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Release of substances from joint grouts based on various binder types and their ecotoxic effects

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Abstract

Background: The leaching of substances and the ecotoxic effects of eluates were studied for joint grouts that are based on various types of binders. Eight products, two of them containing either epoxy resin, polybutadiene or polyurethane binders, or modified cement, were investigated using harmonized leaching tests for construction products in combination with ecotoxicity tests on algae, daphnia, luminescent bacteria, fish eggs and mutagenicity in accordance with CEN/TR 17105. In addition to basic parameters, such as pH, TOC, and inorganic components, organic substances in the eluates were analysed by gas and liquid chromatography in combination with mass spectrometry. Quantitative analyses in combination with ecotoxicity data on selected substances were used to deduce which substances cause the observed ecotoxic effects.

Results: Different patterns of ecotoxic effects were observed in joint grouts with different binder types. The most ecotoxic effects were observed in epoxy resin-based products, followed by polybutadiene-based products. Fewer ecotoxic effects were observed in polyurethane-based products and modified cements. Some of these showed no ecotoxicity. Some of the substances in the eluates were identified and related to ecotoxic effects. 4-Tert-butylphenol and amines probably contributed to the ecotoxic effects of at least one of the epoxy resin-based renders, whereas cobalt is assumed to contribute to the toxic effect on algae of one of the polybutadiene-based products. However, only some of the leached substances could be identified, and only some of the ecotoxic effects can be explained by the available information on the composition of eluates and known ecotoxic profiles of the identified substances.

Conclusions: Ecotoxicity tests on eluates from leaching tests indicate whether environmentally hazardous substances can be leached from construction products. Combined ecotoxicity tests and chemical analysis of eluates from EU-wide harmonized leaching tests for construction products can provide information on substances that cause these effects. This supports the identification and development of environmentally friendly construction products. This study confirmed that ecotoxicity tests in accordance with CEN/TR 17105 are a tool well-suited to support the implementation of the European Commission's zero pollution vision for 2050 and to reduce pollution to levels no longer considered harmful to health and natural ecosystems.

Keywords: Joint grouts, Leaching, Ecotoxicity, Algae, Daphnia, Luminescent bacteria, Fish eggs, Mutagenicity, Chemical analysis, Screening

Background

Construction products can have harmful impacts on the environment [1, 2]. In Europe, the aim to minimize such harmful impacts is specified in the Construction

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Products Regulation [3]. The vision, developed and pursued by the European Commission, is to avoid any harmful pollution of the environment by 2050 [4]. For construction products in (intermittent) contact with water, leaching is one path by which substances are released into the environment. In order to manufacture environmentally benign construction products, reliable and comprehensive test methods are needed to evaluate product performance.

The evaluation of the impact of construction products can involve not only chemical analysis of water samples, but also ecotoxicity tests [5] together with information on the environmental properties of substances. A battery of ecotoxicity tests for eluates from construction products was developed and presented as CEN/TR 17105 [6]. It includes ecotoxicity tests on algae, daphnia, luminescent bacteria, fish eggs, genotoxicity, and mutagenicity. Eluates for these tests are derived from EU-wide harmonized leaching methods for construction products (DSLT, dynamic surface leaching test, prEN 16637-2 [7], and percolation test prEN 16637-3 [8]). Eluates from leaching tests are usually analysed for chemical parameters that can be compared to threshold values. However, the composition of construction products is not always known, and in view of the variety of possible leachable hazardous substances, their analytic identification can be very complex, particularly with organic substances.

On the initiative of the German Environment Agency, the ecotoxicity tests presented in CEN/TR 17105 [6] were investigated in a European round robin test to support the transformation of this document into a Technical Specification (CEN/TS). The objective of this project was to demonstrate that the combination of standardized leaching tests and well-established ecotoxicity tests can be applied to the environmental assessment of construction products. Ecotoxicity tests were performed in 29 laboratories using eluates from the DSLT [7] and the percolation test [8]. The product chosen for the tests was a pavement joint grout used outdoors to fix terrace slabs and therefore in contact with rainwater in its normal use. Usually, prEN 16637-1 [9] defines which of the two leaching procedures is to be applied for a given construction product. In accordance with the possible application scenarios, for this round robin test, eluates from an epoxy resin-based joint grout were prepared using i) plate-like test specimens to simulate water that runs on the surface of grouts exposed in DSLT tests and ii) crushed material from the same joint grout to simulate water seepage by applying column percolation tests. The results confirm the applicability of these ecotoxicity tests for eluates of construction products from both leaching tests [10, 11].

The project also included combined ecotoxicity experiments, basic analysis of eluates, and screening for organic substances on a series of construction products to identify types of construction products that typically show a range of effects and to distinguish and label those products that cause little or no leaching of hazardous substances into the environment, i.e. by awarding the ecolabel "Blue Angel".

The high ecotoxicity of eluates from the epoxy resin-based joint grout to luminescent bacteria and algae led us to investigate more examples of joint grouts that contain different types of binder, i.e. epoxy resin, polybutadiene, polyurethane, and modified cement. These binders stabilize the joint grouts. The joint grouts for outdoor use are used to connect floor plates and prevent the growth of weeds between them. The ecotoxicity of the DSLT eluates was compared with the results of basic chemical analysis. In addition, screening for organics was performed to identify substances causing the ecotoxic effects. For one product, the results from DSLT and percolation tests were compared. In addition, the influence of storage duration between the preparation of test specimens and the leaching tests was investigated for two products. A further aim was to use ecotoxicity data to try to identify substances that cause ecotoxic effects from different types of joint grouts.

Material and methods

Construction products and experiments

Eight joint grouts based on four different binder types were selected (see Table 1) and investigated in various experiments. The joint grouts were obtained as ready-to-use commercial mixtures.

Experiment 1 compared the leaching of substances and the ecotoxicity of eluates obtained by DSLT [7] and percolation tests [8] using MOE1. The leaching of substances and the ecotoxicity of eluates obtained by DSLTs on MOE2 to MOE8 were investigated during experiment 2. The influence of the storage period between the preparation of test specimens and the beginning of the DSLT was investigated in experiment 3. The storage period for test specimens from MOE1 and MOE7 was either 7, 14, or 28 days. A test specimen of each product was wrapped in cling film and stored for 28 days. The numbers of the experiments and the durations of the storage periods are given in the complete results tables (Additional file 1: SI 5 to SI 8).

Preparation of test specimens for DSLT and material for the percolation test

The joint grouts were prepared in accordance with manufacturer's instructions given in technical data sheets, i.e. either used directly, mixed with water or added to sand. To prepare test specimens for DSLT, the mixtures were poured into prepared moulds (25 cm × 14 cm × 0.7 cm

Table 1 Codes of joint grouts based on different binder types

Code	Binder	Description	Experiment
MOE1	Epoxy resin	Two components to be mixed	1, 3a, 3b
MOE2	Polybutadiene	Ready-to-use	2a, 2b
MOE3	Modified cement*	Powder to be mixed with water	2a, 2b
MOE4**	Modified cement*	Powder to be mixed with water	2a, 2b
MOE5	Polyurethane	One component to be added to sand	2a, 2b
MOE6	Epoxy resin	Two components to be mixed and added to sand	2a, 2b
MOE7	Polybutadiene	Ready-to-use	2a, 3a, 3b
MOE8	Polyurethane	One component to be added to sand	2a, 2b

Experiment 1: both DSLT and percolation test, experiment 2a and 2b: DSLT, experiments 3a and 3b: DSLT after different storage durations for test specimens before the leaching test

* Contains organic additives

** MOE4 is a mortar according to EN 998-1:2016 [12] that can be applied for different purposes including filling cracks

internal dimensions). The moulds were lined with cling film beforehand to prevent the joint grout from sticking to the mould. New batches of the joint grouts were opened and used for each experiment on MOE1, MOE2, MOE4, and MOE7, since the products were not stable in the containers once they were opened. The same batches of the products were used for all experiments on MOE3, MOE5, MOE6, and MOE8. One test specimen was prepared for each test assembly.

