

LEACHING OF PHENOLS FROM TIRE SHREDS IN A NOISE BARRIER

Roald Aabøe, Norwegian Public Roads Authorities, NPRA, Norway
Arnt Olav Håøya, RAMBØLL
Tommy Edeskär, Luleå University of Technology, Sweden.

ABSTRACT. As part of the Norwegian Roads Recycled Materials R&D Program (www.gjenbruksprosjektet.net), a large light fill noise barrier has been constructed along highway E6. The structure utilized 25% of all tyres that were collected in Norway in 2002. Four monitoring stations are used to sample leachate from drainage that enter local recipient.

The leaching of anti-oxidizing compounds from tyre shreds is of concern for Norwegian environmental authorities. In national pilot projects where tyre shreds are used as a light fill material special precaution is taken not to harm the surface water recipients.

A five-year monitoring program will document relative effect from different sources and the risk of environmental harm will be evaluated. Ongoing pilot projects indicate that leaching of nonyl-, octyl- or bisphenol from tyre shreds induces no environmental risk if applied under given design conditions. The way of application of recycled material will have an impact on long-term risk and the possibility of reuse or recycling of tyre shreds.

Keywords: Tyre shred, leaching, monitoring, legislation, phenol

R. Aabøe is senior engineer at the Norwegian Public Roads Authorities, Geo- & Tunnel Technology .

A.O. Håøya is senior geologist working at Ramboll AS in Oslo, Norway.

T. Edeskär is MSc in Environmental Engineering and a PhD-student at Luleå University of Technology, Sweden.

INTRODUCTION

The Norwegian Government has identified undesirable properties of chemicals in two white papers from the Storting, (the Norwegian Parliament [1, 2]). The Norwegian Pollution Control Authority has further refined the list of undesirable properties and determined quantitative values (cut-off values) for the various properties [3]. Low biodegradability and a high bioaccumulation potential are considered to be particularly important. Other undesirable properties include toxicity to reproduction, mutagenicity, chronic toxicity, carcinogenic and sensitising properties and ozone-depleting potential. General limit values are set for bioaccumulation, degradability, and acute and chronic toxicity.

Environmental risk characterisation is based on a hazard and an exposure assessment. Conclusions from the assessments vary depending on whether national-, regional- or site-specific considerations are applied. The reasons for this are the different types of scenarios applied for products, emissions and exposure. Emission of phenols from everyday use of tyres is not considered to be a particularly large environmental risk.

An “endocrine disruptor” is a naturally occurring chemical or industrial chemical that can bind to a receptor and prevent normal response, interfere with or act like hormones in animals or people. Such interference may have negative effects on fertility, be mutagenic or have other negative chronic effects on recipient life. As part of several chemicals that are suspected to have such effects Norwegian authorities have focused on nonyl-, octylphenol, their ethoxylates and bisphenol-A [4]. Car tyres (and shredded car tyres) contain phenols for anti-aging purpose.

BACKGROUND

Norwegian Roads Recycled Materials R&D Program [5] is set out to test different possible sustainable applications for shredded tyres. The program focuses on suitable technical application, efficient production line and long-term environmental effects. Shredded tyres have been used as a light fill material in a 450 m long noise barrier along highway E6 in the south Eastern part of Norway. Planning and building the barrier involved no major surprises compared to experiences from other projects [6-8]. The structure contains about 10 000 tons of tyre shreds and due to environmental concerns for a nearby lake the tyres are covered with a membrane. The long-term environmental effects are evaluated in the R&D program. The program also includes three other Norwegian pilot projects containing shredded tyres. This paper focuses on the ongoing monitoring program, environmental authorities' concern for phenol compounds and summarises facts about their eco-toxicological properties and about antioxidants in tyre rubber. Results from three years of monitoring natural leaching from tyre shreds are compared with analysis from water sampled along highway E6, in a storm water basin along E6 and in its surface water recipient flowing from the nearby lake Vansjø.

