Supporting Information:

Confronting Workplace Exposure to Chemicals with LCA: The Examples of Trichloroethylene and Perchloroethylene in Metal Degreasing and Dry Cleaning

Stefanie Hellweg[1], Evangelia Demou[1], Martin Scheringer[1], Thomas E. McKone[2], and Konrad Hungerbuehler[1]*

[1]Swiss Federal Institute of Technology, Safety and Environmental Technology Group, ETH Hönggerberg, CH-8093 Zürich, Switzerland.

[2]University of California Lawrence Berkeley National Laboratory, One Cyclotron Road, 90R3058, Berkeley CA, 94720, USA.

* Corresponding author phone: +41-1-6334337; fax: +41-1-6321189, e-mail: stefanie.hellweg@chem.ethz.ch

Machine technology description

Types I and II are open top, cold-cleaners, with solvent baths and a vapor bath. To prevent vapors escaping to the workplace they have a capturing device at the rim of the baths. In Type II machines the rim also has an electro-cooling apparatus that further enhances vapor capture. Type III machines operate on the same principle, but in this case the baths are all enclosed to prevent solvent evaporation and loss. The Type IV apparatus is a closed system with a refrigerated recirculation system, which recycles the solvent. Type V machines release no exhaust air to the environment. The entire cleaning process takes place in a closed, looped drying and recycling system, including an activated carbon filter to ensure solvent capture. The cleaning chamber opens only after concentrations have reached less than 1 g/m^3.

In the dry-cleaning industry there are five different machine generations. First generation "transfer machines" have a separate washer and dryer. In some countries, such as

Germany, transfer machines are no longer used (1), but in many countries they are still in use, e.g. in the U.S. (2,3). The next four generations are all "dry-to-dry" machines, which eliminate the need for manual transfer of solvent-covered clothing. Second generation machines have a water-cooling system for solvent-laden air. Exhaust air is then vented directly to the atmosphere. Third generation machines have a water-cooling or refrigeration unit incorporated to facilitate vapor recovery. Fourth generation machines are non-vented and have a closed system. The solvent-concentrated air is recovered by passing through a condenser and an activated carbon filter. Even though the same nomenclature is used for the various machines types, in the U.S. and Germany for instance, there are small differences in the technology for the machines between 2nd to 4th generation. However, the differences are minor and are not considered to affect the outcome. Fifth generation machines are broadly used in Germany but not in the U.S. (2,3). In addition to the refrigerated cooling device and the carbon adsorber, the fifth generation also includes an interlocking system, allowing the chamber door to open only after the concentration has reached a specified level.

Data tables

TABLE S1: Machine sizes and batch-times

Machine size	Capacity (kg)	Machine generation	Batch–time (min)
Dry- cleaning			
1	12	First	20-30
2	16	Second	40-55
3	22	Third	40-55
4	28	Fourth	45-65
5	32	Fifth	50-70
Metal-degreasing			
1	40-50		4.8-7.2
2	50-60		6-10.2
3	120-150		8.4-12
4	Approx. 600		20-30
5	Approx. 1000		30-60

TABLE S2: Emissions of dry-cleaning emission (g per kg garment) and metal-degreasing (g per m^2 surface area) for various machine generations and types (data taken or calculated from (1)).