The test specimens were kept under ambient air conditions and removed from the moulds after at least one day. Afterward, the test specimens were conditioned for at least seven days at 21.5 °C ± 1.0 °C, 60% ± 5% relative moisture.

To prepare the test material for the percolation test, the prepared mixture of MOE1 was spread on an HDPE sheet and dried under ambient conditions for 46 days. The dried material was gently deagglomerated (particles < 1 cm) to enable the filling of the glass column (ID 10 cm, length 44 cm). The glass column contained 2.4 kg of the particles that were exposed to the percolation test.

Leaching tests

Test specimens were placed on spacers (2-cm-high glass prisms) in all-glass aquaria (1 test specimen per test assembly) to perform the DSLT [7]. Deionized water (Milli-Q®, conductivity < 5 µS cm^{-1}) was added at a liquid-to-surface-area ratio (L/A) of 25 L m^{-2} (2.5 mL cm^{-2}) and replaced after 6 h. Deviating from prEN 16637-2, which defines eight leaching periods within 64 days and is recommended in CEN/TR 17105, only eluates from the first two leaching periods after 6 h and another 18 h (altogether 24 h) were collected, combined, and then subdivided into aliquots for chemical analysis and ecotoxicity testing. The tests were performed at 20 °C to 22 °C in the dark. A blank control was run with deionized water (Milli-Q®) in an additional leaching vessel for each test series.

For the percolation test [8], 2.4 kg of the deagglomerated particles of MOE1 (residual moisture 0.85%) were packed into a borosilicate glass column (10 cm inner diameter, 30 cm filling height, 1.04 g cm^{-3} bulk density) and exposed to an upward flow of the eluent (doubly deionized water of < 5 µS cm^{-1} conductivity) using a flow rate of 5.62 ml min^{-1}, which corresponds to a linear flow velocity of 30 cm per day $^{-1}$. After saturation of the column, flow was interrupted for 12 h to enable a preliminary equilibration of the test sample. Deviating from prEN 16637-3, which defines seven sampling events after liquid-to-solid ratios of 0.1, 0.2, 0.5, 1, 2, 5, and 10, the accumulated eluate at an L/S (liquid-to-solid) ratio of 2 L kg^{-1} was collected as envisaged for the transformation of the CEN/TR 17105 into a CEN/TS. A sample of the eluent was used as a blank control for the percolation test.

DSLT and percolation tests were both performed at BAM. Aliquots of the eluates from DSLT and percolation tests were frozen at ≤ − 18 °C in either 50 mL PP (polypropylene) containers (for algae, daphnia, luminescent bacteria, and umu and Ames tests), 150 mL PET (polyethylene terephthalate) containers (for fish egg test), or pyrolized glass bottles (for chemical analysis, i.e. GC–MS and LC–ESI–QTOF screening). The samples were shipped in frozen condition to the Hydrotox GmbH for ecotoxicity testing and to TZW Karlsruhe for chemical analysis and stored at ≤ − 18 °C until the start of the respective investigations. Ecotoxicity tests were started within two months after the sampling of the eluates.

Ecotoxicity tests

The test set applied for ecotoxicity testing followed the CEN/TR 17105 [6] guideline for ecotoxicological testing of construction products using the lowest ineffective dilution (LID) concept; this has been described in greater detail by *Heisterkamp* et al. 2021 [10, 11]. This study also includes extensive statistical analyses of ecotoxicity tests for eluate samples obtained from leaching tests. In brief, the algae growth inhibition test was carried out in accordance with ISO 8692 (2012) [13] with the algae species *Raphidocelis subcapitata* (formerly *Pseudokirchneriella subcapitata*). The inhibition of growth was determined after 72 h by measuring the chlorophyll fluorescence. The acute daphnia toxicity test was applied in accordance with ISO 6341 (2012) [14] with *Daphnia magna* using synthetic dilution water. The mobility of the daphnids was evaluated after 24 h and 48 h. The luminescent bacteria test was realized in accordance with ISO 11348 part 2 (2007) [15] using liquid-dried luminescent bacteria while measuring the decrease in luminescence of the marine bacterium *Aliivibrio fischeri* (formerly *Vibrio fischeri*) after an exposure time of 30 min. The fish egg test was carried out in accordance with ISO 15088 (2007) [16] by exposing the fertilized eggs in 24-well plates at 26 °C ± 1 °C for 48 h. Two genotoxicity tests (Ames, umu) were later applied. The umu test was carried out following ISO 13829 (2000) [17] with the bacterial strain *Salmonella typhimurium* TA1535/pSK1002. The bacteria were exposed for 2 h to the eluates with and without metabolic activation (i.e. with or without the metabolic activation system S9), followed by a growth phase of 2 h. The induction of the umuC gene was compared with the spontaneous activation of the control culture. The result given is the smallest dilution step at which an induction rate (IR) < 1.5 is measured. The highest concentration tested corresponds to a dilution level of $D = 1.5$. The Ames fluctuation test (not applied by *Heisterkamp* et al. 2021 [20]) was carried out in accordance with ISO 11350 [18] using the test kit from Xenometrics (Allschwil, Switzerland) with microtiter plates. The test determines the induction of reverse mutations of bacterial *Salmonella typhimurium* strains, which are unable to grow in a histidine-free medium. Under the influence of genotoxic substances, mutations enable the bacteria to produce the amino acid histidine and grow on histidine-free medium. In the Ames fluctuation test, the growth of the bacteria (revertants) is detected by a colour change from violet to yellow. The eluates were examined with the test strains TA 98 and TA 100 with and without metabolic activation (Aroclor 1254-induced S9) after an incubation period of 48 h. Induction rates greater than a ratio of 2 over the baseline were considered genotoxic effects. In accordance with ISO 11350 [18], the highest concentration tested corresponds to a dilution level of $D = 1$, although the sample is diluted by ratio 1.35 through the addition of medium and bacteria suspension.

The LID corresponds to the lowest dilution ratio D, at which effects below the specific threshold were determined. The following effect threshold values were applied for the LID: algae test 5%; daphnia test 10%; fish egg test 10%; luminescent bacteria test 20%; umu test: IR < 1.5; and Ames test: IR < 2.0.

Analytical methods

Basic analyses were performed immediately after sampling at BAM. The conductivity of the eluates was determined in accordance with DIN EN 27888 [19] using a TetraCon® 96 or TetraCon® 325 electrode (WTW); pH was determined in accordance with DIN EN ISO 10523 (2012) [20] using a SenTix41 or Sentix81 pH electrode (WTW); and turbidity was determined by a 2100AN IS turbidimeter (Hach) in accordance with DIN EN ISO 7027 [21]. Total organic carbon (TOC, LOQ 0.1 mg L^{-1}) and total organic nitrogen (TN, LOQ 0.05 mg L^{-1}) were determined by a TOC–VCPH Analyzer (NDIR detector, Shimadzu) in accordance with DIN EN 1484 [22].

Concentrations of anions in eluates were determined by ion chromatography in accordance with DIN EN ISO 10304–1 [23] by an 883 Basic C plus ion chromatograph (Metrohm) using a Metrosep A Supp 5 (250 mm × 4 mm) column. An eluent of carbonate and bicarbonate in water (8 mmol L^{-1} and 1 mmol L−1) was applied for isocratic separation of the anions (see Additional file 1: SI 1 for LOQs).

