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Treatment of tunnel wash waters – experiments with organic sorbent materials. Part II: Removal of toxic metals

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Abstract

In the first part of the article, the column and the bag experiments concerning removal of polycyclic aromatic hydrocarbons (PAHs) and nonpolar oil (NPO) from tunnel wash waters using organic sorbent materials have been described. This part presents the results of removal of toxic metals. The metals of concern (Al, As, Cd, Cr, Cu, Fe, Pb, Mo, Ni, and Zn) were selected based on the priority toxicant pollutants defined in surface water quality criteria. Concentrations of these metals in the collected effluents varied more than the concentrations of PAHs and NPO, and thus only metal contents were considered for statistical analyses. These analyses determined significant differences ($P < 0.05$, $P < 0.01$, and $P < 0.001$) between the mean metal concentrations in the column effluents and those in applied wash water of road tunnel. The results obtained during both experiments revealed that the organic sorbents, and in particular their combination, removed toxic metals more effectively from wash water of road tunnel than from wash water of tunnel electrostatic filters. Among the investigated toxicants, Al and Fe showed the highest levels of reduction in the column experiment, 99.7% and 99.6%, respectively. The lowest reduction levels of 66.0% and 76.2% were found for Pb and Mo, respectively. The results of the bag experiment showed that even one day treatment of wash waters from tunnel electrostatic filters could reduce concentration of some toxicants by more than 70% (Al and Fe) and 80% (Cu).

Key words: electrostatic filters; reduction level; sorbents; tunnel; toxic metals; treatment efficiency; wash water

Introduction

Washing procedures and their frequencies in tunnels depend mainly on types of tunnels and traffic volumes. In Norway, for instance, cleaning of road tunnels is done 2–12 times per year, with water consumption of 40–80 m^3/km of tunnel. In addition, electrostatic filters, for control of air pollution in long and heavily trafficked tunnels, require cleaning/maintenance services once a week, with use of water and soap up to 18 m^3. An application of soap detergents varies between 0.5% and 1% of total water use in road tunnel and electrostatic filters, respectively.

Wash waters from road tunnels and from tunnel electrostatic filters contain a complex mix of organic and inorganic pollutants (Roseth *et al*., 2003). These pollutants originate not only from vehicle-exhaust particles but also from traffic-related materials (brake and tire wear) and emission from asphalt, brake lining, and road paint (Adachi and Tainosho, 2004; Lough *et al*., 2005; Wang *et al*., 2005). Kocbach *et al*. (2006) characterized combustion particles from vehicle exhaust in motorway tunnel of Oslo (Norway) and found substantial amounts of road dust (mineral particles), most likely originating from road abrasion. The size and chemical compositions of combustion particles from vehicle exhaust, particles embedded in the road dust, and particles emitted from traffic-related materials are the main factors that contributed to the adverse health effects (Lin *et al*., 2005).

Studies carried out by Lough *et al*. (2005) showed considerable relation of high emission of traffic pollutants with the traffic volume and fraction of heavy tracks (diesel engines) as well as the relation of emission of noble metals with the presence of old vehicles in traffic stream. In this context, types of vehicle and engine should be considered, which is attributed to the fact that the concentrations of heavy, noble, and toxic metals, such as Ag, Ba, Cd, Pb, Sb, V, and Zn, in nanoparticles can be associated with diesel, whereas contents of Cu, Mn, and Sr in ultrafine particles can be linked to gasoline engine emissions (Chellam *et al.*, 2005; Lin *et al*., 2005).

Most of the pollution components in tunnel wash waters are attached to particles, for instance debris from tire wear make up about one-third of the vehicle-derived particulates in highway runoff (Councell *et al*., 2004), and thus can be easily removed in sedimentation tanks or ponds. However, some pollutants can still pass through the sedimentation traps (Farm, 2002; Lundberg *et al*., 1999), and some of these, e.g., bioavailable components, even in small concentrations, can potentially cause toxic effects

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on aquatic fauna and flora (Boxall and Maltby, 1995). Therefore, the efficient treatment of tunnel wash waters is not only necessary but is also required, due to the fact that the concentrations of toxic metals in surface waters are restricted by standards, guidelines, and criteria established for surface water quality and the protection of aquatic life in freshwater (Alberta Environment, 1999; European Commission, 2006; USEPA, 2006).