TCE emission factors for metal-degreasing	Type I	Type II	Type III	Type IV	Type V
E_{diff} min[a]	0.30	0.17	0.05	0.01	0.00
E_{diff} avg[a]	0.91	0.52	0.13	0.04	0.01
E_{diff} max[a]	7.4	4.2	0.84	0.20	0.12
E_{rc} min[a]	0.98	0.98	0.12	0.03	0.02
E_{rc} avg[a]	5.9	5.9	1.9	0.03	0.02
E_{rc} max[a]	11	11	3.6	0.03	0.02
E_{rep} min[a]	0.39	0.23	0.19	0.02	0.00
E_{rep} avg[b,c]	1.4	0.83	0.68	0.11	0.00
E_{rep} max[c]	11	7,0	5.8	1.3	0.02
PCE emission factors for metal-degreasing	Type I	Type II	Type III	Type IV	Type V
E_{diff} min[a]	0.10	0.06	0.02	0.01	0.00
E_{diff} avg[a]	0.31	0.17	0.04	0.04	0.01
E_{diff} max[a]	2.5	1.4	0.28	0.20	0.12
E_{rc} min[a]	3.3	3.3	0.41	0.10	0.05
E_{rc} avg[a]	19	19	6.2	0.11	0.05
E_{rc} max[a]	36	36	12	0.11	0.06
E_{rep} min[a]	0.15	0.08	0.06	0.01	0.00
E_{rep} avg[a]	0.57	0.33	0.25	0.05	0.00
E_{rep} max[a]	4.9	2.9	2.2	0.77	0.02
PCE emission factors for dry-cleaning	First generation	Second generation	Third generation	Fourth generation	Fifth generation
E_{diff} min		3.4	3.4	1.7	0.20
E_{diff} avg [b]		4.6	4.6	1.9	0.30
E_{diff} max		5.7	5.7	2.1	0.40
E_{rc} min		0.46	0.38	0.26	0.12
E_{rc} avg [b]		1.7	1.40	0.96	0.35
E_{rc} max		6.6	5.5	3.8	1.3
E_{rep} min[c]	<10[d]	1.9	0.32	0.33	0.03
E_{rep} avg[b,c]		2.5	0.42	0.48	0.04
E_{rep} max[c]	<15[d]	3.0	0.53	0.63	0.05

[b] Minimum and maximum emissions of machines with and without vapor degreasing and of plate and sphere shaped metal parts. The average was calculated as the average between minimum and maximum value of size 3 machines (Table S1), as this is the machine size used most (1).
[b] Minimum and maximum values are empiric values. Average values are calculated as the average between min and max, except for E_{rc}, for which empiric information was available.
[c] Emissions were calculated by multiplying the concentrations measured in the cylinder (1) to the cylinder volume and division by the load (79% of the capacity (1)). With respect to second and third generation machines, 50% of this emission amount is emitted to the workplace and the other 50% directly to the environment due to ventilation devices.
[d] In EPA 1995 (4), the total for 'miscellaneous emissions' including losses from opening and closing dryers is given as 10-15 g/kg.

TABLE S3: Emission flows $\dot{E}_{A,x}$ (g/h) of TCE and PCE to workplace air for different machine generations (Type I-V) and sizes. The three components of $\dot{E}_{A,x}$ (Equation 6) were calculated from (1,5). For machine sizes and batch times see Table S1.

Machine type	average load size (kg)		Type I	Type II	Type III	Type IV	Type V
TCE emissions from metal-degreasing (g/h), $\dot{E}_{A,TCE}$							
		Min	132	102	28.3	4.60	0.834
Size 1	45	Max	253	215	50.1	12.3	3.67
		Min	167	124	38.6	6.06	0.890
Size2	55	Max	307	246	70.7	17.2	4.38
		Min	264	187	73.6	10.2	1.15
Size3	135	Max	450	348	122	29.0	5.81
		Min	472	317	147	17.2	1.54
Size4	600	Max	846	621	255	56.8	7.92
		Min	1100	665	398	42.9	1.43
Size5	1000	max	2340	1520	873	192	15.5
PCE emissions from metal-degreasing (g/h), $\dot{E}_{A,PCE}$							
		Min	204.6	190.7	29.1	7.3	2.7
Size 1	45	Max	566.0	550.7	67.7	19.8	8.5
		Min	228.8	208.7	33.7	8.5	2.9
Size2	55	Max	583.7	559.5	75.1	23.1	9.0
		Min	307.5	273.4	51.1	11.5	3.7
Size 3	135	Max	760.2	718.3	106.8	26.2	11.6
		Min	451.9	383.7	83.9	15.7	4.8
Size4	600	Max	1215.3	1125.8	188.7	58.3	17.3
		Min	637.0	455.8	161.7	24.3	3.8
Size5	1000	max	1934.6	1614.5	439.9	147.9	26.1
Machine generation	Load size (kg)		First generation	Second generation	Third generation	Fourth generation	Fifth generation
PCE emissions from dry-cleaning (g/h), $\dot{E}_{A,PCE}$							
		Min	263	72.3	55.1	23.1	3.17
Size 1	12	Max	776	195	144	76.2	17.7
		Min	350	96.4	73.5	30.8	4.23
Size2	16	Max	1040	261	192	102	22.7
		Min	482	133	101	42.4	5.82
Size3	22	Max	1420	357	264	140	32.5
		Min	613	169	129	53.8	7.40
Size4	28	Max	1810	456	337	178	41.4
		Min	701	193	147	61.6	8.46
Size5	32	max	2070	520	384	203	47.3

TABLE S4: Volume, air exchange rates and number of workers exposed (1,5).