Samples for the analysis of cations were acidified with concentrated sulphuric acid to pH < 2 immediately after collection. Concentrations of cations in eluates were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7000 ICP-OES, Thermo Scientific) in accordance with DIN EN ISO 11885 [24]. Cations with LOQs greater than LAWA Gfs values (no-effect levels defined by the BUND/Länder-Arbeitsgemeinschaft Wasser) [25] and samples with very low concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, iCAP Q equipped with a fast valve, Thermo Scientific) in accordance with DIN EN ISO 17294–2 [26]. Argon (5.0, Linde) was applied as a carrier gas (0.5 l min^{-1}), an auxiliary gas (1.5 l min^{-1}), and a plasma gas (15 l min^{-1}) in both devices. External calibration was applied for both methods using mixed standards.^{115} In was used as the internal standard for ICP-MS. ^{68}Zn and ^{115}In were analysed in KED mode by ICP-MS using argon (5.0) as a cell gas (see LOQs in Additional file 1: SI 1).

Eluates from all products were screened at BAM for organic substances using GC–MS. Selected organic substances, i.e., benzyl alcohol, 2-ethylhexanoic acid, 4-tert-butylphenol, 1–3-benzenedimethanamine, and *N,N*-dimethyl-1-dodecanamine were quantified at

BAM in eluates from MOE1 and MOE7 (see Additional file 1: SI 2 for the analytical procedure).

Screening by GC–MS at TZW was done in accordance with DIN EN 15768 (2015-05) [27]. As sample preparation, the eluates were extracted by liquid–liquid extraction under acidic (pH 2) and alkaline (pH 10) conditions with dichloromethane. After drying the organic phase, the extracts were combined and reduced to a volume of 1 mL. For the semi-quantitative analysis, several labelled internal standards were used. The measurements were carried out by GC–MS using RTX-5 (60 m × 250 µm × 0.25 µm, Restek) as a separation column.

For non-target screening by liquid chromatography, a LC system Agilent 1200er series and direct injection (100 µL) on reversed phase column Zorbax C18 (150 mm × 2.1 mm, 3 µm, Agilent) was used for separation. The mobile phase was a water-acetonitrile gradient with the addition of 0.1% formic acid. For high-resolution mass spectrometry, an ESI–QTOF (5600, Sciex) was coupled to the LC system. Separations were done in the negative and positive ionization mode.

To expand the qualitative investigation of the eluates, a liquid chromatographic method coupled to an UV detector (LC-DAD) was used: the LC system (1100 series, Agilent) was used with a reversed phase column Nucleodur C18 Gravity (150 mm × 2 mm, 3 µm, Macherey Nagel) and a water acetonitrile gradient with 10 mmol L^{-1}phosphoric acid. Detection was done with a diode array detector (1100er series, G1315B, Agilent).

Additional details on the liquid–liquid extraction and the three analytic methods are listed in Additional file 1: SI 3.

Results

General observations

The difference between test specimen masses before and after the leaching experiments was interpreted as water uptake by the test specimens. The values include water that remained on the surfaces when the test specimens were removed from the test assemblies. The uptake of water during the first two elution steps of the DSLT varied between 1% and 17% of the original mass of the investigated products (see Additional file 1: SI 4). The epoxy resin-based products (about 12%) and the modified cements (about 11%) took up the greatest amounts of water, whereas water uptake was lower in the polybutadiene-based products (about 6%) and lowest in the polyurethane-based products (about 2%). This resulted in different intensities of water contact for the different types of joint grouts during the DSLT experiments.

Basic analysis of eluates

Basic parameters such as pH, conductivity, turbidity, TOC, and TN are easily analysed and are applied as indicators of possible effects on the environment. The joint grouts based on epoxy resin (MOE1 and MOE6) and polyurethane (MOE5 and MOE8) caused an increase of pH in the eluates to values between pH 8 and pH 9.5. As expected, the pH of eluates from the two modified cements was higher, i.e. between pH 11.5 and pH 12. In contrast, the pH values of eluates from the polybutadiene products (MOE2 and MOE7) were acidic, i.e. about pH 4.

Increased electric conductivity indicates leaching of ions. This was observed mainly in the modified cements. In these products, electrical conductivity increased from less than 5 µS cm^{-1} to 3 mS cm^{-1}, while it ranged between 100 µS cm^{-1} and 400 µS cm^{-1} in DSLT eluates from epoxy resin products and between 44 µS cm^{-1} and 64 µS cm^{-1} in eluates from polybutadiene products and was in the range of the blank values in eluates from polyurethane products. For MOE1 (epoxy resin), the highest value, i.e. 600 µS cm^{-1} was observed in the L/S 2 fraction from the percolation test.

Turbidity was measured only in the L/S 2 fraction from MOE1 and the DSLT eluate of MOE8. The values were less than 10 FNU. In accordance with prEN 16637-3:2021, centrifugation of the eluates is required for samples of turbidity above 100 FNU.

The content of TOC in the eluates is a sum parameter indicating whether large amounts of organic substances are leachable. The highest TOC values were observed in the epoxy resin products, i.e. concentrations between 320 mg L^{-1} and 560 mg L^{-1} in DSLT eluates and even about 1300 mg L^{-1} in the L/S 2 fraction from the percolation test on MOE1. The TOC concentrations in eluates from the polybutadiene products were around 40 mg L^{-1}. The TOC concentration in eluates from one of the modified cements (MOE3) was between about 60 mg L^{-1} and 100 mg L^{-1}, whereas it was much lower in the other modified cement (MOE4), i.e. less than 6 mg L^{-1}. The lowest TOC values were observed in the polyurethane products, i.e. between about 0.6 mg L^{-1} and 5 mg L^{-1}.

Considerable amounts of organic substances that contain nitrogen, as indicated by TN values, were observed only in eluates from the epoxy resins. TN values were between 30 mg L^{-1} and 80 mg L^{-1} in DLST eluates and 270 mg L^{-1} in the L/S 2 fraction from MOE1. Small TN values of up to 0.5 mg mL^{-1} were observed in one of the polybutadiene-based joint grouts, one of the modified cements, and one of the polyurethane-based joint grouts. TN values were below LOQ in the three other products.

DSLTs were repeated for all products, resulting in two to five independent results for each product. The differences between repeated tests hint at the robustness of

Table 2 Selected cations in DSLT eluates from different grouts

Code	Binder	n	As in µg L^{-1}	Al in µg L^{-1}	Ba in µg L^{-1}	Co in µg L^{-1}	Cu in µg L^{-1}	Cr in µg L^{-1}	Mn in µg L^{-1}	Mo in µg L^{-1}	Ni in µg L^{-1}	Pb in µg L^{-1}	Sb in µg L^{-1}	Zn in µg L^{-1}
LAWA GfS			3.2		175	2.0	5.4	0.3		35	7.0	1.2	5.0	60
MOE1	ER	5	0.38		1.73		8.14		5.6	10.3		2.93	0.26	25.4
MOE6	ER	2	0.39		14.7		13.3				5.63			
MOE2	PB	2	0.19		6.38	1395	25.4		272			27.7		33.0
MOE7	PB	5			3.65		6.49		829		3.16	2.03	0.18	
MOE3	MC	2		515	1292		4.45				16.0		0.79	
MOE4	MC	2		24,400	31.5		2.09	4.62		6.40	3.14		0.73	
MOE5	PU	2			1.49		2.15				3.55	0.82	0.07	
MOE8	PU	2			1.40		3.11				1.90			

Selection criteria: elements that are included in the LAWA list of threshold values (LAWA GfS, 'Geringfügigkeitsschwellenwert') from 2016 [31] complemented by aluminum and manganese; concentrations in the range of the LOQs (limits of quantification) are not included; mean values from number of experiments (n),

Abbreviations for binders: *ER* epoxy resin, *PB* polybutadiene, *MC* modified cement, *PU* polyurethane the leaching method as well as the homogeneity of the investigated material. The pH data, ranges of conductivity, TOC, and TN were very similar in repeated tests for all products. The highest values were less than twice that of the lowest values, despite TOC for one product and TN for two products. In those cases, the measured data were very small. The complete set of measured basic data is presented as Additional file 1: SI 5.

