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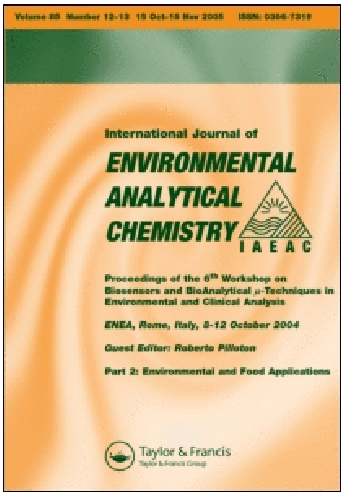

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Groundwater Contamination Assessment by Problem-Specific Selection of Analytical Parameters

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GROUNDWATER CONTAMINATION ASSESSMENT BY PROBLEM-SPECIFIC SELECTION OF ANALYTICAL PARAMETERS

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The approach outlined in this work permits a systematic, substance-specific and use-specific examination and evaluation of abandoned waste deposits and other waste sites with regard to emissions from these into groundwater. Examination and evaluation are based on a clear reduction of the number of substances to be measured and evaluated to those which permit an estimation of the potential risk involved in a use of affected groundwater for drinking purposes (priority contaminants).

Useful results for practical application are:

- a list of the priority contaminants to be analyzed;
- the transfer and persistence potential of these contaninants in groundwater; and
- concentrations of these contaminants at the site of use being still tolerable.

Thus, a parameter package is provided which permits a scientifically founded, problem-adapted and economic examination and evaluation of abandoned sites of waste deposits in view of their contamination potential and the resulting risk for groundwater use.

KEY WORDS: Groundwater contamination, inorganics, chlorinated hydrocanbons, waste disposal sites.

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INTRODUCTION

Contrary to contaminated industrial sites where hazards often do not arise until there is a different use of the site (e.g. excavation of ground for construction work) or direct contact with "open" deposits of weakly mobile and persistent contaminants (e.g. by playing children), most hazards arising from abandoned and still operating sites for waste disposal are almost exclusively produced by emissions from such sites. In Figure 1, the emission routes for substances from contaminated sites have been depicted and also their possible transfer to places where they may produce exposure. The most important emission route leads to groundwater.

Which substances may be emitted from an abandoned site into groundwater and in which amounts and which would be the hazards posed by them near the site for catchment of water for later use for human consumption will depend on the substances present. It has to be established whether a specific substance was either deposited, or may form, and on the amounts of that substance involved. The physical and chemical properties of the emitted substances with regard to their migration inside the deposited

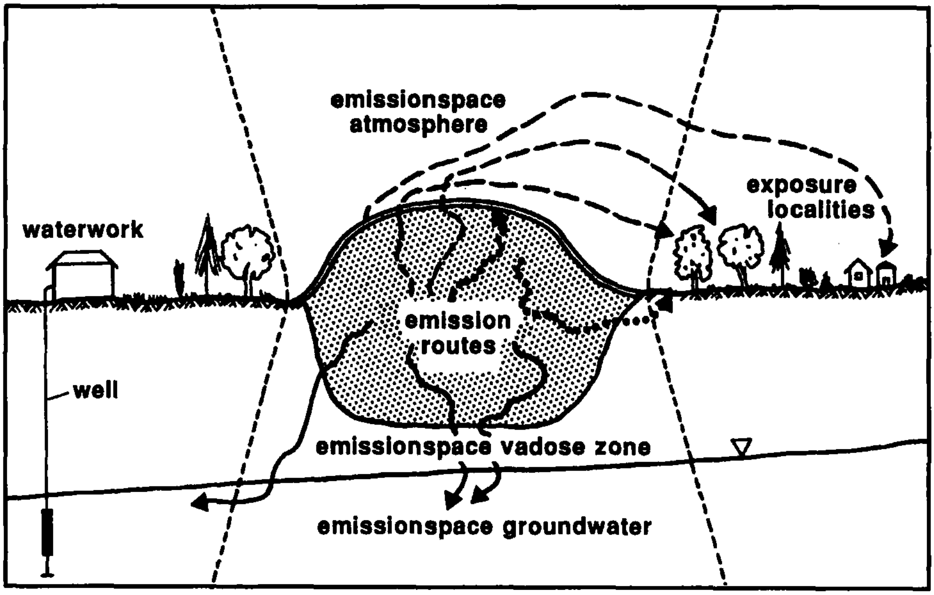

Figure 1 Emission routes for contaminants from an abandoned waste disposal site.

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material, in the vadose zone and in groundwater are of importance, as are the existing underground conditions at the site and the toxicity of the substance in the event of its use for drinking water.

Normally, the range of substances present in an abandoned site is not even approximately known. The same applies to the results of chemical conversion in the deposited material. To obtain corresponding information, the inside of the deposit is often made accessible by drilling, followed by sampling and analysis of the waste materials or their residues. This is certainly the wrong approach because a recording of substances *in* abandoned deposits of any type is not meaningful for three reasons. Firstly, an extremely narrow grid of sampling sites is necessary. However, even in the case of very small distances in terms of area and space, representative sampling is not possible and extremely high costs arise. Secondly, the number of substances recorded by such an approach will be huge but most of them cannot be considered because they can either not be identified or, if this is possible, there are no yardsticks for evaluation or their concentrations are too low. Thirdly, even if all substances present at an abandoned site are known, it is not possible to determine those substances which are emitted from the deposits and which may pose hazards to drinking water supply at totally different sites, because it is impossible to record the physical, chemical and biological interactions taking place within the wastes deposit.

Thus, the best approach consists in chemical-analytical examination of many cases of groundwater contamination caused by emissions from abandoned sites. This means that those substances which constitute a hazard for the utilization of waters for human consumption must be recorded on a representative basis. In the present communication, the results obtained by systematic studies and the conclusions to be drawn with regard to the selection and evaluation of problem-specific analytical parameters are shown.

EMISSION OF SUBSTANCES INTO GROUNDWATER FROM ABANDONED SITES

Characterization and quantification with the aid of contamination criteria

Composition by type of substance and substance content of groundwaters are considerably modified by the leachates from abandoned sites. Although in individual cases, the concentration of substances may also become reduced under the influence of an abandoned deposit (e.g. sulphate degradation in a reduction zone), the influence of leachates from abandoned sites in almost all cases becomes statistically evident as a concentration rise. There are exceptions, e.g selenium: The data for largely unaffected groundwaters exhibited higher concentrations than those for groundwaters influenced by leachates.

In Table 1, the results for groundwaters influenced by leachates and sampled in effluents from ca. 250 abandoned sites in west Germany have been listed. Calculated mean, median and other percentile values as well as the maximal values of the different inorganic parameters have been compiled. Compared to inorganic substances, there are far more organic ones which may contaminate groundwater in effluents from abandoned sites. Thus, in extensive studies in west Germany and in the United States[1] using GC-MS analysis, ca. 1200 organic groundwater contaminants could be recorded in leachates from abandoned contaminated sites. Of these, only a comparatively small number could be detected more than once and exhibited concentrations well above 1 µg/L (USA) or 0.1 µg/L (West Germany). Detection frequency of the foremost part of the organic contaminants identified (> 1000) was below 0.1%. In statistical terms, this means that these were identified less than once in 1000 samples each of groundwater downstream of waste deposits!