LIGHT FILL NOISE BARRIER

“Huggenesvollen” noise barrier is situated along E6 highway in Rygge municipality South-Eastern Norway (Figure 1). The soil in the area mainly consists of marine clay and some fine sand. The ground under the 450 m long barrier consists of 2-3 m sand over a 10-15 m wide deposit of soft marine clay. The natural drainage is towards the sensitive recipient lake Vansjø. To protect this recipient, run-off from the tyre shreds was drained away from the lake.

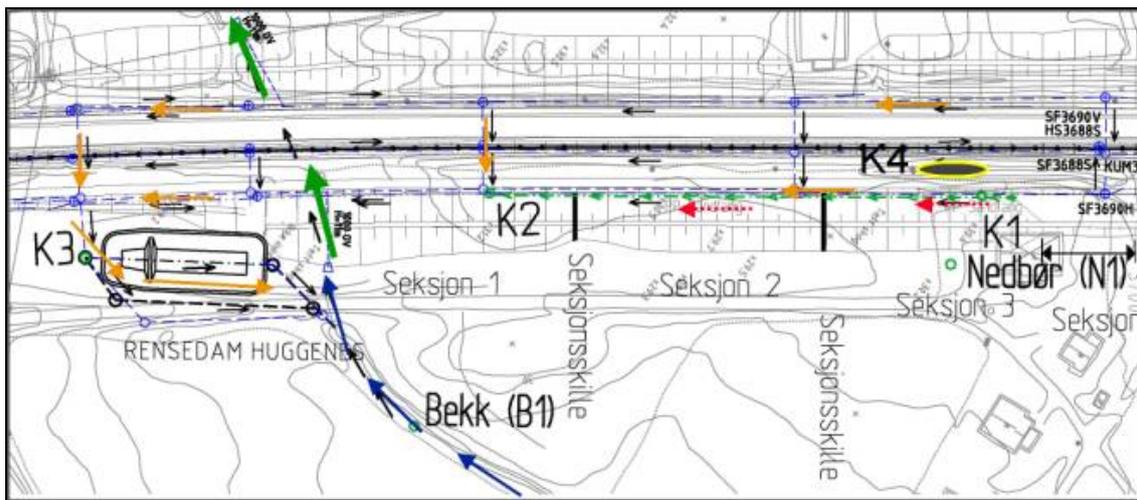


Figure 1. Samples are taken from the monitoring stations K1-3 and B1 over a five-year period starting 2003. The surface water samples are analysed for phenols, PAHs and metals. These stations document variations in runoff from shredded tyres, drainage and recipient not affected by surface water from the road. K4 has been used to sample runoff from the paved road. Arrows indicate the different directions of water flow. All of the water will mix with water from B1 in the end.

Run-off from surface water is gathered in the road drainage system, and is lead to a storm water basin that flows out into a small stream (B1, Figure 1). The core of the noise barrier is up to 5 m thick, and the barrier is built in several sections divided by 1-meter wide vertical layers of clay. The utilised fractions of shredded tyres are generally 5 – 30 cm, and the structure contains about 1 million tyres. In the construction process it was assumed that that shredded tyres can be compressed up to 15 %. The compression was performed by bulldozers and wheeled loaders.

Figure 2 shows a cross section at monitoring station K1 (section 3). In accordance with the demand from environmental authorities a needle punched bentonite membrane (Bentofix) was chosen to enclose the tyre shreds. This type of membrane was selected due to its physical properties (durability and self repairing properties) and easy installation. A 0.5 m thick layer of local soil was placed on top of the membrane (slope 1:1.5). Monitoring of surface water from four stations gives a five-year time line of chemical variations in water quality from shredded tyres (K1), from road water drain

(K2), from mixing at storm water basin (K3) and in water coming from the lake Vansjø (B1). Water from road pavement is periodically monitored at station K4.