Inorganic anions and cations

Concentrations of anions were low in most of the eluates. However, relatively high concentrations of sulphate were observed in eluates from one of the modified cements (MOE4, 35 mg L^{-1} and 48 mg L^{-1}), whereas less sulphate was leached from the other modified cement (MOE3, 0.4 mg L^{-1} and 4 mg L^{-1}). For one out of three batches of MOE1 (epoxy resin-based), sulphate concentrations in DSLT eluates amount to up to 60 mg L^{-1}, whereas the sulphate concentrations in DLST eluates from the other two batches and in the L/S 2 fraction from the percolation test were lower (below 10 mg L^{-1} or in the range of blank values and LOQ). This was also the case with the MOE1 batch that was used for the interlaboratory study [10, 11]. The sulphate concentration in eluates from the other epoxy resin-based joint grout (MOE6) was about 2 mg L^{-1}. Chloride was detected in eluates from the modified cements (MOE4: 3 mg L^{-1} to 4 mg L^{-1}; MOE3: 0.4 mg L^{-1} in only one sample) and the epoxy resin-based products (MOE1: about 3 mg L^{-1}; MOE6: 1 mg L^{-1} to 2 mg L^{-1}). Fluoride and nitrate were detected at low concentrations only in some of the samples of the modified cements, the polybutadiene-based product MOE2 and the epoxy resin-based product MOE1. Bromide was detected in eluates from the epoxy resin-based product MOE1 (0.2 ml L^{-1} to 0.6 mg L^{-1}). Concentrations of nitrate and phosphate were in the range of the blank values for all samples. The ratios between results from repeated experiments were usually below 2. Anion concentrations of all samples are presented as Additional file 1: SI 6.

Elements that were detected in eluates and for which no-effect levels are defined in Germany (LAWA GfS, Geringfügigkeitsschwellenwerte, insignificance threshold values [25]) are summarized in Table 2. In addition, data on aluminium and manganese are included in the table, since differences between the investigated products were observed for these two elements. The results for all analysed cations are presented as Additional file 1: SI 7. As with the anions, many cations were detected in the range of blank values, LOQs, or only in some of the samples in repeated experiments. Barium, copper, nickel, and antimony were detected in eluates of the majority of the products. Lead, zinc, molybdenum, and arsenic were found in eluates from only a few products. Several elements were detected only in specific products, i.e. cobalt in eluates from the polybutadiene-based product MOE2, chromium in eluates from the modified cement MOE4, aluminium in eluates from the two modified cements, and manganese in the eluates from the two polybutadiene-based products and, at low concentration, in eluates from one epoxy resin-based product.

Concentrations in the range of or slightly exceeding the LAWA GfS values were observed for copper and nickel. The concentration of barium in the eluates from the modified cement MOE3 was above the LAWA GfS value, while the concentrations in the eluates from the other products was below the LAWA GfS value. The concentrations of arsenic, molybdenum, antimony, and zinc in all eluates were below the LAWA GfS values. Eluate concentrations in repeated experiments usually varied by a factor of up to 2. The ratio was higher for arsenic from different batches of MOE1 (ratio 3.5) and for barium, copper, and lead in different experiments on MOE7 (ratio 4 to 8).

There was no trend for the eluate concentrations of anions and cations when the duration of storage of MOE1 and MOE7 test specimens was varied before starting the DSLT.

Ecotoxicity of eluates

The results of the ecotoxicity tests are summarized in Table 3. The ecotoxicity of eluates from the different joint grouts differed considerably, whereas similar patterns were observed for many parameters in products that are based on the same type of binder.

Strong ecotoxic effects on luminescent bacteria and algae were observed in eluates from the epoxy resin-based products. The ecotoxic effect on luminescent bacteria was considerably lower in the eluates from MOE6 than in the one from MOE1, whereas ecotoxic effects on algae were greater in DLST eluates from MOE6 than in eluates from MOE1. Elevated ecotoxicity on luminescent bacteria and algae was observed in eluates from the polybutadiene-based product.

Daphnia and fish eggs were affected mainly by eluates from the epoxy resin-based products.

The umu tests indicated genotoxicity of the epoxy resin-based product MOE1, while the Ames test indicated genotoxic effects of the modified cements MOE3 and MOE4. Only low LID values for algae and daphnia or no ecotoxic effects were observed in the eluates from the polyurethane-based products MOE5 and MOE8, respectively.

Table 3 Summarized results from ecotoxicity tests on eluates from different leaching experiments on joint grouts

Code	Binder	*n*	Leaching test	Algae LID_A	Daphnia LID_D 48 h	Fish egg LID_{Egg}	Luminescent bacteria LID_{lb}	Umu LID_{EU}	Ames
MOE1	ER	6	DSLT	384 to 1536	64 to 192	8 to 12**	1536 to 3072	3**	1**
MOE1	ER	1	Percolation test	3072**	256 to 512**	24 to 32**	12,288 to 16,384**	6 **	1
MOE6	ER	1*	DSLT	3072	192	16	96	≤ 6	1
MOE2	PB	1*	DSLT	32	≤ 2	≤ 2	16	≤ 1,5	1
MOE7	PB	5	DSLT	8 to 12	≤ 2 to 3	≤ 2***	24	≤ 1,5***	1***
MOE3	MC	1*	DSLT	3	≤ 2	≤ 2	≤ 2	≤ 1,5	≥ 2
MOE4	MC	1*	DSLT	inconsistent	4	≤ 2	≤ 2	≤ 1,5	2
MOE5	PU	1*	DSLT	4	3	≤ 2	≤ 2	≤ 1,5	1
MOE8	PU	12	DSLT	≤ 2	≤ 2	≤ 2	≤ 2	≤ 1,5	1

Test specimens or deagglomeated particles of grouts were exposed to either DSLT or percolation test. The storage periods for test specimens varied between 7 and 28 days for DSLT. Part of the test specimens were covered by cling film during storage. The test material for the percolation test was cured and stored for 46 days before the test

LID ranges represent data from independent experiments. Ames test: can also indicate cytotoxicity

LID of corresponding blank samples was ≤ 2 for algae, daphnia, fish eggs and luminescent bacteria, ≤ 1.5 for umu test and 1 for Ames test

* Test on algae was performed for eluates from a repeated experiment since blank sample of the first experiment was toxic toward algae, **only one eluate was tested twice, *** only one eluate was tested

Abbreviations for binders: *ER* epoxy resin, *PB* polybutadiene, *MC* modified cement, *PU* polyurethane

GC–MS and LC–ESI–QTOF screening for organic substances in eluates

It is challenging to seek information on organic substances that can be expected to cause ecotoxic effects. Often the available product information does not contain adequate data, and a product eluate presents a "black box" for an investigation. As a general parameter, the content of TOC in eluates indicates whether large amounts of organic substances can be leached. However, there is no information on the toxicity of the leached mixture of substances. Another option is to identify substances and search for information on their ecotoxic effects.

Only organic substances in the eluates that are accessible for the applied preparation, separation, and detection methods can be captured by current analytical procedures. Thus, different substances were identified by GC–MS and LC–ESI–QTOF (see Additional file 1: SI 10 and SI 12). The obtained substance lists were checked for substances that were declared in formulas or other product information—as far as available—and for substances that are labelled with H-phrases for environmental and health hazards [28]. The ECHA page for substances was also checked for substances that have been registered under REACH [28], as were the production volumes as a plausibility check for the identification of the substances.

Substances were identified in eluates from the eight joint grouts by GC–MS at BAM (see Additional file 1: SI 10) and for eluates from MOE1 by LC–ESI–QTOF and GC–MS at TZW (see Additional file 1: SI 12).