A selection of substances and substance groups for analytical and methodological reasons was largely excluded by the approach used since in these examinations, the preparation of samples (acid or basic/neutral extractable substances, volatile substances and pesticides) and analysis (essentially GC-MS) were directed at the objective of covering as many groundwater contaminants as possible. It became evident that a mere 128 organics with a detection frequency of > 1% (USA) or > 0.1% (Germany) could be identified in effluents from abandoned sites. In Table 2, the essential organic groundwater contaminants from the region of west Germany have been listed, by a number of statistical parameters of their concentration and in the order of their detection frequency (> 3%). 12 out of 19 contaminants with a detection frequency of ≥ 10% were readily volatile halogen compounds. Of these, 5 were alkane derivatives, 4 alkene derivatives and 3, chlorine-substituted benzenes. Among the 7 halogen-free contaminants, benzene and its alkyl derivatives (4 compounds) were predominant, the others were 2 phenols and naphthaline.

Volatile halogenated compounds also exhibited the highest average concentrations. Particular mention must be made of dichloromethane, (38 mg/L and 871 µg/L, respectively), cis-1,2-dichloroethene (22 mg/L and 234 µg/L, respectively) and vinyl chloride (ca. 1.7 mg/L and 85 µg/L, respectively). Thus, also the quantities found confirmed a significant dominance of these compounds as groundwater contaminants from abandoned deposits[2,3].

It must be assumed that only certain substances are demonstrated frequently and in elevated concentrations downstream from abandoned deposits. These are largely persistent under the strongly reducing conditions in "reduction zones", exhibit intensive

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Table 1 Statistical parameters of inorganic constituents from contaminated groundwater in Western Germany.

Parameter		DL[1]	Analytical attempts[2] (n)	(n) >DL	DF[3] [%]	Concentration mean A[4]	Concentration mean B[5]	Percentile concentration 50%	Percentile concentration 75%	Max.
Main cations										
Calcium	[mg/l]	5.0	318	317	99.7	177.0	175.0	156.0	229.0	785.0
Magnesium	[mg/l]	2.0	321	320	99.7	39.3	38.1	22.0	42.3	436.0
Sodium	[mg/l]	5.0	338	337	99.7	140.0	128.0	45.6	130.0	3600.0
Potassium	[mg/l]	1.0	217	217	100.0	34.4	32.9	12.0	36.0	350.0
Ammonium	[mg/l]	0.02	276	231	83.7	14.4	11.0	0.41	6.2	945.0
Iron (total)	[mg/l]	0.01	335	330	98.5	10.3	9.6	2.0	11.0	240.0
Manganese	[mg/l]	0.01	329	311	94.5	1.6	1.5	0.43	1.2	33.1
Main anions										
Hydrogen carbonate	[mg/l]	18.0	233	233	100.0	527.0	519.0	408.0	661.0	2458.0
Chloride	[mg/l]	1.0	360	360	100.0	218.0	202.0	74.2	168.0	6020.0
Sulfate	[mg/l]	1.0	352	350	99.4	218.0	194.0	122.0	223.0	8560.0
Nitrate	[mg/l]	0.5	347	244	70.3	58.7	25.6	2.5	24.3	11500.0
Trace elements										
Aluminium	[µg/l]	40.0	168	135	80.4	947.0	596.0	80.0	573.0	59600.0
Lead	[µg/l]	0.05	334	129	38.6	7.6	6.3	< 0.05	2.1	450.0
Cadmium	[µg/l]	0.05	335	126	37.6	40.3	1.5	< 0.05	0.3	13000.0
Chromium (total)	[µg/l]	10.0	279	179	64.2	39.5	21.2	< 10.0	< 10.0	5120.0
Copper	[mg/l]	10.0	275	189	68.7	26.5	24.5	< 10.0	20.0	577.0
Nicker	[µg/l]	10.0	249	187	75.1	116.0	22.9	13.0	24.0	23200.0
Mercury	[µg/l]	0.2	232	39	16.8	< 0.2	< 0.2	< 0.2	<0.2	3.4
Strontium	[µg/l]	40.0	205	201	98.0	604.0	580.0	399.0	764.0	5580.0
Zinc	[µg/l]	10.0	328	276	84.1	921.0	410.0	64.5	220.0	168000.0
Trace anions										
Arsenic (III/V)	[µg/l]	0.2	253	172	68.0	61.0	45.4	1.3	6.0	4000.0
Nitrite	[mg/l]	0.1	285	107	37.5	0.77	0.49	< 0.1	0.3	79.0
Selenium (IV/VI)	[µg/l]	0.2	112	20	17.9	0.22	0.10	< 0.2	< 0.2	14.0
Boron (total)	[µg/l]	20.0	259	253	97.7	949.0	832.0	181.0	530.0	31200.0
Fluoride	[mg/l]	0.5	97	57	58.8	< 0.5	< 0.5	< 0.5	0.50	1.7
Phosphate (total)	[mg/l]	0.1	207	113	54.6	2.3	1.8	0.1	0.60	115.0

[1] Detection limit
[2] Number of investigated wells
[3] Analytical attempts above detection limit
[4] mean of all values
[5] mean of all values excluding maximum values

migration into and spread in groundwater. Substances of low persistence and poor transfer behaviour of a degree that may correspond to immobility cannot be demonstrated with a high frequency or be present in groundwater in high concentrations even if they frequently occur or form in wastes in large amounts. As an immediate consequence, only substances which are frequently found can be present in high concentrations in effluents from abandoned deposits. This is clearly recognizable from Table 2 where also concentrations have been shown to exhibit a tendency to drop with a decreasing frequency of detection. This also explains the phenomenon that substances with a frequency of detection of ≥ 0.1% (ca. 1000 substances) could no longer be detected in concentrations of > 1 µg/L.

These significant findings must be considered when establishing lists of parameters for an examination of groundwater contamination from abandoned and other deposits of

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Table 2 Statistical parameters of organic constituents from contaminated groundwater in Western Germany.