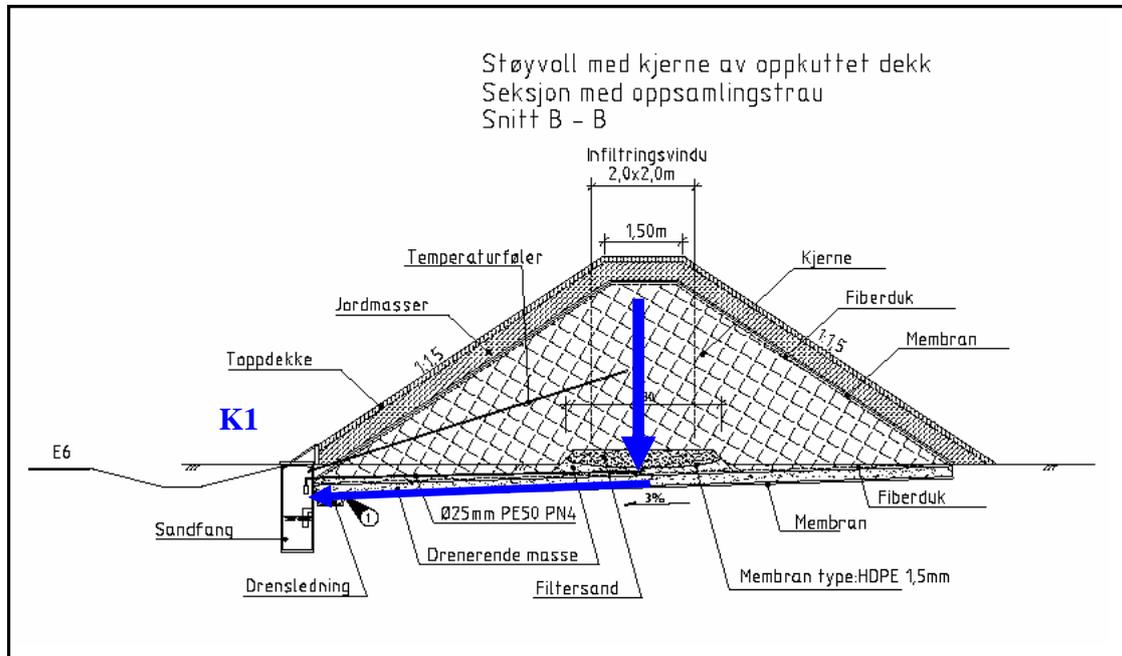


Figure 2. A cross section that shows light fill core of shredded tyres, collection of infiltrated water and tubes for monitoring temperature and setting. Infiltrated water is collected in 5 litre glass bottles.

ENVIRONMENT AND ANTIOXIDICING PHENOLS FROM TYRES

Antiaging agents include antioxidants and other antidegrading agents. Antioxidants are added to the rubber mixture in order to protect the rubber from degradation from oxygen, heat, UV-radiation and chemical oxidation from other chemicals, for example metals. No single antioxidant compound is effective against all of these degradation processes [9]. The primary antioxidants within the tyre materials consist mainly of secondary amines and substituted phenols. Most commonly used secondary amines is the p-phenylene diamines (PPD), because they also have other functions in the rubber matrix. The phenolic antioxidants are usually used in non-black compounds where the amine oxidants cannot be used because of discolourating reaction products. The most effective antioxidants are the hindered bisphenols [10].

Antidegradants are used as additives in the car tyre production with a mass contribution of respectively 1,5 % of the total car tyre. The most widely used antidegradant is *N*-(1,3 dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine (6-PPD) [11]. The antioxidant phenol is included in the mentioned 1,5% of the tyre weight but the average proportion between PPD and phenols has not been found.

Studies on phenols in tyre leachate have been performed by several authors through leaching tests in laboratories and in in situ monitoring programs from various engineering applications.

Håøya 2002 studied leaching of phenols according to CEN/TC 292 under neutral conditions. Table 1 shows leached amount at L/S 10 and the measured concentration in the eluate (tyre shred 5x5 cm).