Benzyl alcohol was identified in the eluates from all products, but not in the blank. No other organic substances were identified by GC–MS in eluates from the polyurethane-based products and modified cements. The signal of 2-ethylhexanoic acid was prominent in extracts from the eluates of the polybutadiene-based products. Possibly, its cobalt salt was used as a siccative for the polymerization of polybutadiene to produce MOE2, while the manganese salt was used to produce MOE7 (see results on cations above).

Similar results were obtained for MOE1 eluates by GC–MS analysis at TZW and BAM. Additional substances, e.g., bis(2-ethylhexyl)fumarate, bis(2-ethylhexyl) maleate, and benzyl dodecyl dimethylammonium cations were indicated by LC–ESI–QTOF analysis at TZW.

Attempts to combine ecotoxicity and screening results for organic substances

Results from screening analysis in both laboratories and ecotoxicity data on selected tentatively identified substances are summarized in Table 4. The table includes substances that are labelled by H-phrases on environmental hazards. In addition, benzyl alcohol was included, since it is used as a solvent in various products and is supposed to affect the solubility of other organic substances in eluates. 2-Ethylhexanoic acid was included, since it was characteristic for the polybutadiene-based products.

Quantitative data on selected organic substances in eluates from MOE1 and MOE7 depending on storage time

Certain substances were quantified in eluates of MOE1 and MOE7 to check the presumption that a higher

Table 4 Ecotoxicity and classification of selected substances that were tentatively identified in eluates from grouts

Substance	CAS	H-phrases	Substance identified by			Ecotoxicity data		
			TZW LC–MS	TZW GC–MS	BAM GC–MS	Fish	Daphnia	Algae
4-tert-Butylphenol*	98-54-4	H410		MOE1	MOE1	rainbow trout LD50 (96 h) = 5.1 mg L^{-1}	EC50 (48 h) = 3.9 mg L^{-1}	*Selenastrum capricornutum* EC50 (72 h) = 14 mg L^{-1}, EC10 or NOEC (72 h) = 0.32 mg L^{-1}
Benzyl alcohol*	100-51-6			MOE1	MOE1 to MOE8	*Lepomis macrochirus* LC50 (96 h) = 10 mg L^{-1}	EC50 (48 h) = 360 mg L^{-1}	*Pseudokirchnerella subcapitata* EC50 (72 h) = 770 mg L^{-1}, NOEC (72 h) = 310 mg L^{-1}
N,N-Dimethyl-1-dodecanamine *	112-18-5	H410		MOE1	MOE1	*Danio rerio* or *Oncorhynchus mykiss* LC50 (96 h) = 0.26 mg L^{-1} to 1.13 mg L^{-1}	EC50 (48 h) = 0.056 mg L^{-1} to 0.93 mg L^{-1}	different species EC50 (72 h) = 0.016 mg L^{-1}, EC10 or NOEC (72 h) = 0.0026 mg L^{-1}
N,N-Dimethyl-1-tetradecanamine	112-75-4	H410			MOE1	different species LC50 (48 h) = 0.43 mg L^{-1} to 1 mg L^{-1}	EC 50 (48 h) = 0.056 mg l^{-1} to 0.93 mg L^{-1}	different species EC50 (72 h) = 0.016 mg L^{-1} EC10 or NOEC (72 h) = 0.0026 mg L^{-1}
Bis(2-ethylhexyl) fumarate	141-02-6	H411	MOE1			no data	EC50 (48 h) > 100 mg L^{-1}	QSAR estimation EC50 > 1.19 mg L^{-1}, NOEC ≥ 1.19 mg L^{-1}
Bis(2-ethylhexyl) maleate	142-16-5	H410	MOE1			Zebra fish LC50 (96 h) > 100 mg L^{-1}	EC50 (48 h) = 59.5 mg L^{-1}	different species EC50 (72 h) > 100 mg L^{-1} (nominal) and 0.62 mg L^{-1} (measured), NOEC (72 h) = 3.7 mg L^{-1} (nominal) and 0.052 mg L^{-1} (measured)
Benzothiazole-2-thiol (2-Mercapto-benzothiazole)	149-30-4	H400 (acute) H410 (long term)	MOE1			rainbow trout LC50 (96 h) = 0.73 mg L^{-1}	EC50 (48 h) = 29.8 mg L^{-1}	*Selenastrum capricornutum* EC50 (72 h) = 0.5 mg L^{-1} NOEC (72 h) = 0.066 mg L^{-1}
2-Ethylhexanoic acid*	149–57-5				MOE2 MOE7	*Oncorhynchus mykiss* EC50 (96 h) = 180 mg L^{-1}	EC50 (48 h) = 85.4 mg l^{-1}	*Desmodesmus subspicatus* EC50 (72 h) = 485.1 mg L^{-1} EC10 or NOEC = 231.2 mg L^{-1}
1,3-Benzenedimethanamine*	1477-55-0	H412			MOE1 MOE6	Rainbow trout LC50 (96 h) > 100 mg L^{-1}	EC50 (48 h) = 16 mg L^{-1}	*Desmodesmus subspicatus* EC50 (72 h) = 12 mg L^{-1}, NOEC (72 h) = 6.25 mg L^{-1}

Table 4 (continued)

Substance	CAS	H-phrases	Substance identified by			Ecotoxicity data		
			TZW LC–MS	TZW GC–MS	BAM GC–MS	Fish	Daphnia	Algae
2,3-Epoxypropyl-o-tolyl ether	2210-79-9	H411		MOE1		*Oncorhynchus mykiss* LC50 (96 h) = 2.8 mg L^{-1} to 5.1 mg L^{-1}	EC50 (48 h) = 3.3 mg L^{-1}	no data
Benzyldodecyldimethylammonium cation, possibly from Benzyldodecyldimethylammonium bromide	7281-04-1	H400	MOE1			no data	no data	no data

Selection criteria for substances: confirmed by reference substances (substances marked by *) and/or substances classified as H400, H410 or H411

Analytical laboratories (TZW and BAM) and methods applied to identify substances in MOE eluates are indicated, TZW analyzed only MOE1 eluates by LC–MS and GC–MS, BAM analyzed eluates from MOE1 to MOE8 only by GC–MS; for MOE codes, see Table 1. Origin of H-phrases: ECHA website on registered substances [34], Origin of ecotoxicity data: ECHA website (Brief profiles of substances)

degree of evaporation of volatile constituents or chemical reactions during storage of the test specimens can affect the ecotoxicity of the eluates. This includes TOC and TN as sum parameters, the solvent benzyl alcohol, two amines that were identified in eluates from MOE1, and 2-ethylhexanoic acid that appeared in relatively high concentrations in eluates from MOE7. The prepared test specimens were stored for 7, 14, or 28 days before the DSLT was started. In addition, one test specimen of each product was covered by cling film to avoid evaporation during storage (experiment 3). Results from the uncovered test specimens from this experiment and from the first DSLT using MOE1 test specimens after 12 days of storage (experiment 1) are presented in Fig. 1. All results are listed in Additional file 1: SI 5 and SI 11. Concentrations of most parameters in eluates, i.e. TOC and TN for both products, 4-tert-butylphenol and *N,N*-dimethyl-1-dodecanamine from MOE1, and 2-ethylhexanoic acid from MOE7, were in similar ranges for the different durations of storage. The concentrations of 1,3-benzenedimethanamine decrease with time in experiment 3, but the data point from experiment 1 does not fit that trend. The concentrations of benzyl alcohol were lower in the eluates from MOE7 than from MOE1 and decrease with storage time for both products. The results for the covered test specimens were in the ranges of the results for the uncovered test specimens.