					Concentration				*Mean logarithmic values*	
						Percentile				
Parameter	*DL*[1] *[µg/l]*	*Analytical attempts*[2] *(n)*	*(n) >DF*	*DF*[3] *[%]*	*Mean [µg/l]*	*50% [µg/l]*	*75% [µg/l]*	*Max. [µg/l]*	*log*	*[µg/l]*
Tetrachloroethene	0.1	277	195	70.4	56.1	1.4	3.7	6500.0	0.62	4.2
Trichlorothene	0.1	277	154	55.6	1010.0	2.3	11.0	128000.0	1.06	11.5
cis-1,2-Dichloroethene	4.0	153	46	30.1	22100.0	166.0	1150.0	411000.0	2.37	234.0
Benzene	1.0	127	38	29.1	141.0	13.5	38.0	1795.0	1.24	17.4
1,1,1-Trichloroethane	0.1	206	47	22.8	16.5	1.0	7.4	270.0	0.25	1.8
m/p-Xylene	0.1	92	21	22.8	39.9	2.8	4.9	447.0	0.53	3.4
Trichloromethane	0.1	236	52	22.0	76.2	1.4	10.1	2800.0	0.32	2.1
1,2-dichloroethane	5.0	16	3	18.8	107.0	< 5.0	< 5.0	210.0	1.86	72.4
Chloroethene (VC)	1.0	136	24	17.7	1690.0	99.5	1950.0	12000.0	1.93	85.1
Toluene	0.1	127	21	16.5	73.2	3.5	11.0	911.0	0.61	4.1
Dichloromethane	10.0	114	17	14.9	38100.0	438.0	16800.0	499000.0	2.94	871.0
Tetrachloromethane	0.1	201	29	14.4	1.2	0.2	0.3	23.0	0.48	3.0
4-Methylphenol (p-cresol)	1.0	124	17	13.7	42.0	8.6	20.7	283.0	1.08	12.0
Chlorobenzene	0.1	93	12	12.9	52.9	2.3	6.5	388.0	0.67	4.7
2-Methylphenol (o-cresol)	0.5	124	16	12.9	10.0	5.9	9.2	63.3	0.66	4.6
1,2-Dichlorobenzene	0.1	90	11	12.2	1.4	0.9	2.1	6.6	-0.08	0.83
1,4-Dichlorobenzene	0.1	90	11	12.2	31.9	2.2	37.5	265.0	0.53	3.4
Naphthalene	0.1	124	15	12.1	2.2	1.1	2.1	12.6	0.16	1.5
Ethylbenzene	0.1	124	14	11.3	32.2	4.4	62.5	160.0	0.82	6.6
o-Xylene	0.1	127	12	9.5	13.8	4.7	19.6	69.0	0.77	5.9
2,4,6-Trichlorophenol	0.1	124	11	8.9	3.2	0.6	1.5	24.1	-0.15	0.71
3,5-Dimethylphenol	0.1	124	10	8.1	16.2	6.9	35.6	61.0	0.60	4.0
Phenol	0.1	124	10	8.1	2.2	1.5	3.6	5.6	0.24	1.7
1,1,2-Trichloroethane	0.5	140	11	7.9	36.0	3.0	70.0	190.0	0.88	7.6
1,3-Dichlorobenzene	0.1	90	7	7.8	11.5	1.1	38.2	74.0	0.23	1.7
trans-1,2-Dichloroethene	5.0	134	10	7.5	57.1	50.0	95.0	135.0	1.61	40.7
Cumol, $C_6H_5CH(CH_3)_2$	0.1	90	5	5.6	2.4	3.1	4.5	4.7	0.20	1.6
1,1-Dichloroethane	10.0	130	7	5.4	52.7	53.0	90.0	110.0	1.64	43.7
Acenaphthene	0.1	124	6	4.8	6.3	1.3	17.1	32.0	0.19	1.6
2,4-Dichlorphenol	0.1	124	6	4.8	3.5	0.9	9.6	17.2	-0.07	0.85
3-Chlorophenol	0.1	124	6	4.8	12.7	12.3	20.8	22.8	1.02	10.5
p-Cymol, $p\text{-}CH_3C_6H_4CH(CH_3)_2$	0.1	90	4	4.4	1.9	1.5	2.6	3.5	0.22	1.7
2-Ethyltoluene	0.1	90	4	4.4	0.6	0.6	0.8	1.0	-0.21	0.62
2,4,5-Trichlorophenol	0.1	127	5	3.9	7.1	1.3	16.6	31.9	0.23	1.7
1,3,5-Trimethylbenzene	0.1	90	3	3.3	1.7	< 0.1	< 0.1	4.0	-0.02	0.95
Phenanthrene	0.1	124	4	3.2	1.5	0.6	2.6	4.4	-0.48	0.33
Tribromomethane	1.0	130	4	3.1	3.0	2.5	4.5	6.0	0.39	2.5

[1] Detection limit [2] Number of investigated wells [3] Analytical attempts above detection limit

wastes[4]. It will be shown in the following how problem-specific parameters for examination can be selected by scientifically founded criteria.

The "contamination factor" as a criterion of contamination

The influence of leachate emissions from abandoned deposits on groundwater may be characterized and quantified by a comparison of statistical parameters of substance-

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specific concentrations in uninfluenced groundwaters of different origin[5] and in groundwaters contaminated through leachates from abandoned deposits (Table 1). For inorganic substances, the geogenic background must be taken into consideration, for organic substances, in part, the share of ubiquitous pollution. The contamination factor (CF) of a substance designates the ratio between the concentration in the contaminated area and that in the uninfluenced area[6]. Thus, it indicates the factor by which the concentration of a substance in the contaminated area is higher than the concentration in the uninfluenced area. It constitutes a relative measure of the intensity of the influence. The contamination factor can be calculated only if the concentration in the uninfluenced area forming the denominator of the fraction is larger than zero which is the rule for geogenic inorganic parameters. Where, as it is the case with organic parameters and a few inorganic trace substances, the concentration in the uninfluenced area equals zero or is below the detection limit, a contamination factor cannot be calculated.

The ratio between the average (excluded maximal values) for contaminated groundwaters (cf. Tablel) and the average for uninfluenced groundwaters serves as a measure of the intensity of the influence of the individual inorganic parameters. Principally, a contamination factor may also be calculated for other statistical parameters (median, percentile and maximal values). In this case, a subscript index would facilitate distinction.

With the exception of nitrate, lead and cadmium, the contamination factors (CF_{mean}) exhibited levels of > 2 for all inorganic parameters studied (Table 7–1). Values of > 20 were reached by ammonium (CF_{mean} 64.7), arsenic (CF_{mean} 37.8), chromium (CF_{mean} 36.6) and boron (CF_{mean} 23.9). Values of > 10 were reached by phosphate (CF_{mean} 12.9), aluminium (CF_{mean} 11.9), cadmium (CF_{mean} 11.5) and potassium (CF_{mean} 11.3). These figures document the considerable increase or mostly adverse modification of the natural contents of these substances in groundwaters.

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"Emission frequency" as a criterion of contamination

By definition, detection frequency of the emission of a substance is the percentage share of cases of detection of a substance having penetrated into groundwater through leachate from an abandoned deposit. A differentiation should be made as to whether an emitted substance (contaminant) may naturally occur in groundwater or not. For almost all inorganic contaminants, this is the case, however not for the purely anthropogenic organic ones. For this reason, the geogenic content of naturally occurring inorganic water ingredients must be known to enable a recognition of a rise in their contents. The natural geogenic background concentration of anthropogenic organic contaminants equals zero which means, that, as a rule, frequency of analytical detection and frequency of a detection of their emission are identical. While with regard to the contamination factor, the intensity of the rise is important, the mere fact of the presence of a rise is decisive for the frequency of detection.