Table 1. Phenols and total organic carbon (TOC) from leachate test at neutral pH at L/S 10 (CEN/TC292) from tyre shreds [12] (tyre shred 5x5 cm). Three parallel samples are tested

Compound	Range [mg/kg TS]	L/S10 Range [μ /l] ¹
4-tert-Octylphenol	0.002 – 0.05	2 – 5
Octylphenoletoxilates (1-10)	0.01 – 0.03	1.5 – 2.4
4-n-Nonylphenol	1.001×10^{-5} – 0.003	0.01 – 0.03
iso-nonylphenol (technical)	0.005 – 0.007	0.5
Nonylphenoletoxilates (1-10)	0.14 – 0.18	13.8 – 16.5
Bisphenol-F	0.007 - 0.03	2.2 - 2.5
Bisphenol-A	0.02 - 0.06	5.6 - 14.3
TOC	53 - 61	2900 - 6100

Table 2. Predicted no effect concentrations (PNEC) for fresh water, sediment and soil. Acceptable upper limit for 4 and 1 day average (once every 3 year on average) are listed for nonylphenol in freshwater and seawater.

Criteria/unit	Nonyl-phenol	Ref.	Octyl-phenol	Ref.	Bisphenol A	Ref.
PNEC _{f.water} μ g/l	0.33	[15]	0.122	[13]	1.6**	[16]
PNEC _{sedimen} μ g/kg wet weight	300	[15]	6.5	[13]	26	[16]
PNEC _{soil} mg/kg	0.039	[15]	5.9	[13]	23	[16]
4 day average * f.water μ g/l	<5.9	[14]				
1 hour average * f.water μ g/l	<27.9	[14]				
4 day average * saltwater μ g/l	<1.4	[14]				
1 hour average * saltwater μ g/l	<6.7	[14]				

* Once every 3 year on average

** Based on effects on the population as reproduction and mortality

Table 2 shows the predicted no effect concentrations (PNEC) for the selected phenols [13-16]. The values are collected from draft reports and are the best available knowledge for a safe environmental acceptance criterion. Compounds of phenol combine in the

natural environment until the particles are decomposed (half-life <1 year). Increased concentrations of the examined phenols in surface water (recipient) are not detected.

Bisphenol A is a solid at room temperature and will normally appear as flakes or powder. The substance is soluble in water with 300 mg/l at 20°C, and $\log K_{OW} = 3.4$. This value indicates a low to moderate potential for bioaccumulation in aquatic species, and a moderate adsorption in soil. Bisphenol A has low biodegradability combined with high acute toxicity. Aquatic toxic data are reported for fresh water and salt-water fish, invertebrates and algae. These data cover conventional consequences as reproduction and mortality, but also endocrine disrupting effects [16]. Investigations indicate that Bisphenol A acts as the hormone estrogen on fish. Acute aquatic toxicity range from 1-10 mg/l, and algae is the most sensitive specie.

The endocrine effects on aquatic invertebrates that are exposed for bisphenol A are for the time being not well understood [16]. It seems like endocrine-disrupting effects might be the most sensitive consequence. Still the PNEC values for bisphenol A are based on effects on the population, as for example reproduction and mortality. Recipients where sensitive species live should not have concentrations that exceed these PNEC values over longer periods of time.

Nonylphenol is a pale, very viscous liquid that has a weak phenolic smell and $\log K_{OW} = 3.8 - 4.77$. The substance is very dangerous for organisms that live in water, and can cause undesirable long-term effects in the water environment. Sediments or mud will easily adsorb it. Nonylphenol is bioaccumulated in organisms and can enter the aquatic environment directly as nonylphenol or as nonylphenoethoxilates. In the natural environment nonylphenoethoxilates rapidly break down to nonylphenol. Based on available data, nonylphenol is biodegradable and the speed of degradation is influenced by the adaptation of microorganisms. It has been demonstrated [14] that nonylphenol can be degraded by photochemical processes in 10 to 15 hrs (half-life) in bright summer sun when nonylphenol is near the water surface

Nonylphenol and its ethoxilates show estrogenic effect on fish. Most tests indicate that this effect will start at ca. 10 – 20 µg/l [15]. Nonylphenol is considered an endocrine disruptor chemical and induces production of vitellogenin in male rainbow trout. This is a process normally occurring in female fish in response to estrogenic hormones during the reproductive cycle. It also induces precocious development of ovaries and an intersex condition in some fish species [14].