Parameter	Unit	Metal-degreasing	Dry-cleaning
Volume of inner box (near-field), V_A	m^3	100[a]	100[a]
Volume of outer box (far-field), V_B	m^3	300–500[a]	300–500[a]
Air exchange rate with the environment, k_L	h^{-1}	6–6.5 for type I and II machines 5.5–6 for type III–V	6–10
Air exchange rate between box A and B, k_A[b]	h^{-1}	7–7.5 for type I and II machines 6–6.5 for type III–V	8–12
Number of workers exposed ('n_{pop}' in Equation 4)	-	Near-field: 1.5-3 (average 2.25) for type I and II machines, and 1–1.6 (average 1.3) for type III to V Far-field: 3-10 (average 6.5) for type I and II machines, and 2-8 (average 5) for type III to V	Near-field: 1-1.5 (average 1.25) Far-field: 4-5 (average 4.5)

[a] The total room volume is the sum of V_A and V_B.

[b] $k_B = k_A \cdot V_A / V_B$

TABLE S5: PCE and TCE concentrations[a], (g/m^3), for various machine types, in both near- and far-field. Bold values surpass the MAK value.

Concentration / machine Type		Type I	Type II	Type III	Type IV	Type V
TCE Concentrations from metal-degreasing						
Near-Field Concentration, C_A (g/m^3)	Min	0.24	0.19	0.06	0.01	0.002
	Average	**1.21**	**0.84**	**0.45**	0.08	0.009
	Max	**4.63**	**3.02**	**1.98**	**0.43**	0.04
Far-field Concentration, C_B (g/m^3)	Min	0.07	0.05	0.02	0.03	0.0005
	Average	**0.34**	0.23	0.12	0.02	0.003
	Max	**1.30**	**0.85**	**0.52**	0.11	0.01
PCE Concentrations from metal-degreasing						
Near-Field Concentration, C_A (g/m^3)	Min	**0.38**	**0.85**	0.06	0.02	0.006
	Average	**1.23**	**1.08**	0.27	0.07	0.02
	Max	**3.84**	**3.20**	**1.00**	**0.34**	0.06
Far-field Concentration, C_B (g/m^3)	Min	0.11	0.10	0.02	0.004	0.002
	Average	**0.34**	0.30	0.07	0.02	0.006
	Max	**1.07**	**0.90**	0.26	0.09	0.04
Concentration / machine generation		First generation	Second generation	Third generation	Fourth generation	Fifth generation
PCE emissions from dry-cleaning						
Near-Field Concentration, C_A (g/m^3)	Min	0.33	0.09	0.07	0.03	0.004
	Average	**1.46**	**0.38**	0.28	0.14	0.03
	Max	**3.74**	**0.94**	**0.69**	**0.37**	0.09
Far-field Concentration, C_B (g/m^3)	Min	0.11	0.03	0.02	0.01	0.001
	Average	**0.46**	0.12	0.09	0.04	0.009
	Max	**1.15**	0.29	0.21	0.11	0.03

[a] Calculated according to Equation 2.