Inorganic substances

For inorganic substances, the arithmetic mean concentration in uninfluenced groundwater (in the case described, loose rock aquifers) have been defined as mean geogenic background[5]. The number of values measured and found to be above this geogenic background will show the per cent frequency of detection of the emission of a substance. In cases where the background level was below the detection limit, the latter has been used as a substitute (fluoride, nitrite, mercury). The substance/element having the highest frequency of detection was hydrogen carbonate (85.5%, followed by boron (85.7%), sodium (83.4%), chloride (79.2%) and magnesium (76.0%). The frequency of detection was less for lead (38.3%), nitrite (35.4%), aluminium (33.0%), selenium (22.3%), cadmium (14.9%) and mercury (14.7%).

A comparison of the detection frequency of emissions with the respective contamination factors has shown that a high contamination factor must not necessarily mean a high frequency of detection. Thus, aluminium and cadmium have comparatively high contamination factors of 11.9 and 11.5, respectively while their frequency of detection is low (33.9 and 14.9%, respectively). Also the reverse situation may occur. Inorganic substances having high contamination factors and at the same time, a high frequency of detection may be considered as particularly typical of emissions from abandoned deposits into groundwater. Contamination factors of > 10 and detection frequencies of > 50% were seen for arsenic (37.8; 61.3%), ammonium (64.7; 53.6%), boron (23.9; 85.7%), potassium (11.3; 74.2%) and chromium (36.6; 56.3%).

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Organic substances

The analytical detection sensitivity of a number of organic substances may be high enough to record also ubiquitous contamination which cannot be attributed to emissions from abandoned deposits. Thus, the analytical detection limit for trichloroethene, tetrachoroethene and trichloromethane is 0.1 μg/L while ubiquitous contamination is of an order of up to 0.4 μg/L. For this reason, analytical detection of these substances in the concentration range of ubiquitous contamination cannot be interpreted as evidence for emission from an abandoned deposit.

To determine the frequency of detection of emissions of organic substances, therefore, a so-called 'relevance limit' has been established, i.e. the concentration above which detection of an organic substance can be attributed, with a considerable reliability, to emission from an abandoned deposit. In almost all cases, the relevance limit will correspond to the detection limit. Only for single volatile chlorinated hydrocarbons, the relevance limit has been fixed at 1 μg/L. Since for example in the case of tetrachloroethene, only 67 (24.4%) out of 195 values measured above the analytical detection limit of 0.1 μg/L were below the relevance limit of 1 μg/L, the frequency of the detection of emissions was a mere 46.2% while the frequency of analytical detection was 70.4% (Table 2).

Tetrachloroethene with a detection frequency of 46.21%, trichloroethene (40.79%) and cis-1,2-dichloroethene (30.07%) were those organic substances which could be preferentially detected in groundwaters influenced by abandoned deposits. On the whole, only 7 substances were detected with a frequency of > 20% and 19, with one of > 10%. 49 substances exhibited a detection frequency of > 1%[7].

"Mean emitted concentration" as a criterion of contamination

The mean emitted concentration of a substance is a suitable quantitative measure of the influences emanating from a substance. By definition, this corresponds to the difference between the mean concentration in influenced groundwaters and the mean concentration in uninfluenced groundwaters from a defined source. In the case of organic substances, the small ubiquitous influence has a negligible bearing on the difference, so that the mean emission concentration will correspond to the mean concentration in the influenced groundwaters.

Inorganic substances

The highest mean emission concentration was exhibited by hydrogen carbonate (281 mg/L), followed by chloride (169 mg/L), sulphate (135 mg/L), sodium (111 mg/L) and calcium (92 mg/L). It becomes evident that CO_2 which in the bioreactor, i.e. the abandoned deposit, is formed in considerable quantity and also converted to HCO_3^- constitutes one of the principal substances emitted. This likewise applies to Na^+ and Cl^- which are eliminated together in the form of common salt (NaCl). Since demolition rubble has always made up a considerable share of the wastes volume, SO_4^{2-} and Ca^{2+} are also counted among the substances emitted by this route most frequently and in the highest absolute quantities.

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Organic substances

For calculation of the mean emission concentrations of the organic substances, the individual concentration values are converted into logarithmic form because some single values may be so high that arithmetic means of non-logarithmic concentration data cannot serve as evidence and do not offer a possibility for comparison. Since concentration values below the detection limit cannot be converted into logarithmic form, only values measured above the detection limit will be included in the mean emission concentration of the organic substances. Such approach is also meaningful because there is a low frequency of detection for most organic substances which is equivalent to a high share of values measured below the detection limit. If these values were included in calculations, most mean emission concentrations would be below the detection limit.

In the order of mean emission concentrations, the first place is occupied by dichloromethane (871 µg/L); it is followed by cis-1,2-dichloroethene (123 µg/L), vinylchloride (85 µg/L), 1,2-dichloroethane (72 µg/L), 1,1-dichloroethane (44 µg/L), trans-1,2-dichloroethene (41 µg/L) and benzene (17 µg/L). Also here, the dominance of volatile halogenated organic compounds in groundwater downstream of abandoned deposits becomes evident.

COMPARISON OF RESULTS FROM WEST GERMANY AND THE USA

Inorganic substances

In the United States, the statistical variance of the concentration near sites was used for recognition of the essential inorganic contaminants and evaluation of emissions from waste deposits[8]. Calculation of the variance considered both the concentrations in unaffected areas (upstream area, unaffected wells) and those in the contaminated downstream area. There should be a low variance between concentrations of a water

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ingredient from different sampling points at a site if an inorganic substance is not involved in emission. Variance should become larger where an inorganic contaminant is identified in emissions.

As far as possible on the basis of the available data material, the statistical variance of the concentrations of 16 inorganic ingredients was calculated for 253 sites in the USA[8]. Three essential facts were revealed:

Firstly, distribution of inorganic substances with high variance levels is not accidental. If at a site, a substance takes part in emission, there will always be other substances which likewise surpass variance limits. The reason for this is that emission always involves more than a single substance.

Secondly, the spectrum of substances emitted from a number of sites may be used to characterize leachate emission from a certain type of site.

Thirdly, tabulation of the frequency of occurrence of the individual contaminant in emissions may be applied to establish an order of their relative importance of site types as emitters.

Taking into consideration the last point, the inorganic substances have been listed in Table 3 by the number of waste disposal sites in the USA where they could be detected as a contaminant above a certain variance limit. For comparison, the same inorganic substances have been listed in Table 3 in the order of their contamination factors as detected in West Germany.

While in the USA, As, Cd, Na, Hg, Zn and Nil were the six inorganic contaminants most frequently found in groundwaters contaminated by abandoned and operating waste disposal sites at levels significantly above the background, the elements involved in West

Table 3 Ranking of inorganic constituents in disposal site leakage events based on high parameter variance of the USA compared to west German contamination factors and detection frequencies > background concentrations (only parameters determined in both investigations).