Discussion

Combination of leaching and ecotoxicity tests

In a few studies, the ecotoxic effects of eluates from construction products and the occurrence of—mainly organic—substances in these samples were investigated in combined approaches to identify hazardous substances that are released from construction products and cause ecotoxic effects [29–40]. The combination of the harmonized leaching tests and the ecotoxicological test battery as included in CEN/TR 17105 [6] was applied on several types of construction products [29–31], on biocide release from renders [32], on reactive fire-retardant coatings [33], and on roof membranes [34]. DSLT experiments were combined with tests for phytotoxicity and for the mutagenic and genotoxic potential of eluates from microfine cement, including PCE-based (polycarboxylate ether) superplasticizers [35]. For steel coatings, DSLT was combined with tests on luminescent bacteria and/or tests on estrogenic activity [36–38], including bioluminescence detection on TLC (thin-layer chromatography) plates. In another study on steel coatings, test specimens were shaken in water and the eluates investigated for estrogenic and other effects on a human cell line, for bioluminescence in bacteria, for photosynthesis activity and growth of algae, and for effects on water fleas [39]. Leachates from batch experiments on recycled concrete were nontoxic to daphnia, freshwater algae and duckweed [40]. In order to be able to compare the ecotoxicity of different construction products, it is useful if the approach to the investigation of possible ecotoxic effects is harmonized. The present study confirms the applicability of CEN/TR 17105 and its further validated transition into CEN/TS 17459.

Basic analysis of eluates as indicator for possible environmental impact

Basic analyses of the eluates indicate whether environmental effects are possible due to pH changes, the

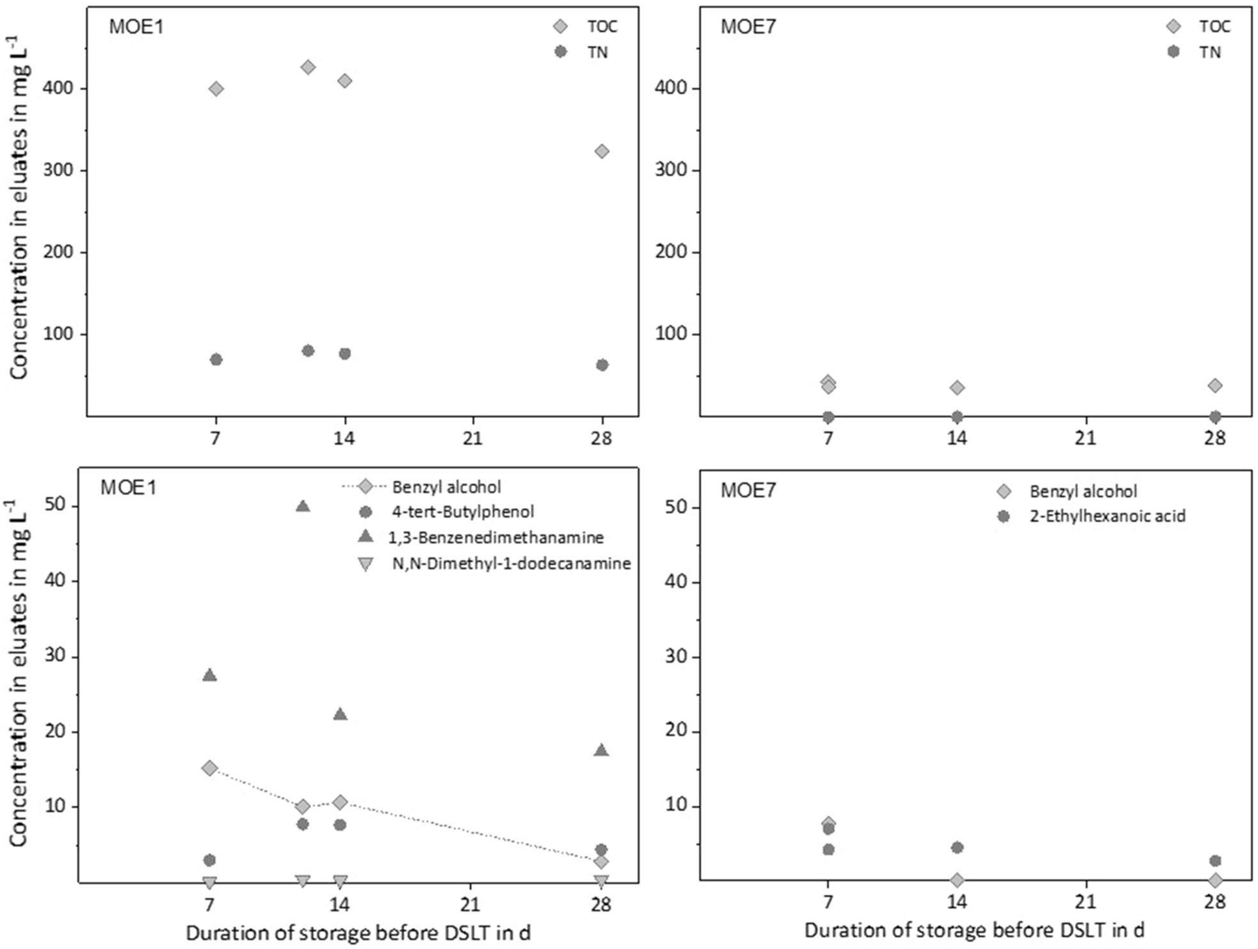

Fig. 1 Concentration of TOC, TN, and selected organic substances in eluates from MOE1 and MOE7. Eluates originate from DSLT (combined sample of eluate 1 and 2)

release of ions, or large amounts of organic matter. In summary, the results on the eluates from joint grouts indicate that the greatest effects on pH and the leaching of ions came from modified cement, whereas the greatest amounts of organic substances were leached from epoxy resin-based products. In addition, the eluates from the epoxy resin-based products held the greatest amounts of nitrogen-containing substances. This observation has prompted us to pay special attention to nitrogen-containing substances when screening for organic substances in the eluates. The polyurethane-based products had the least effect on pH, conductivity, and TOC. In addition, their observed TN values were in the lower range. The observation of fewer ecotoxic effects of eluates from the modified cements and the polyurethane-based products agrees with the fact that relatively low amounts of organic substances were found in these eluates.

Ecotoxicity caused by inorganic anions and cations

Results on inorganic anions and cations can be compared with environmental quality standards, for example, the LAWA GfS values [25]. These values are defined for groundwater, and its application for assessing eluates requires transfer steps. However, these calculations have not been defined so far. This needs to be taken into account when the data are examined.

Overall, results on anion leaching do not indicate possible ecotoxic effects. Considering safety factors that were applied to define LAWA GfS values, the obtained concentrations of cations in the investigated eluates do not suggest any effects in ecotoxicity tests. As an exception, concentrations that were clearly above the LAWA GfS values were observed for cobalt and lead in eluates from the polybutadiene-based product MOE2. Cobalt compounds can be used as a siccative during the production of polybutadienes. Alternatively, manganese compounds can be used for this purpose (see data on MOE2 and MOE7 in Table 2). The observed concentration of cobalt in the MOE2 eluate was about 1.4 mg L^{-1}, which is higher than the LC50 for freshwater invertebrates (0.61 mg L^{-1}) and the EC50 (0.31 mg L^{-1}) for freshwater algae as indicated in the REACH database on the ECHA website [28]. The cobalt concentration falls below the EC10 or NOEC of 0.076 mg L^{-1} only at a dilution by a factor of 32, resulting in about 0.04 mg L^{-1} Co. As the LID_A for the MOE2 eluate was determined to be 32, it is obvious that cobalt causes a significant part of the ecotoxic effect of this eluate on algae. However, the effect on luminescent bacteria is probably caused by another component in the eluate, since the EC10 or NOEC value for microorganisms (3.73 mg L^{-1}) is higher than the determined concentration. Data on the ecotoxicity of cobalt are scarce. It is known that cobalt sulphate can be contained in wood preservatives as a formulation additive and may contribute to the ecotoxicity of mixtures on algae [41]. Cobalt is assessed as relatively important compared with other components of the wood preservative, since it is easily leached due to its high solubility in water. Although the concentration of lead in the eluate of MOE2 is greater than the LAWA GfS value, an effect in ecotoxicity tests is not expected. The lowest EC50 for this element is reported for the alga *Pseudokirchneriella subcapitata* [EC50 (72 h) 20.5 µg L^{-1} to 364 µg L^{-1}] [28]. The minimum value is in the range of the analysed concentration of lead. Lead is less toxic to *Daphnia magna* [EC50 (48 h) 280 µg L^{-1} to 364 µg L^{-1}] and microorganisms (EC10 1 mg L^{-1}) [28].