1 Materials and methods

Two laboratory experiments were conducted in columns and bags filled in with four organic sorbent materials. The sorbents were characterized by: A (peat-based material), Po (organic material adsorbing oil contaminants), Pm (mixture of organic materials adsorbing oil and metal contaminants), M (wet bark adsorbing metal contaminants), and Po-M (combination of two organic materials Po and M). The column experiment was allowed to run for one month and the focus was mainly on the efficiency of treatment of wash water from roof, walls, and road surface of motorway tunnel, whereas the bag experiment was established for one day to determine the efficiency of filtration bags treating wash water from electrostatic filters of road tunnel. More samples and results were collected from the column experiment and thus more data for statistical analyses were available. These analyses were performed using a *t*-test for independent samples. The *t*-test determined significant differences (and identified significance levels $P < 0.05$, $P < 0.01$, and $P < 0.001$) between the mean concentrations of toxic metals in the effluents from the columns and those in applied wash water of road tunnel.

1.1 Methods

Ten toxic metals (Al, As, Cd, Cr, Cu, Fe, Pb, Mo, Ni, and Zn), related to the European, American, and Canadian criteria for priority toxic pollutants in surface waters (Alberta Environment, 1999; European Commission, 2006; USEPA, 2006), were measured in the samples of tunnel wash waters and in the effluents collected from the columns and the bags. Concentrations of these toxicants were determined with ICP-MS (Thermo Finnigan Element 2, Waltham, USA) and ICP-AES (Optima 3000 DV, Perkin-Elmer, USA), after filtration on a 0.45-μm filter.

2 Results and discussion

2.1 Column experiment

Extreme concentrations of toxic metals in the effluents from the columns filled in with the organic sorbents (A, Pm, Po, M, and Po-M) were compared with the respective concentrations in both background samples, i.e., the effluents from the empty column (E) and wash water of road tunnel (TW) (Table 1). However, two elements (As and Cd) were not considered for comparison, due to both of them in all tested TW had concentrations below their limits of quantitation (LOQ), 25.0 and 1.2 μg/L, respectively.

The measured concentrations of toxic metals (presented in Table 1) revealed that TW contained most of these elements (except Mo) at the levels exceeding their limited concentrations defined by standards for surface water quality and the protection of aquatic life (Alberta Environment, 1999; European Commission, 2006; USEPA, 2006). From the group of considered toxic metals, six parameters (Pb, Cr, Cu, Zn, Al, and Fe) had higher values than guidelines established by the Canadian Council of Ministers of the Environment (CCME) for the protection of aquatic life in freshwater (Alberta Environment, 1999). Within this group, five elements (Cr, Cu, Zn, Al, and Fe) were found with concentrations above their maximum levels described in the USEPA (2006). In addition, two elements (Ni and Pb) had higher contents than their limited values classified by the European Commission (2006) in the Environmental Quality Standards (EQS) for priority substances in inland and other surface waters.

The results of the treatment of TW by the organic sorbent materials revealed high reduction levels of toxic metals (Table 1). The highest reductions were achieved for Zn, Fe, and Al in the effluent from the column filled in with the sorbent combination Po-M. By these reductions, minimum concentrations of Zn, Fe, and Al in Po-M effluent were below their limited criteria established for water quality guidelines in Canada and in the USA

Table 1 Extreme concentrations and maximal reductions of toxic metals in the background samples (TW and E) and the effluents from the columns filled in with organic sorbent media (A, Pm, Po, M, and Po-M)

Element	Concentration (min (max)) (μg/L)							Reduction (%)
	TW	E	A	Pm	Po	M	Po-M	
Ni	< 6.0 (52.5)	< 6.0 (19.7)	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0	88.6*
Pb	< 18.0 (53.0)	< 18.0	< 18.0	< 18.0	< 18.0	< 18.0	< 18.0	66.0*
Mo	15.4 (21.0)	14.5 (18.4)	< 5.0 (21.6)	8.6 (16.2)	5.4 (16.7)	< 5.0 (7.3)	< 5.0 (11.4)	76.2*
Cr	4.0 (107.0)	3.7 (9.4)	< 2.5 (4.3)	< 2.5 (5.6)	2.6 (5.1)	< 2.5 (4.7)	< 2.5 (4.1)	97.7 *
Cu	11.1 (177.0)	< 4.0 (25.6)	< 4.0 (21.5)	< 4.0 (24.1)	< 4.0 (25.5)	5.5 (29.0)	< 4.0 (23.6)	97.7 *
Zn	105.0 (1,560.0)	80.5 (194.0)	30.1 (171.0)	18.4 (555.0)	44.2 (1,770.0)	47.4 (197.0)	17.6 (185.0)	98.8
Al	467.0 (26,100.0)	473.0 (2,490.0)	173.0 (707.0)	108.0 (602.0)	187.0 (888.0)	206.0 (1,030.0)	74.0 (643.0)	99.7
Fe	2,590.0 (26,800.0)	2,800.0 (3,900.0)	449.0 (1,540.0)	359.0 (3,360.0)	574.0 (1,790.0)	187.0 (1,920.0)	104.0 (1,060.0)	99.6