	United States		*Western Germany*		
Chemical rank	*Number of sites*	*Percentage of sites*	*A contamination factor (mean values)*[1]	*B detection frequency % > background*[2]	*Product A x B*
1	As (28)	As (18.7)	As (58)	Na (97)	As (4176)
2	Cd (21)	Mg (18.6)	Al (18)	Cl (92)	Na (1067)
3	Na (18)	Zn (16.5)	Cd (17)	Mg (89)	Ni (900)
4	Hg (16)	Ni (14.8)	Mn (12)	Ca (87)	Mn (876)
5	Zn (14)	Na (14.3)	Ni (12)	SO_4 (75)	Cl (720)
6	Pb (13)	Cd (14.1)	Na (11)	Ni (75)	Al (720)
7	Ni (13)	Hg (11.4)	Cl (8.8)	Mn (73)	SO_4 (345)
8	Se (12)	Ca (10.3)	Fe (6.9)	As (72)	Fe (3310
9	Mg (11)	Cu (9.6)	Pb (6.4)	Cu (62)	Mg (320)
10	Mn (11)	Se (8.8)	Zn (4.9)	Zn (49)	Cd (306)
11	Cu (9)	Pb (8.2)	Cu (4.9)	Fe (48)	Cu (304)
12	SO_4 (9)	Mn (7.4)	SO_4 (4.6)	Pb (45)	Pb (288)
13	Cl (7)	Al (6.7)	Mg (3.6)	Al (40)	Zn (240)
14	Fe (7)	SO_4 (6.5)	Ca (2.7)	Se (27)	Ca (235)
15	Ca (6)	Cl (5.1)	Se (1.0)	Cd (18)	Se (18)
16	Al (4)	Fe (4.4)	Hg (1.0)	Hg (18)	Hg (18)

[1] normalized evaluation numbers between 1 and 100 (path-specific maximum: KF_{mean} NH_4 (64.7) = 100)

[2] normalized evaluation numbers between 1 and 100 (path-specific maximum: DF HCO_3 (85.8%) = 100).

Germany were As, Al. Cd, Mn, Ni and Na. It should be noted that in both studies, arsenic has been the most important inorganic contaminant. In addition to arsenic, cadmium, sodium and nickel in both investigations belonged to the respective group of the six most important inorganic substances emitted. The importance of a number of other inorganic substances varied considerably in the two investigations and could not be explained on scientific grounds. This applies e.g. to aluminium and mercury. It is also difficult to understand the low importance of chloride vs. sodium in the American investigation since the foremost part of the sodium is leached from the waste material together with chloride (as NaCl).

Organic substances

Also for the organic substances the comprehensive data set from the USA was used for verification of the findings. There has been a much better chance for comparison than in the case of inorganic substances, since evaluation was performed by the same criterion, i.e. frequency of detection.

A good coincidence was seen for the 25 most frequently detected organic groundwater contaminants, taking into account concentrations of > 1 µg/L (USA) and > relevance limit (West Germany) (Figure 2). 20 out of 25 substances (80%) were identical. In both cases, evaluation showed a preponderance of volatile halogenated aliphatic substances (6 alkanes and 5 alkenes each and 4/2 aromatic chlorine compounds). In addition, there were 6/5 halogen-free hydrocarbons and 4/7 oxygen-containing substances (phenols and ketones).

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Standardization of contamination criteria and derivation of principal contaminants

For an integral substance-specific evaluation of the variety of contaminants with regard to their relevance for specific emission routes, a linkage of the criteria of contamination, frequency of detection and emission concentration, would be meaningful. Since however, the ranges of values for these two criteria differ in an extreme way, a linking of absolute values would result in a correspondingly imbalanced weighting.

Thus, linkage must be preceded by standardization to value ranges of equal size. The standardized figures are referred to as evaluation numbers (EN). All values are standardized to fit the 1–100 range, since the resulting numerical values are better understood and easier to compare because of e.g. the common use of percentage data. This can be achieved both by using formulae for calculation[7], or graphically as shown in Figure 3.

In the case of mutually independent parameters, the evaluation number must be multiplied to derive an integrated statement. Where a contamination criterion is of no relevance for a substance, 1 is defined as the lowest evaluation number because evaluation numbers of < 1 or even zero would, if multiplied, result in an extreme attenuation or extinction of the importance of the other parameters. The evaluation number 100 is assigned to the respective maximum (specific maximum for the emission route, waste deposition–leachate–groundwater, which however, as in the present case, is possible only where the results of an investigation are of representative characters).

Substances which occur both frequently and in high concentrations in groundwater downstream of abandoned deposits are defined as (emission route-specific) principal contaminants. The importance of principal contaminants may be quantified as the

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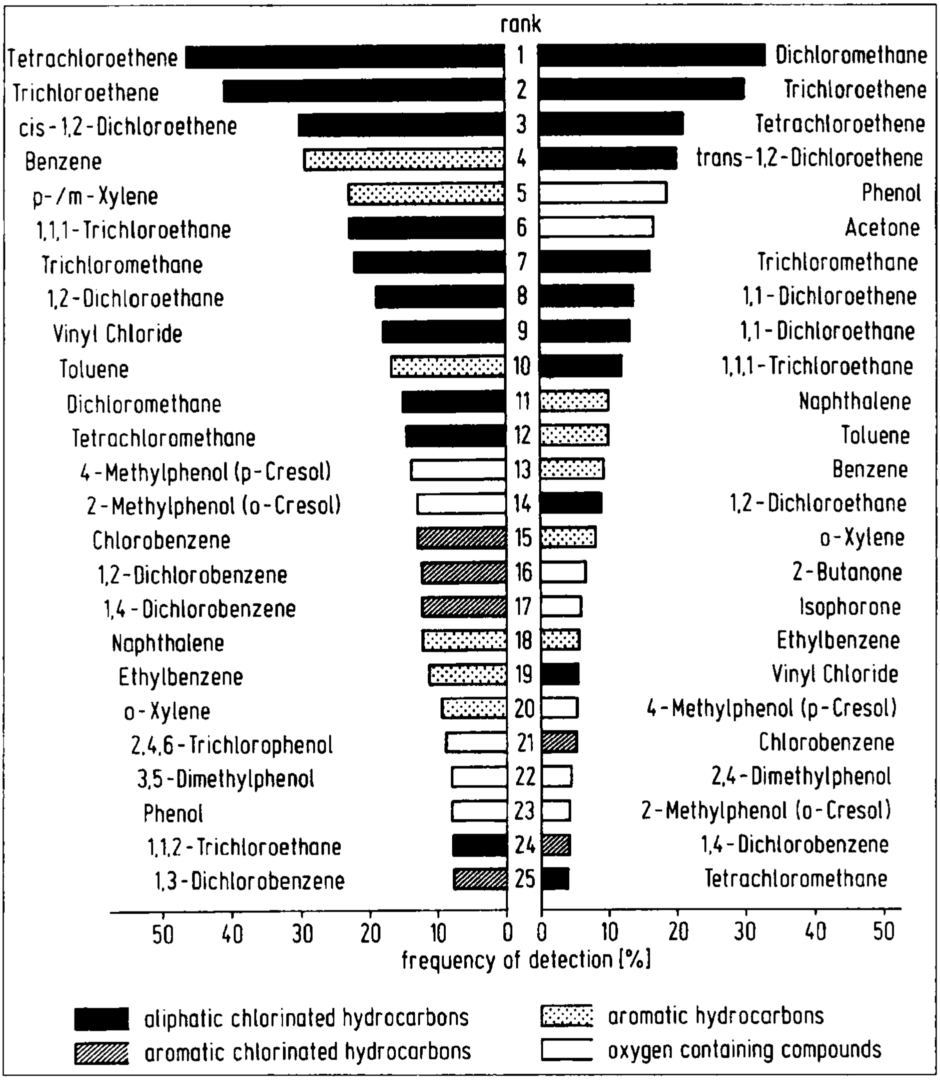

Figure 2 Ranking of frequency detection ($\geq$ 1 µg/L) of principal organic contaminants in groundwaters downgradient from waste-sites in Germany and the Untied States.

product of the two evaluation numbers for frequency of detection and emission concentration. The higher the product (maximum 10^4), the more important is the contaminant. Examples may be taken from Table 4. (The contamination factor is not used for the determination of principal contaminants because it is a relative variable and if at all, could be used for inorganics only).