Ecotoxicity caused by organic substances

TOC and TN values indicate whether large amounts of organic carbon and nitrogenous compounds, respectively, are being released. Further investigations are necessary to find out whether these contain environmentally hazardous substances. This includes qualitative testing to identify environmentally hazardous substances, but also quantitative testing to determine if critical concentrations are being reached. In order to evaluate the findings, ecotoxicological data on the substances found must be available. Gas and liquid chromatography coupled with mass spectrometry are commonly used methods for this purpose. GC–MS and LC–ESI–QTOF screening for organic substances in eluates were applied for this study.

It is remarkable that several nitrogen compounds, i.e. mixtures of amines, were identified in extracts from eluates of the epoxy-resin-based products. Amines are used to cross-link epoxy resins. Different mixtures, i.e., 2,2,4-trimethylhexane-1,6-diamine and 1,3-benzenedimethanamine (MOE1) or 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine) and 1,3-benzenedimethanamine (MOE6), were probably applied to produce the two different epoxy-resin-based products. Ecotoxicity data suggest that eluates from these products are highly toxic to algae and luminescent bacteria, moderately toxic to daphnia, and less toxic to fish eggs. The detected amines, especially *N,N*-dimethyl-1-dodecanamine and *N,N*-dimethyl-1-tetradecanamine, exhibit high toxicity to algae [EC50 (72 h) = 0.016 mg L^{-1}], but are also relatively toxic to daphnia [EC (48 h) = 0.056 mg L^{-1}]. These substances are probably involved in the ecotoxicity of the eluates, but do not explain the observed pattern of ecotoxic effects on different species. The concentration of *N,N*-dimethyl-1-dodecanamine in the eluates was determined to be about 0.4 mg L^{-1}. An about 150fold dilution of the eluates is required to obtain the EC10 or NOEC (72 h) of 0.0026 mg L^{-1} for algae. However, the lowest observed ineffective dilutions (LID) were greater (up to about 1500, see Table 3), i.e. ecotoxic effects on algae were only partly caused by this substance. Amines were detected only in eluates from epoxy resin-based products. This is also confirmed by the fact that considerable concentrations of TN were detectable only in eluates from epoxy resin-based products, but not in eluates from the other products (see Additional file 1: SI 5).

Possibly, 4-tert-butylphenol can contribute to the effect on algae of eluates from epoxy resin-based joint grouts. Concentrations in the eluates from MOE1 ranged between 3 mg L^{-1} and 8 mg L^{-1} (n = 5). A dilution of a factor of up to 30 was necessary to reach the EC10 or NOEC of 0.32 mg L^{-1} for algae. Fish and daphnia are more sensitive to 4-tert-butylphenol (see data in Table 4), i.e., tert-butylphenol can be involved in MOE1 eluates' observed toxicity to these species (LID_{Egg}: 8–12, LID_D: 64–192, see Table 3). In a study of ecotoxic effects of epoxy resin-based coatings for steel [37], 4-tert-butylphenol, which is used as hardener, was identified as the main substance causing acute and estrogenic effects of eluates from these coatings. Additional substances are supposed to contribute to these effects. The concentrations of 4-tert-butylphenol in DSLT eluates from MOE1 were in the range of the concentrations in eluates from both epoxy resin-based coatings for steel (2.6 mg L^{-1} and 4.3 mg L^{-1} [37]) that displayed estrogenic effects. Therefore, estrogenic effects can be assumed also for the eluate from MOE1, although they were not tested in the present study. In a further study of two epoxy resin-based coatings [38], toxicity to bacteria and estrogenic effects of two epoxy resin-based coatings and the concentration of 4-tert-butylphenol in the eluates were decreased when the test specimens were exposed to UV radiation prior to the leaching test. In addition, several phenols that can contribute to the estrogenic effects were identified. Some of them occurred only after UV radiation, e.g., the concentration of bisphenol A was considerably increased after UV radiation. In another study [39], bisphenol A was identified in eluates from corrosion protection coatings, including epoxy resin-based products. Estrogenic and anti-androgenic effects, inhibition of bioluminescence, and effects on the reproduction of water fleas and algal growth were partially related to this substance, although other substances were assumed to contribute to the effects. The concentrations of 1,3-benzenedimethanamine in the DSLT eluates from MOE1 (17 mg L^{-1} to 50 mg L^{-1}, $n=5$) were in the range of E50 values for daphnia and algae. Therefore, this substance could have only little effect on these organisms in diluted eluates. Concentrations of other substances that can cause ecotoxic effects of eluates from MOE1, e.g., substances listed in Table 4, are unknown. Therefore, their contribution to the observed ecotoxicity of these eluates cannot be discussed. Furthermore, there can be other ecotoxic substances in the eluates that have not been identified. The calculation of the mixture toxicity of the quantified environmentally hazardous substances is described in [31].

It is suggested that eluates from the polybutadiene-based joint grouts MOE2 and MOE7 contain substances that are toxic to algae and luminescent bacteria and rather non-toxic to daphnia and fish eggs. None of the tentatively identified substances from the eluates of these products fulfils this ecotoxicity profile. For 2-ethylhexanoic acid, EC50 values for fish, daphnia, and algae are considerably higher than the concentrations observed in DSLT eluates from MOE 7 (3 mg L^{-1} to 7 mg L^{-1}, $n=5$, see Additional file 1: SI 11 and Table 4).

In the present study, only small ecotoxic effects on algae and daphnia were observed in one of the polyurethane-based products (see Table 3). This fits well with the fact that no substances other than benzyl alcohol were identified in these eluates. In a study on polyurethane-based coatings for steel [37], eluates from two out of three polyurethane-based coatings did not cause any ecotoxic effect. For the third product, zinc was assumed to cause toxic effects on algae. 4-toluenesulfonamide and 4-tolueneethylsulfonamide were identified in the eluates. However, in another study [36], 30 substances released from polyurethane including p-toluenesulfonamide were identified. Several of the identified substances caused bacterial toxicity to *Aliivibrio fischeri.*

Eluates from fire-retardant coatings—products with and without epoxy-resin—contained substances that cause ecotoxic effects on bacteria, algae, and daphnia [33]. Several phenol derivatives that are labelled environmentally hazardous were tentatively identified in the eluates.

The toxicity of eluates from renders that include organic binders was related to biocidal active substances [32], i.e. the toxicity of eluates to bacteria was dominated by the isothiazolinone OIT, while toxic effects on algae were dominated by terbutryn.

Ecotoxic effects of eluates from EPDM (ethylenepropylen diene-monomer rubber) roof membranes on luminescent bacteria, algae, and daphnia were related to zinc and benzothiazole, and ecotoxic effects of eluates from FPO (flexible polyolefin) roof membranes on algae were related to 1,1,1-trimethylolpropane [34].

Both the literature data and the results of this study underscore the importance of organic substances used in additives for potential environmental impacts of construction products.