Calculation of PNEC values has been based on both short term and long-term studies of nonylphenol and fish, aquatic invertebrates and algae. Nonylphenol is expected to adsorb easily by soil and sediments. Recipients where sensitive species live should not have concentrations that exceed these PNEC values over longer periods of time.

The US EPA water quality criteria for nonylphenol (draft) [14] state an upper limit for concentration that should not have unacceptable effects on fresh- or seawater organisms.

“1 and 4 day average more than once every three years on the average” values are listed in Table 2.

Octylphenol is a solid that is soluble in water with 19 mg/l at 22°C, and its log K_{OW} = 4.12. This log K_{OW} value indicates a moderate potential for bioaccumulation in aquatic flora and fauna. Available data indicate that octylphenol has a low solubility in water but will be absorbed by organic matter in soil, sediments and mud. Octylphenol seems to be degradable, even though the microorganisms might need some time to adapt. Both nonyl- and octylphenol are primarily found in sediments. Organisms that live in the sediments and organisms that live of these are vulnerable groups considering exposure to octylphenol.

Octylphenol is regarded acute toxic for aquatic organisms, and can cause long-term effects in the aquatic environment. It is also reported to have estrogenic effects. The safety factor that is used for octylphenol is 50 due to uncertainties concerning the sensitivity some invertebrates have shown. The safety factor for nonylphenol is 10. Recipients were sensitive species live should not have concentrations that over longer periods exceed these PNEC values.

ENVIRONMENTAL MONITORING – PHENOLS

Environmental monitoring of structures containing tyre shreds in Norway has been going on since 2001. The oldest structure that is part of this project is from 1991. Monitoring at “Huggenesvollen” started before the construction in 2002 and is now part of a five-year monitoring program [17]. Figure 3 summarises the results from the first series of sampling. Suggested environmental acceptance criteria (PNEC from Table 2) are for comparison shown by the first bar from the right, for all except for “other nonylphenols”. The first bar from the left shows concentration in water that infiltrated tyre shreds (K1, Figure 1 and Figure 2). Here 4-t-octylphenol slightly exceeds PNEC values. Along the highway, while snow was melting on icy ground and salty road, surface water was collected in the dyke at the side of the road (K4). Although there was only one water sample, these concentrations show the highest measured values for all monitored phenol compounds. Water quality in the storm water basin (K3) reflects the general runoff from the highway. Here no values exceed the PNEC values. Water coming from the lake Vansjo (B1) does not exceed PNEC, but both octyl- and bisphenol A were detected. Surrounding land is used for agricultural purposes..

Three years of leaching from tyre shreds is documented at the Solgard project (Figure 4) [18]. The water at Solgard was collected directly under the tyre shreds. Figure 4 shows that 4-n-nonyl-, 4-t-octyl- and bisphenol-A are comparable or below PNEC values (Figure 3). Increased concentration of octyl- and nonylphenol may be due to decomposing etoxilates.