When using the emission route considered here, the inorganic substances, hydrogen carbonate, sodium, calcium, magnesium, potassium and sulphate were found to attain the highest products from the evaluation numbers for the frequency of detection and the emission concentration, i.e. they were the most obvious principal contaminants (Table 4). Boron exhibited remarkable features: Its geogenic occurrence is limited to traces but,

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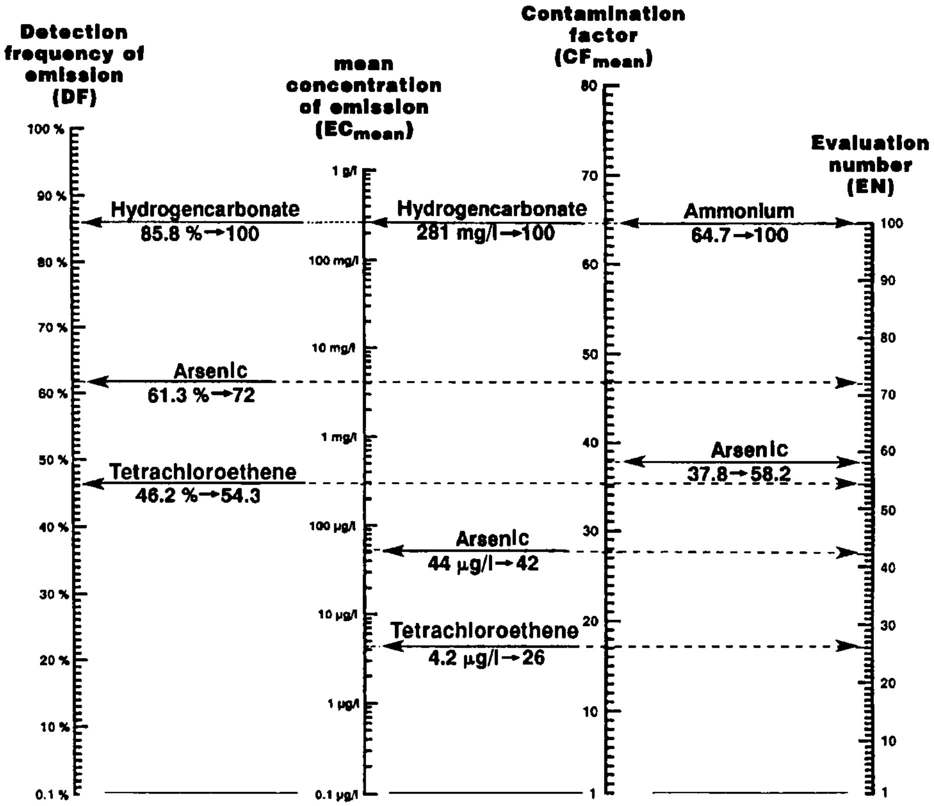

Figure 3 Standardization of contamination criteria.

Table 4 Emission route-specific contaminants.

Substance	[1]*EN*$_{DF}$	[2]*EN*$_{EC}$	*Product*
Hydrogencarbonate	100.0	100.0	10000
Sodium	97.2	93.8	9117
Chloride	92.4	96.6	8926
Calcium	87.0	92.2	8048
Magnesium	88.7	83.5	7406
Potassium	86.6	85.1	7370
Sulfate	75.4	95.1	7171
Boron	99.9	60.9	6084
Manganese	73.2	64.3	4740
Arsenic	71.7	41.6	2983
Nickel	75.2	36.4	2737
Chromium	66.0	36.5	2409
Nitrite	41.8	57.5	2404
Lead	45.2	26.9	1216
Cadmium	18.2	18.6	339

[1] Evaluation number of detection frequency

[2] Evaluation number of emission concentration

similarly to HCO_3, it can be detected in all emissions from abandoned deposits (EN_{DF} = 99.9). Within the order of principal contaminants, it is the first trace element following the principal elements. This situation, jointly with its geochemical mobility and simple analysis, has underlined the excellent suitability of boron as a screening parameter to recognize leachate emissions from abandoned deposits[6].

Among the organic substances, the list of principal contaminants is headed by the volatile chlorinated hydrocarbons, cis-1,2-dichloroethene (EN = 1731), trichloroethene (EN = 1568) and tetrachloroethene (EN = 1406). They are followed by benzene (EN = 1225), dichloromethane (EN = 1119), 1,2-dichloroethane (EN = 1015) and vinyl chloride (EN = 984), to name the most important ones.

DERIVATION OF PROBLEM-SPECIFIC ANALYTICAL PARAMETERS (PRIORITY CONTAMINANTS)

Knowledge of the inorganic and organic contaminants with regard to their importance on the emission route in itself does not suffice for a problem-specific risk estimation of groundwater contamination. This becomes evident e.g. by the fact that the seven essential and principal inorganic contaminants are without toxicological relevance in the event of a use of the contaminated groundwater for human consumption. They are unsuitable to estimate the risk for a use as drinking water that emanates from an abandoned deposit. Thus, the use-specific toxicity of principal contaminants is important and must also be taken into account.

A substance-specific 'toxicity potential' of the principal contaminants may be quantified by means of a screening evaluation scheme specifically developed at the Institute for Water, Soil and Air Hygiene for that purpose[7,9,10]. It essential features have been depicted in the right hand part of Figure 4. Examples of the toxicity potential of a number of contaminants have been shown in Table 5.

To derive the analytical parameters which are decisive for contamination studies (priority contaminants), the necessary variables describing the contaminants, i.e. the frequency of detection in emissions, the concentration in emissions and the toxicity potential (all in the form of evaluation numbers) are multiplied. An overview of the approach is presented in the flow sheet depicted in Figure 4. Partial differences in the approach result from the mere fact that the geogenic share in the concentration of inorganic contaminants must be taken into consideration.