Comparison of leaching tests

The epoxy resin-based product MOE1 was investigated in DSLT and the column test. The concentrations of TOC, TN, most of the leached anions and cations, and a few quantified organic substances were higher in the eluate from the column percolation experiment than in the mixture of the first two eluates from the DSLT (see Additional file 1: SI 8 for summarized data). In the ecotoxicity tests, the LIDs were greater for the L/S 2 fraction from the percolation test than for the combined eluates from the first two elution periods from DSLT (see Additional file 1: SI 9).

It is supposed that the larger surface area of the crushed material causes greater water contact by percolation than in the DSLT of the product in monolithic form. The duration of water contact was 24 h for the first two immersion periods of the DSLT and 12 h without eluent flow for pre-equilibration plus 25.9 h of percolation in the column test. However, the water volume used per mass of test material differed considerably, i.e. it was 2 L per kg of test material in the column test and 9 L per kg of test specimen in the DSLT.

Usually, emissions observed in percolation tests are reported as emissions per mass of test material, whereas the emissions during the DSLT are reported as emissions per surface area, e.g., mg m^{-2}. Since the masses of the test specimens in the DSLT were recorded, emissions during DSLT were also calculated in relation to masses (see Additional file 1: SI 8) to compare the two leaching methods. The mass-related emissions were greater during DSLT than during the percolation test for many parameters. Despite the greater surface area of the granulated MOE1 material, this was probably caused by the higher ratio of water volume per mass of test material in the DSLT and indicates high water solubilities of these parameters from the associated substances. Admittedly, this observation applies only to the actual test conditions, i.e. the test material and its water uptake during the DSLT, the dimensions and mass of test specimens, and the water volume per surface area.

Investigation of the first two DSLT eluates or fractions at early stages of the percolation experiments provides evidence of hazardous substances or mixtures that can be easily leached. Substances that are mobilized after longer periods of water contact and substances that are formed only during longer period of water contact may have been overlooked. This can be relevant for construction products that are in contact with water for longer periods of time under service conditions. Furthermore, information on emission processes that allows conclusions about release mechanisms can help optimize products.

Construction products, especially freshly manufactured test specimens, can change during storage. This can have an influence on the leaching of substances. Therefore, it is necessary to test the storage period for construction products and to specify it in the leaching procedures. A slightly decreasing trend with increasing storage time for benzyl alcohol was observed for the joint grouts MOE1 and MOE7. For the other chemical parameters, no trend was observed for the period of 1 to 4 weeks of storage (see Additional file 1: SI 5, 6, 7 and 11 and Fig. 1). This was also the case with the ecotoxicological studies (see Additional file 1: SI 9). For test specimens from these products, the storage time may vary during this period without any influence on results of ecotoxicity tests being expected.

Conclusions

- This paper provides new knowledge on substances of concern in joint grout eluates and their ecotoxicological effects. Some eluates showed ecotoxic effects even at very high dilutions. This can be of concern in the environment, when similar or lower dilution levels are reached under use conditions.
- Ecotoxicity data were successfully used to identify substances that may cause ecotoxic effects from different types of joint grouts. As expected, due to the complex mixture toxicity in the investigated eluates not all effects can be allocated to specific substances.
- The results using joint grouts show as an example that ecotoxicological effects of construction product eluates can now be adequately described and compared across different product types with the help of a standard battery of acute ecotoxicity tests with sublethal effects and standardised leaching tests. For a deeper understanding of long-term effects of construction product leachates on aquatic biota further research using chronic tests is needed.
- Eluates from joint grouts based on different binders caused different patterns of ecotoxic effects, while the two products that were investigated for each of four different binder types caused similar effects in many cases.
- Among the investigated products, the most significant ecotoxicity was observed in epoxy resin-based products, followed by polybutadiene-based products. Polyurethane-based products and modified cement caused fewer or no ecotoxic effects on the tested organisms. This can be a motivation use an ecolabel, e.g., Blauer Engel (Blue Angel) to indicate products that cause fewer effects on the environment due to leaching.
- At present, the combination of ecotoxicity tests and modern analytical techniques, such as GC–MS and LC–ESI–QTOFS–MS, completed by ecotoxicity data on substances, allows the identification of substances to explain the results of ecotoxicity tests. However, toxicity usually cannot be explained by single substances, and a complete overview of the composition of eluates is not available. The development of methods for the comprehensive detection and description of environmentally hazardous substances remains highly demanded for the scientific community. Identification of substances that can be leached from construction products causing ecotoxic effects can stimulate optimization of product formulas.
- Concentrations of and ecotoxicity data on substances are required to assess the contribution of substances to observed ecotoxic effects. Several amines can be leached from epoxy-resin-based joint grouts and are supposed to be involved in ecotoxic effects. Inorganic components, e.g., cobalt in polybutadiene-based joint grouts, are also leached from joint grouts and could cause ecotoxic effects.
- The results of ecotoxicity tests and chemical analysis are relatively robust across the durations of the storage of test specimens of joint grouts prior to leaching tests in the range of 1 to 4 weeks.

Abbreviations

BAM: Bundesanstalt für Materialforschung und -prüfung; CEN/TC: European Committee for Standardization/Technical Committee; CEN/TR: European Committee for Standardization/Technical Report; CEN/TS: European Committee for Standardization/Technical Specification; CPR: Construction Products Regulation; DE-UZ: Umweltzeichen Blauer Engel; DIN: Deutsches Institut für Normung; EN: European Standard; DSLT: Dynamic surface leaching test; EAD: European Assessment Document; EC50: Volume percentage causing 50% effect; EPDM: Ethylenepropylen diene-monomer rubber; ESI–QTOF: Electrospray ionization–quadruple-time-of-flight mass spectrometer; FPO: Flexible polyolefin; ICP-MS: Inductively coupled plasma mass spectrometry; ICP-OES: Inductively coupled plasma optical emission spectrometry; ISO: International Organization for Standardization; LAWA: Bund/Länder-Arbeitsgemeinschaft Wasser; LC: Liquid chromatography; LC-DAD: Liquid chromatography coupled with a diode array detector; LID: Lowest ineffective dilution; LOQ: Limit of quantification; L/S: Liquid-to-solid ratio given in L kg^{-1}; n.d.: Not determined; NOEC: No observed effect concentration; PCE: Polycarboxylate ether; PET: Polyethylene terephthalate; PERC: Percolation test; PP: Polypropylene; TOC: Total organic carbon; TLC: Thin-layer chromatography; TN: Total nitrogen; TZW: Technologiezentrum Wasser.

Supplementary Information

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Additional file 1: SI 1. Limits of quantification (LOQs) for anions and cations. **SI 2**. Analytical methods on organic substances applied at BAM. **SI 3**. Analytical methods on organic substances applied at TZW. **SI 4**. Data on test assemblies. **SI 5**. Results for TOC, TN, pH, conductivity and turbidity of eluates. **SI 6**. Concentration of anions in eluates from DSLT and percolation test. **SI 7**. Concentration of cations in eluates from DSLT and percolation test. **SI 8**. Comparison of emissions from MOE1 in DSLT and percolation test. **SI 9**. Results from ecotoxicity test on eluates from joint grouts. **SI 10**. Results from GC-MS Screening at BAM. **SI 11**. Results for selected organic substances in eluates of MOE1 and MOE 7 after different duration of storage of test specimens before leaching tests. **SI 12**. Data from TZW.

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Author contributions

US drafted the manuscript; US and UK were responsible for the leaching tests and part of the chemical analysis; IH, MK, and SG were responsible for the ecotoxicity tests; OH was responsible for part of the chemical analysis; and OI was involved in the study design. All authors contributed to the manuscript.

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Availability of data and materials

The original data sets of the ecotoxicity tests are available from Ines Heisterkamp. The original data sets of chemical analysis are available from Ute Schoknecht and Oliver Happel.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

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