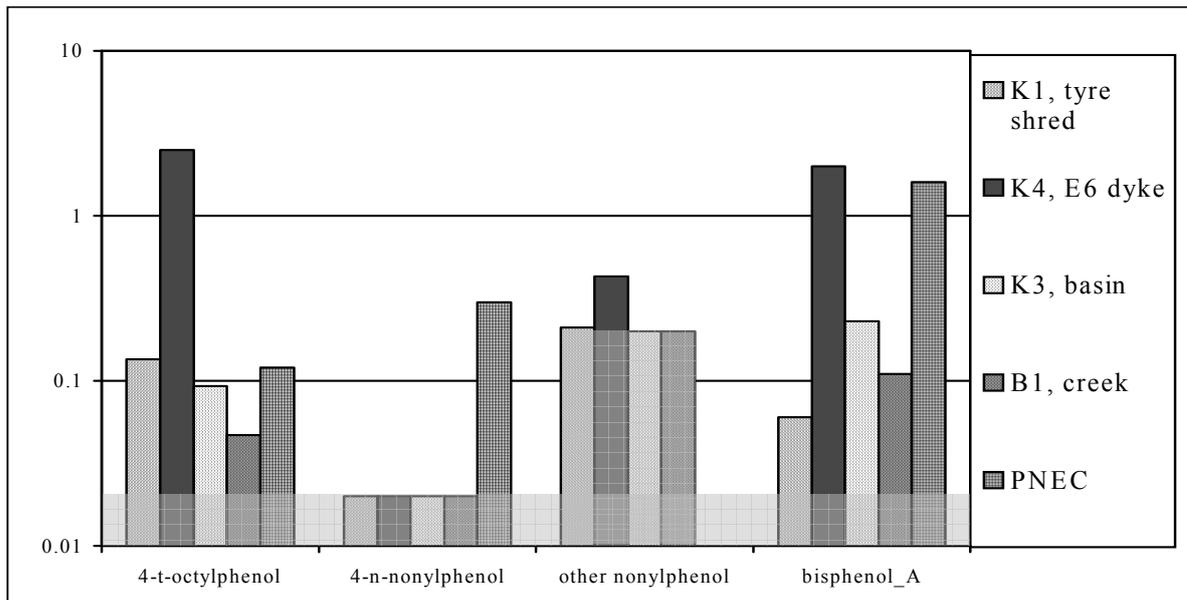


Figure 3. Phenol concentrations (log-scale) from monitoring stations (µg/l) at “Huggenesvollen” along highway E6. Values represent leaching the first 6-month period. Predicted no effect concentrations (PNEC) are here suggested as environmental acceptance criteria. Detection limits are overlaying in grey. “Other nonylphenols” may use PNEC for 4-n-nonylphenol. Collection system consists of HDPE-membrane, PE-tube and glass bottle.