By definition, the height of the product of the three evaluation numbers is a measure of the relevance of a contaminant on the emission route and with regard to a defined risk for uses/exposure. Since the screening scheme presented is aimed at toxicological evaluation of a substance for oral intake with drinking water, the product formed from the three evaluation numbers is merely a measure of the relevance of a groundwater contaminant from abandoned deposits for estimation of a possible risk to drinking water. To assess other risks of use or exposure potentials, different basic data must be introduced into the toxicological model of evaluation, resulting in different evaluation numbers for the toxicity potential and thus for other priority contaminants specific to routes and uses. Contrary to the principal contaminants which only depend on the route of emission, priority contaminants are also specific to a risk for use or exposure situation.

The highest product of the three evaluation numbers which is theoretically possible, i.e. 10^6 is not reached in reality. The highest evaluation numbers were attained by the inorganic priority contaminants, arsenic, boron, manganese, chromium (VI), nitrite and

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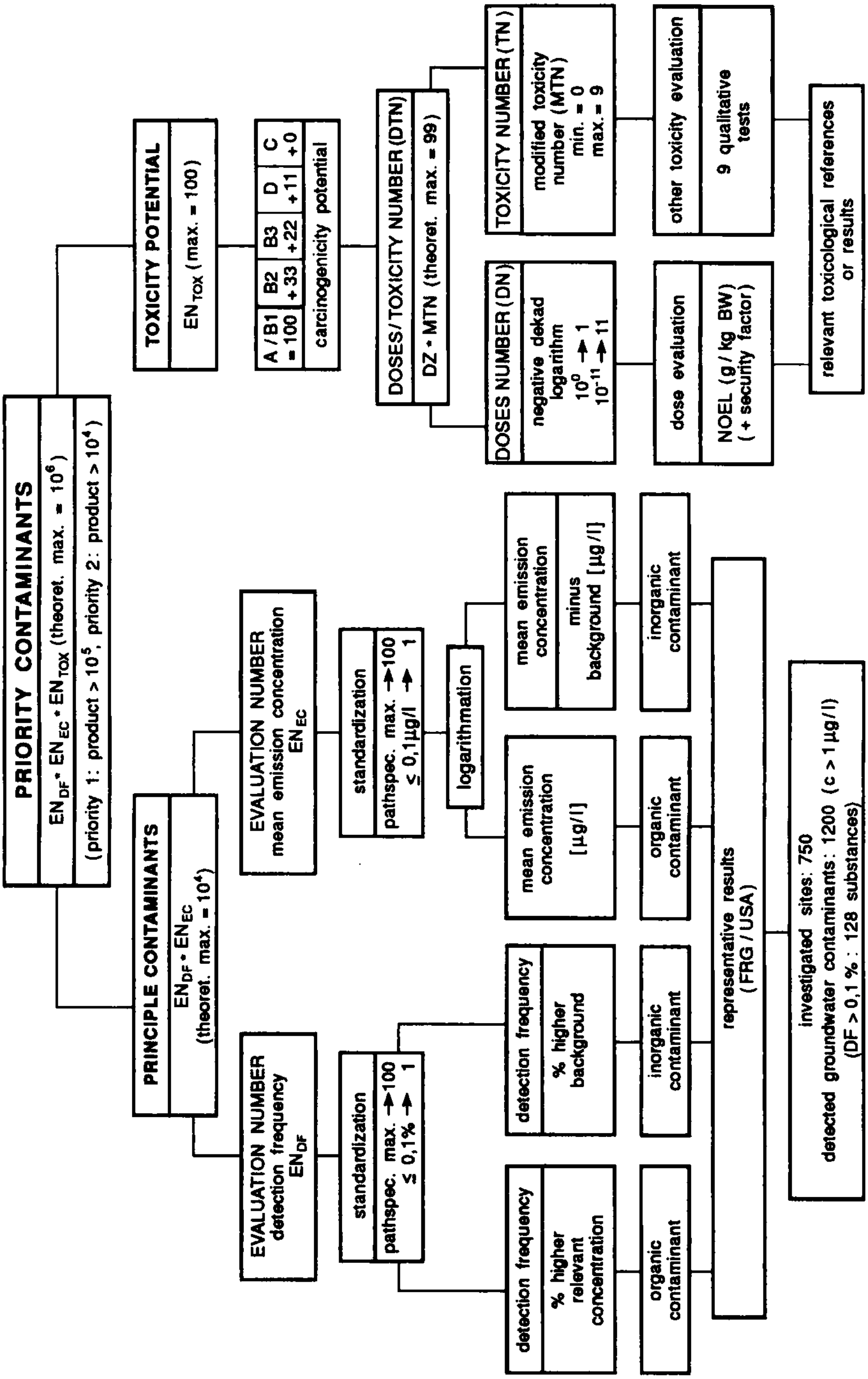

Figure 4 Flowsheet for the determination of priority pollutants.

Table 5 Examples of toxicity potentials of inorganic and organic contaminants.

Substance	EN_{TOX}
Ammonium	10
Arsenic	100
Cadmium	71
Sulfate	1
Nitrate	8
Boron	31
Tetrachloroethene	68
Chloroethene (VC)	100
Phenol	50
Dichloromethane	46
Benzene	100
Naphthalene	42

nickel (Table 6) as well as by the organic priority contaminants, benzene, 1,2-dichloroethene, vinylchloride, tetrachloroethene, trichloroethene and dichloromethane (Table 6).

Substances having evaluation numbers $> 10^5$ have been defined as contaminants of first priority. Contaminants exhibiting numbers between 10^5 and 10^4 are assigned to the second priority group. Contaminants with evaluation numbers $\leq 10^4$ are no longer considered as belonging to a priority group. This is of decisive importance for the selection of the best suitable parameters for the investigation of groundwater near abandoned sites and waste deposits.

Thus, the priority contaminants systematically developed in this study are the most suitable parameters for investigation of emissions into groundwater from abandoned and still operated deposits and a recognition of their toxicologically founded risk potential for a use of such groundwaters in the production of drinking water. In the method developed by the Institute for Water, Soil and Air Hygiene for the examination of groundwater contamination by abandoned deposits[6], the second analytic step (analysis of problematic

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Table 6 Emission route-specific and exposure-specific priority contaminants.

Substance	[1]EN_{DF}	[2]EN_{EC}	[3]EN_{TOX}	*Product*
Arsenic	71,7	41,6	100	2,98*10^5
Boron	99,9	60,9	31	1,89*10^5
Manganese	73,2	64,3	33	1,55*10^5
Chromium (VI)	66,0	36,5	61	1,47*10^5
Nitrite	75,2	36,4	43	1,17*10^5
Benzene	34,6	35,4	100	1,22*10^5
1,2-Dichloroethane	22,6	44,9	100	1,01*10^5
Chloroethene (VC)	21,4	46,0	100	9,84*10^4
Tetrachloroethene	54,3	25,9	68	9,56*10^4
Trichloroethene	48,1	32,6	59	9,25*10^4
Dichloromethane	18,2	61,5	46	5,15*10^4

[1] Evaluation number of detection frequency

[2] Evaluation number of emission concentration

[3] Evaluation number of toxicity potential

substances) includes substances from both priority groups in each case. This approach permits a specific, problem-oriented examination and analysis of groundwater contamination by abandoned deposits (Figure 5).

