29	-1.52

<i>Unchlorinated aromatic hydrocarbons</i>						
Benzene	2.74	0.60	1.82	-1.54	-2.30	
Toluene	2.75	0.60	2.27	-	-1.85	
12-xylene	2.71	-	-0.58	-	-	
13-xylene	2.89	(0.74)	-0.96	-	-	
14-xylene	2.89	(0.30)	-0.30	-	-	
Ethylbenzene	2.93	(0.74)	-1.51	-	-	
Naphthalene	1.92	0.85	0.35	-	-	
<i>Chlorobenzenes</i>						
MCBz	2.57	1.04	1.30	-	-2.00	
12-DCBz	2.08	1.40	0.11	-	-	
HCBz	2.12	-	1.80	0.22	-5.00	
<i>Chlorophenols</i>						
245-TeCP	-	1.56	0.35	-	-	
246-TeCP	-0.09	0.78	1.00	-1.70	-4.00	
2346-TeCP	-	-	-	-	-	
2356-TeCP	-	(1.56)	-	-	-	
PeCP	0.18	1.95	1.60	-0.48	-2.00	
<i>Chlorinated neutral pesticides</i>						
Aldrin	0.15	2.78	4.33	1.06	-1.00	
Dieldrin	-1.69	3.40	3.05	1.48	-4.00	
Endrin	-3.11	-	4.22	-	-4.00	
44'-DDD	-	-	3.19	0.47	-	
24'-DDE	-	-	-	0.47	-	
44'-DDT	0.58	3.54	3.44	-0.47	-3.00	
Lindane	-1.31	3.15	3.77	0.12	-2.52	
Heptachlor	2.09	2.86	3.05	0.53	-	
<alpha>-Chlordane	-0.03	3.00	3.52	0.21	-4.00	
<i>Polychlorinated aromatic compounds</i>						
Arochlor 1242	1.75	-	3.00	-	-3.30	
Arochlor 1248	3.55	0.85	3.40	-	-3.30	
Arochlor 1254	2.44	≈10	4.00	-	-3.30	
Arochlor 1260	2.86	≈10	3.00	-	-3.30	
PCBs	-	-	-	2.37	-3.30	

Appendix (continued)

Name, symbol, abbreviation or formula ^b	Volatility ^c log <i>H</i> (Pa·m ³ mol ⁻¹)	Persist. ^d (acr.), log <i>t</i> _{1/2} (d)	Aquat. chronic toxic., ^e log LEC ⁻¹ (ppm ⁻¹)	Carcinog., ^f log <i>b</i> * ₁₀₁ ppm ⁻¹ (d)	Drink. water norms, ^g log LQG (ppm)
<i>Other compounds</i>					
2-cresol	-0.79	(1.26)	-	-	0.70
3-cresol	-1.09	(0.30)	-	-	0.70
4-cresol	-1.04	(0.30)	-	-	0.70
<i>n</i> -DOP	0.05	0.70	0.80	-	-

^a If several equally appropriate values were available, the arithmetic mean was used for physicochemical properties and the maximum value for toxicity. Physicochemical properties are at 25 °C.

^b For abbreviations, see Table 1.

^c Coefficient of Henry's law [15, 17, 10-12, 16].

^d Half-life in aerobic (aquatic) environments, as reported, estimated by linear models of percent reduction and test duration, or calculated from first-order decay coefficients determined in sewage or in river water [16, 19, 10-12, 17, 18].

^e Greatest toxicity for all aquatic systems and end points, as logarithm of the reciprocal of the lowest LEC (lowest effective concentration) value [10-13].

^f 95% upper confidence limit for cancer potency as estimated with the linearized multistage model [2, 1, 9, 12].

^g Lowest relevant national health norms or guidelines for acceptable concentrations in potable water [7, 8, 2, 12].

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