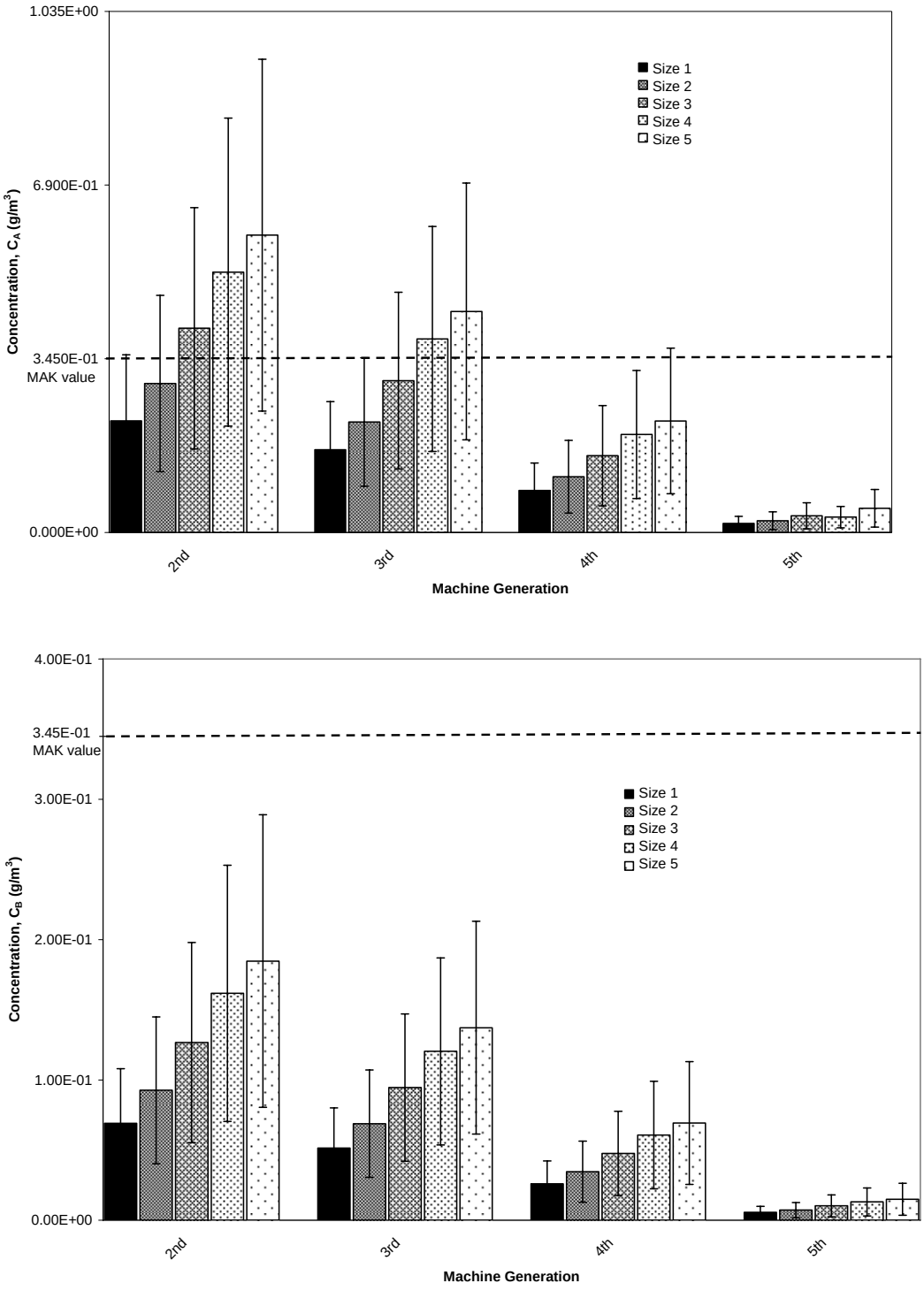

Figure S1: Near- and far-field concentrations for PCE in dry-cleaning (various machine generations and sizes).

TABLE S6: Machine Distribution

Industrial Sector	Germany (1999)		United Kingdom (2002-2004)
Metal Degreasing	100% Type V 301 Type V (TCE)[a] 1351 Type V (PCE)[b]		Majority are open-topped vapor degreasers (i.e. Types I and II)[c] ~6,000 hot-vapor degreasers in the UK[d]
	Generation	Germany (2001)	U.S. (1995)[f]
Dry Cleaning	1st	-	34%
	2nd	-	32%
	3rd	-	34%
	4th	-	
	5th	100% (4700)[e]	Less than 1% (2002)

a. Ref. (6)
b. Ref. (7)
c. Ref. (8)
d. Ref. *(9)*
e. Ref. *(10)*
f. Ref. (4)

TABLE S7: Net solvent consumption and amounts of waste solvents generated in g per m^2 metal surface and kg garment for various machine types/generations (two significant figures). The indicated data sources either provided average values (avg) or data ranges (min/max).