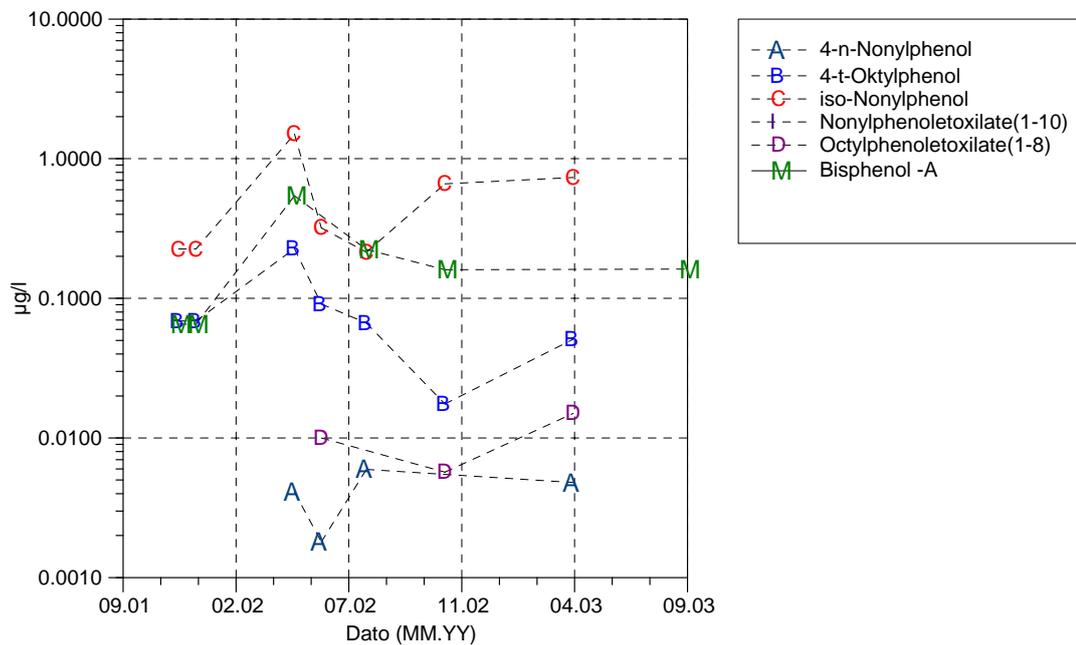


Figure 4. Monitoring station at Solgard production area Moss municipality. Concentration represents variations in the period 2001-03. Samples represent water that has infiltrated crushed rock (1m) and shredded tyre (1.5 meter). Water is collected in lysimeter 5x5 meter similar to Figure 2 [18]. Analyses below detection limit are left out (total of 7 samples). The collection system consists of PVC-membrane, PE-tube and glass bottle.

DISCUSSION

Norwegian Roads Recycled Materials R&D Program is in a dialog with Norwegian Pollution Control Authority to find a sustainable solution for application of tyre shreds in light fill road structures. The R&D Program has adapted the European standard for characterisation of waste and the Norwegian guidelines for environmental risk assessment [19] to a method for evaluating long term environmental risks from recycled materials in a road structure [20].

Leaching tests have been performed by Zelibor 1991 [21], O'Shaughnessy 2000 [22] and Håøya 2002 [12] among others. Zelibor and O'Shaughnessy state that concentration of phenols in leachate ranges from <1-50µg/l. Results from Table 1 are in the same range, but field samples are generally <1 µg/l (Figure 3 and Figure 4).

Table 3. Generalised phenol and etoxilate concentrations in laboratory L/S10 eluate and field leachate

Compound	L/S10 Range [µ/l]	Field leach. [µ/l]	PNEC -f.water [µg/l]
4-tert-Octylphenol	≈ 1	≈ 0.1	0.12
Octylphenoletoxilates (1-10)	≈ 1	≈ 0.01	-
4-n-Nonylphenol	≈ 0.01	< 0.01	0.33 - 6
iso-nonylphenol (other)	≈ 1	≈ 1	(0.33 – 6)
Nonylphenoletoxilates (1-10)	≈ 10	< 0.01	-
Bisphenol-A	≈ 10	≈ 0.1	1.6

Table 3 summarises temporary findings from laboratory and field measurements in the ongoing monitoring program. Field concentrations are by approximately 10 – 100 times smaller than laboratory concentrations. No change is found in the case of nonylphenols. Field concentrations are in a range that is acceptable when comparing to a conservative predicted no effect concentration.

CONCLUSION

The ongoing monitoring program and R&D on the application of shredded tyres indicate that leaching of mentioned phenols are at its max during the first year and are then reduced to levels that, when applied in a properly designed road structure, will be acceptable for sensitive recipients. Ongoing pilot projects indicate that leaching of nonyl, octyl- or bisphenol from tyre shreds induces no environmental risk if applied under given design conditions.

ACKNOWLEDGMENTS

The field measurements and the paper is a joint investment between the Norwegian Roads Recycled Materials and Ragn Sells which is contractor for collecting and processing of scrapped tyres.