EVALUATION OF GROUNDWATER CONTAMINATION BY ABANDONED DEPOSITS FROM THE ANGLES OF EMISSION ROUTE AND USE

For an evaluation of emissions from abandoned deposits specific to the route of emission, other phenomena must be considered in addition to the substances to be determined and evaluated in examination programmes (priority contaminants).

Thus, the site of groundwater use and the site of a possible exposure to pollutants will, as a rule, not be identical with the site where contaminants are emitted (abandoned deposit) and be located at an obvious distance. On the route from the site where contamination takes place to the site of use/exposure, the concentration of the emitted priority contaminants will be modified by processes of dilution, sorption and degradation. The final concentration at the site of use and/or exposure will be essentially determined by the concentration of a priority contaminant at the site of contamination, its persistence and mobility and the local subsoil conditions (hydrogeological parameters of substance transport).

Also in this respect, standardized approaches have been developed by the the Institute for Water, Soil and Air Hygiene Institute permitting an establishment of the transfer and persistence potentials of priority contaminants on the basis of standardized physico-chemical substance parameters[7].

Having knowledge of the concentrations of priority contaminants at the source of contamination (abandoned site) and their substance-specific transfer and persistence potentials, the possible transport of the respective contaminants in groundwater to the water works can be estimated or modelled. However, the local (site-specific) geohydrological conditions must be known. Information to this effect should be provided by the person being technically responsible for an abandoned deposit.

Finally, the resulting acute or long-term contaminant concentration at the site of use and their toxicological/hygienic tolerability are decisive for the evaluation of a possible risk to water use due to emissions from an abandoned deposit. Where the tolerable concentrations at the place of use are known or have been fixed, the maximal concentrations which are tolerable at the site of contamination may be inferred by calculation, e.g. using a transport model. Owing to the site-specific differences in the route for transfer from the site of contamination to that of use (geographic distance, thickness of the aquifer, dilution, organic carbon and clay content of the aquifer, geochemical environment etc.), the tolerable emission concentration will differ for each site despite the existence of fixed tolerable concentrations at the site of use (water works).

This demonstrates the decisive advantage of an individual local evaluation which is guided by consideration of use and exposure. It constitutes also the most essential argument to reject general limit values for contaminants which are not specific to use. The same is true for values above which restoration is required to target values for restoration as practised e.g. in the Netherlands List and other lists which only consider substance concentrations at the site of contamination.

How can hygienically and toxicologically tolerable limits be fixed for groundwater to be used as drinking water? In Germany, reference may be made to the limit values for

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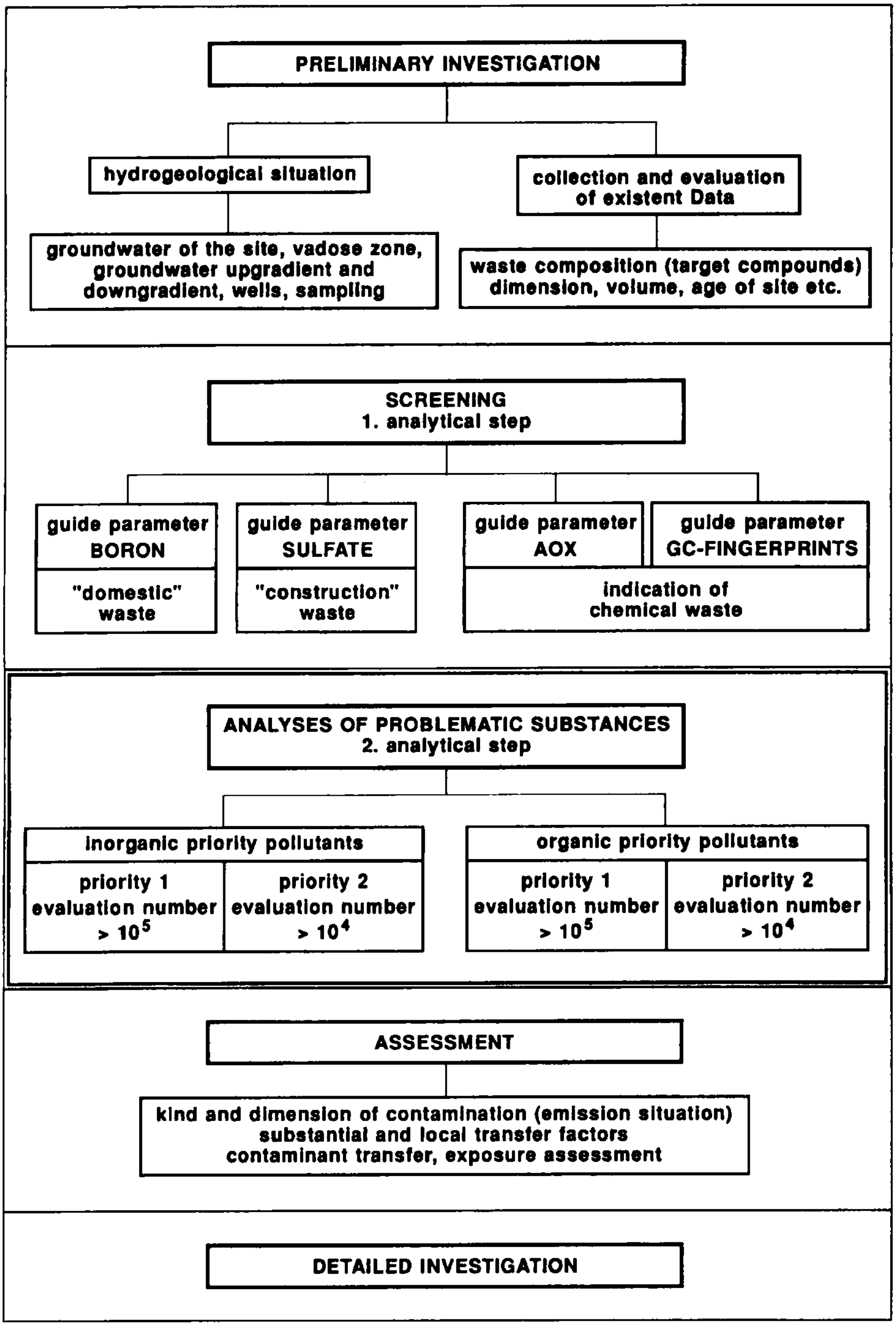

Figure 5 Flowchart for the investigation and evaluation of groundwater contamination by waste disposal sites.

the Drinking Water Regulations, however only insofar as possible contaminants from abandoned deposits are listed in the Regulations. It should be mentioned that the limit values of the Drinking Water Regulations were established not only under aspects of toxicology but also under such of water catchment as outlined in the DIN 2000 standard[11], they must, however, not disagree with the toxicological limit values.

For this reason, a yardstick considering both hygienic and toxicological contamination criteria is proposed for the evaluation of groundwater-contaminating abandoned deposits in areas where ground waters, at least partially, are to be used for drinking water production. Also for this purpose, the Institute for Water, Soil and Air Hygiene has developed a scheme permitting the establishment of adequate concentration ranges from the substance-specific evaluation numbers[7,9,10].

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