TCE	Type I	Type II	Type III	Type IV	Type V
Net consumption of fresh TCE[a]	70	70	50	39	39
Mass of waste solvent mixture per m^2 going into distillation (solvent and pollutants)	702	702	702	702	702
Waste solvent mass in distillation[a]	700	700	700	700	700
Pollutants[b]	2	2	2	2	2
Solvent losses from distillation[a] (this amount of waste solvent is incinerated)	38	38	39	39[c]	39[c]
Recovered solvent	662	662	661	661	661
Recovery rate	94%	94%	94%	94%	94%
PCE	**Type I**	**Type II**	**Type III**	**Type IV**	**Type V**
Net consumption of fresh PCE[a]	90	90	57	44	44
Mass of waste solvent mixture per m^2 going into distillation (solvent and pollutants)	776	776	776	776	776
Waste solvent mass in distillation[a] (this amount of waste solvent is incinerated)	774	774	774	774	774
Pollutants[b]	2	2	2	2	2
Solvent losses from distillation[a]	42	42	44	44[c]	44[c]
Recovered solvent	732	732	730	730	730
Recovery rate	94%	94%	94%	94%	94%
Amounts (g per kg garment) / Machine generation	First generation	Second generation	Third generation	Fourth generation	Fifth generation
Total consumption of fresh PCE					
Min	300[d]	100[e]	40[e]	20[e]	
Max	500[d]	150[e]	80[e]	40[e]	10[e]
PCE into distillation[e]					
Min	320[f]	280[g]	280[g]	230[f]	
Avg					170[e]
Max	320[f]	280[g]	280[g]	240[f]	
Waste PCE into incineration					
Min	10[h]	14	14	12[e]	
Avg					8.3[e]
Max	160[h]	14	14	12[e]	

[a] Ref. *(11)*

[b] 4.8 g/l according to Mannheim et al. *(11)*. The densities of TCE and PCE are 1,465 g/cm3 and 1,62 g/cm³, respectively.

[c] Assumption: Same as Type III machines.

[d] Ref. *(12)*.

[e] Ref. *(13)*.

[f] From these amounts, 94-95% are recovered in case of fourth and fifth generation machines*(13)*. Values for first generation machines calculated as the difference of total consumption and total emissions to air.

[g] Assumption: Average between first and fourth generation machines (only distillation residues).

[h] Ref. *(4)*. From this amount, approximately 16 g/kg account for distillation residues (and the remaining fraction for filter residues).

TABLE S8: Inventory data for the distillation of 1 kg PCE or TCE containing waste-solvent mixture (calculated with *(14)*).

Inventory flow	Name of corresponding data set in *(15)*	Unit		Amount
Electricity	electricity, medium voltage, production UCTE, at grid	kWh	Min	0.004
			Average	0.033
			Max	0.110
Cooling water		m^3	Min	0.004
			Average	0.027
			Max	0.070
Steam	heat, heavy fuel oil, at industrial furnace	MJ	Min	1.2
			Average	3.4
			Max	7.5
Nitrogen	Nitrogen, liquid, at plant	kg	Min	0.0000012
			Average	0.0003
			Max	0.0011
Outlet air[a]		Nm^3	Min	0.024
			Average	0.062
			Max	0.151

[a] The carbon content is between 10g and 20 g carbon per Nm^3. Assumption: consisting of emissions of PCE or TCE, depending on the solvent distilled.

TABLE S9: Inventory data for the incineration of 1 kg of PCE and TCE (calculated with *(16)*, two significant figures).

Inventory flow	Name of corresponding data set in *(15)*	unit	TCE	PCE
Use of heating oil	Heavy fuel oil, at regional storage	kg	0.38	0.42
Use of heating gas	Natural gas, at long-distance pipeline	Nm^3	0.0017	0.0017
Use of drinking water	tap water, at user	kg	8.7	8.7
Use of NaOH	sodium hydroxide, 50% in H2O, production mix, at plant	kg	2.3	2.5
Use of HCl	hydrochloric acid, 30% in H2O, at plant	kg	0.0078	0.0078
Use of NH_4OH	chemicals inorganic, at plant	kg	0.0030	0.0030
Steam production	heat, heavy fuel oil, at industrial furnace 1MW	MJ	17	17
Electricity (net production)	electricity, medium voltage, production UCTE, at grid	kWh	0.060	0.060
CO_2		kg	1.9	1.9
NO_x as NO_2		kg	0.00026	0.00026
NMVOC		kg	0.0000030	0.000003
particles		kg	0.000038	0.000038
NH_3		kg	0.000011	0.000011
CO		kg	0.000022	0.000022
Cl as HCl (air)		kg	0.00025	0.00026
Cl^- to water		kg	0.81	0.85

TABLE S10: Number of workers and population number per scale, used as weighting factors $n_{pop,x}$ (Equation 4).