REFERENCES

1. Miljøverndepartementet, *Report no. 8 to the Storting (1999-2000) - Summary in English*. 2000. <http://www.dep.no/md/engelsk/publ/stmeld/022051-040012/index-dok000-b-n-a.html>
2. Miljøverndepartementet, *Report to the Storting No. 58*. 1997. <http://www.dep.no/md/engelsk/publ/stmeld/022001-040002/index-dok000-b-n-a.html>
3. SFT, *Hazardous chemicals - Criteria for undesirable properties*, in *State of the Environment Norway (SOE)*, www.sft.no, Editor. 2004, Norwegian Pollution Control Authority: Oslo. http://www.environment.no/templates/PageWithRightListing_3257.aspx
4. SFT, *Few chemicals with endocrine effects in consumer products in Norway*, www.sft.no, Editor. 1996. <http://www.sft.no/publikasjoner/kjemikalier/1392/TA1392.html>
5. SVV, N.R.N., *National Roads Recycled Materials R&D Program*. 2004. www.gjenbruksprosjektet.net
6. ASTM, *Standard Practice for Use of Scrap Tires in Civil Engineering Applications*. American Society for Testing and Materials. 1998.
7. EPA, *Beneficial Use of Scrap Tires*. 2002, Division of Solid and Infectious Waste Management, Scrap Tire Unit.: State of Ohio. p. 2.
8. Nauska, J., J. Forsman, *Noise barrier made of shredded tyres, experiences in Finland.*, S.O.p.n. 110157A, Editor. 2002, SCC Viatek (Ramboll).
9. Hofmann, W., *Rubber Technology Handbook*. 1989, New York: Hanser Publishers.
10. Ciullo, P.A., N. Hewitt, N., *The Rubber Formula*. Noyes Publications, Norwich, New York. 1999.
11. BLIC, *Life cycle assessment on an average European car tyre.*, B. Bureau de Liaison des Industries du Caoutchouc (BLIC), Editor. 2001.
12. Håøya, A.O., *E6 Rygge Kommune - Miljørisikovurdering ved bruk av kvernet*, S. AS, Editor. 2002, Statens vegvesen, Vegdirektoratet.
13. Brooke, D., C Watts, R Mitchell & I Johnson, *ENVIRONMENTAL RISK ASSESSMENT REPORT: 4-TERT-OCTYLPHENOL (CAS NO: 140-66-9) DRAFT*, U.E. Agency, Editor. 2003, National Centre for Ecotoxicology and Hazardous Substances.
14. EPA, U.S.E.P.A., *AMBIENT AQUATIC LIFE WATER QUALITY CRITERIA FOR NONYLPHENOL - DRAFT*. 2003, U.S. ENVIRONMENTAL PROTECTION AGENCY, Office of Water. <http://www.epa.gov/waterscience/criteria/nonylphenol/draft-nonylphenol.pdf>
15. Union, E., *European Union Risk Assessment Report. 4-Nonylphenol (branched) and Nonylphenol*. 2001, National Centre for Ecotoxicology and Hazardous Substances (U.K.).
16. Union, E., *Risk Assessment of Bisphenol-A. Draft*. 2002, National Centre for Ecotoxicology and Hazardous Substances (U.K.).
17. Håøya, A.O., G.T. Unsgård, *Miljøovervåknig 2001-03 - Avrenning fra kvernet bildekk*. 2004, Scandiaconsult AS. www.gjenbruksprosjektet.net
18. Håøya, A.O., R. Olsson, S. Torsøe, *Civil Engineering Rubber. Pilotprosjekt: Solgård - Moss. Arbeidsbeskrivelse med foreløpige resultater*. 2002, Scandiaconsult AS for Ragn Sells.
19. SFT, *Risikovurdering av forurenset grunn.*, S. forurensningstilsyn, Editor. 1999. <http://www.sft.no/publikasjoner/kjemikalier/1629/ta1629.pdf>
20. Petkovic, G., C. Engelsens, A.O. Håøya, G. Breedveld, *Environmental impact from the use of recycled materials in road construction: Method for decision-making in Norway*. Resources, Conservation & Recycling, 2004 in press(RECYCL 1677). www.sciencedirect.com
21. Zelibor, J.L. *Leachate from Tire Samples, The RMA TCLP Assessment Project: Radian Report. Education Seminar on Scrap Tire Management, Scrap Tire*. in Management Council, Washington, D.C., September, pp. 381-391. 1991.
22. O'Shaughnessy, V., V.K Garga, *Tire-reinforced earthfill. Part 3: Environmental assessment*. 2000(Canadien Geotechnical Journal, Vol. 37, pp. 117-131).

Draft reports [13, 15, 16] are distributed by:

Environment Agency's Project Manager Steve Dungey. U.K. National Centre for Ecotoxicology and Hazardous Substances. Environment Agency. Chemicals Assessment Section. Isis House, Howbery Park, Wallingford. OX10 8BD, UK. Fax: +44 (0)1491 828556. <http://www.environment-agency.gov.uk/>