Scale	Number of persons exposed
Near-field workplace *(1)*	Dry-cleaning: 1-1.5 (average 1.25) Metal degreasing: 1.5-3 (average 2.25) for type I and II machines, and 1–1.6 (average 1.3) for type III to V
Far-field workplace (1)	Dry-cleaning: 4-5 (average 4.5) Metal degreasing: 3-10 (average 6.5) for type I and II machines, and 2-8 (average 5) for type III to V
Continental scale *(17)*	367,000,000
Global scale *(17)*	Moderate zone: 2,120,000,000 Tropical zone: 2,290,000,000 Arctic zone: 99,100,000

TABLE S11: Weighted Risk Characterization Ratios (*weightedRCR*) for dry-cleaning. The numbers refer to a fictitious emission flow of 1000 tonnes/day to workplace air. Later transfer to outdoor air is not considered here.

	Min	Average	Max
weightedRCR (A) MAK based	1.2E+05	1.9E+05	3.2E+05
weightedRCR (B) MAK based	9.4E+04	1.7E+05	3.3E+05
weightedRCR (total) MAK based	2.2E+05	3.6E+05	6.5E+05
weightedRCR (A) TLV based	2.5E+05	4.0E+05	6.6E+05
weightedRCR (B) TLV based	2.0E+05	3.4E+05	6.8E+05
weightedRCR (total) TLV based	4.5E+05	7.5E+05	1.3E+06
weightedRCR (A) HLV Uses based (8h)	4.1E+07	6.5E+07	1.1E+08
weightedRCR (B) HLV Uses based (8h)	3.2E+07	5.6E+07	1.1E+08
weightedRCR (total) HLV Uses based (8h)	7.3E+07	1.2E+08	2.2E+08

TABLE S12: Characterization factors (CF, Equation 5) for workplace emissions and outdoor emissions.

		Workplace (emission to indoor air at the workplace, considering also later transfer to outdoor air)			Environment (emission to ambient air) *(17)*
		Metal degreasing type I and II	Metal degreasing type III to V	Dry cleaning	
MAK based					
	Min	35	35	-	
TCE	Max	35	35	-	34
	Min	6	6	5.7	
PCE	Max	6	6	5.9	5.5
TLV based					
	Min	35	35	-	
TCE	Max	36	36	-	34
	Min	6	6	5.77	
PCE	Max	7	7	6.24	5.5
Environmental HLV based (adjusted to 40h exposure/week)					
	Min	3400	2600	-	
TCE	Max	12000	8600	-	34
	Min	79	61	46	
PCE	Max	260	190	130	5.5

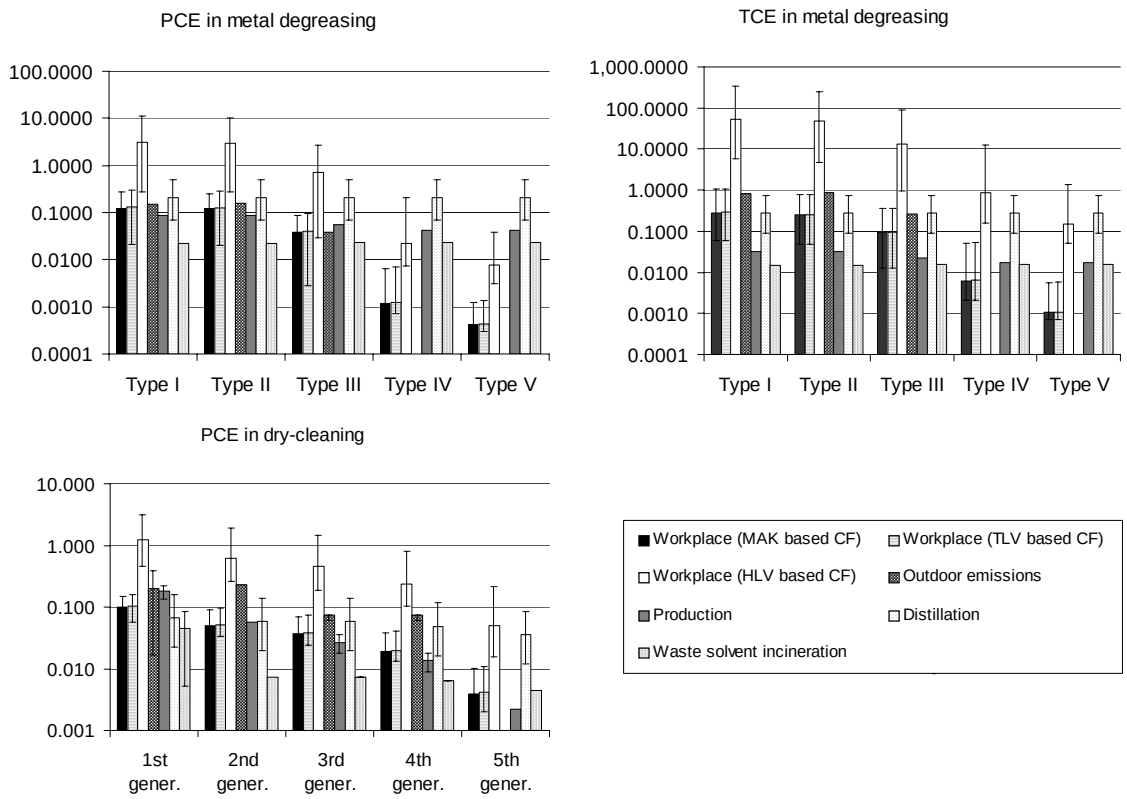

Figure S2: Human Toxicity Potential on the basis of characterization factors (in 1,4-dichlorobenzene-equivalents, $HTP_{workplace,CF}$ in Equation 6) from the use of PCE (left) and TCE (right) in the degreasing of 1 m^2 metal surface (top) as well as from the use of PCE in the dry-cleaning of 1 kg of garments (bottom). The uncertainty ranges show the range of minimum and maximum emissions (see Tables 2-4 and S8). In contrast to Figure 3, the bars for workplace include the direct effects of workplace emissions as well as the potential subsequent outdoor effects (emissions released at the workplace will eventually reach the environment through ventilation).

TABLE S13: Contribution of solvent emissions to the total human health potential considering the complete life cycle of TCE and PCE use in metal-degreasing and dry-cleaning. Emissions were weighted with the *weightedRCR* (two significant figures).

TCE in metal-degreasing – MAK based	Type I	Type II	Type III	Type IV	Type V
Fraction of impact from TCE outdoor emissions of total impact	83%	83%	68%	37%	37%
Fraction of impact from TCE emissions at the workplace of total impact	0.31%	0.27%	0.15%	0.021%	0.0036%
Remaining emissions from production and disposal	17%	17%	32%	63%	63%
TCE in metal-degreasing – environmental HLV based					
Fraction of impact from TCE outdoor emissions of total impact	2.2%	2.5%	3.5%	11%	26%
Fraction of impact from TCE emissions at the workplace of total impact	97%	97%	95%	72%	30%
Remaining emissions from production and disposal	0.44%	0.49%	1.7%	18%	44%
PCE in metal-degreasing – MAK based					
Fraction of impact from PCE outdoor emissions of total impact	54%	54%	30%	11%	11%
Fraction of impact from PCE emissions at the workplace of total impact	1.6%	1.6%	0.60%	0.025%	0.0087%
Remaining emissions from production and disposal	45%	45%	69%	89%	89%
PCE in metal-degreasing – environmental HLV based					
Fraction of impact from PCE outdoor emissions of total impact	8.5%	8.6%	10%	10%	11%
Fraction of impact from PCE emissions at the workplace of total impact	85%	84%	67%	7.7%	2.8%
Remaining emissions from production and disposal	7.0%	7.1%	23%	82%	87%
PCE in dry-cleaning – MAK based	First generation	Second generation	Third generation	Fourth generation	Fifth generation
Fraction of impact from PCE outdoor emissions of total impact	52%	71%	58%	61%	18%
Fraction of impact from PCE emissions at the workplace of total impact	0.58%	0.43%	0.61%	0.41%	0.30%
Remaining emissions from production and disposal	47%	28%	42%	39%	81%
PCE in metal-degreasing – environmental HLV based					
Fraction of impact from PCE outdoor emissions of total impact	18%	29%	19%	26%	9%
Fraction of impact from PCE emissions at the workplace of total impact	66%	59%	68%	58%	50%
Remaining emissions from production and disposal	16%	12%	14%	16%	41%

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