* Maximal reduction calculated with respect to limits of quantitation (LOQ). TW: wash water of road tunnel; E: the effluents from the empty column; A: peat-based material; Po: organic material adsorbing oil contaminants; Pm: mixture of organic materials adsorbing oil and metal contaminants; M: wet bark adsorbing metal contaminants; Po-M: combination of two organic materials Po and M.

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(Alberta Environment, 1999; USEPA, 2006). In addition, all minimum concentrations of these metals in the effluents from other sorbents were also lower than their guideline values defined by the American Criteria (USEPA, 2006). Contents of two other metal elements, Cr and Cu, were both effectively reduced (97.7%) in the effluents (Table 1). The ranges of Cr concentrations in the effluents from all sorbents did not exceed the Canadian and the American guidelines.

In the case of Cu concentrations, only minimums were below the limited values in freshwaters recommended by the Canadian and the American criteria (Alberta Environment, 1999; USEPA, 2006). The lowest reduction levels, among all measured toxic metals (Table 1) were found for Ni, Pb, and Mo. Nevertheless, concentrations of Ni and Pb in the effluents from all sorbents were below their LOQ. Contents of Mo in all effluents, the same as in TW, did not exceed the guideline concentration in surface waters. In some cases, maximum concentrations of Mo, Cu, and Zn in the effluents from the sorbents (except the combination Po-M) were higher than their maximums in TW and the effluents from E, which was found only at the very beginning of the experiment (initiate application of TW into the columns) and was identified as the effect of leaching out of these metals from the sorbents.

The range of the concentrations of toxic metals in TW was wide enough to influence their mean concentrations, which were higher than the mean contents of these toxicants in the effluents from all sorbents (Table 2). The differences, however, were only statistically significant ($P < 0.05$) between the mean concentrations of Mo in TW and in the effluents from Pm, Po, M, and Po-M. More statistically significant differences were found between the mean contents of toxicants in the effluents from the sorbents and in the background effluent from E. This was related to significantly lower ($P < 0.05$) mean concentrations of Cu, Zn, and Al, highly significantly lower ($P < 0.01$) mean concentration of Cr and extremely significantly lower ($P < 0.001$) mean concentrations of Mo and Fe in the effluents from the sorbents than those in the effluent from E (Table 2).

A comparison between the mean concentrations of toxic metals in the background samples and in the effluents from the sorbents revealed that the contents of Cr, Zn, Al, and Fe were the lowest in the effluents (with statistical significance) from the combination Po-M. In addition, only these effluents contained all measured metals at the minimum levels that corresponded to guidelines, standards, and criteria for toxic metals in surface waters (Alberta Environment, 1999; European Commission, 2006; USEPA, 2006). Thus, the sorbent combination was found to be an effective medium for the treatment of TW.

2.2 Bag experiment

Contents of toxic metals in the effluent from the bag filled in with the sorbent combination (BF) were compared with contents of these metals in both background samples, i.e. the effluents from the empty bag (EB) and wash water of tunnel electrostatic filters (WF) applied during the experiment (Table 3).

Two elements (As and Cd) were not considered for comparison, due to their concentration in tested WF and the effluent from EB and BF (the same as in TW and the effluent from the columns) were below their LOQ, 25.0 and 1.2 μg/L, respectively. The measured contents of other metals (except Mo) in WF and in both effluents exceeded concentrations of toxicants limited by guidelines, standards, and criteria for surface water quality and the protection of aquatic life (Alberta Environment, 1999; European Commission, 2006; USEPA, 2006). In this context, concentrations of six metals (Cr, Pb, Cu, Zn, Al, and Fe) were above their limits classified by the Canadian guidelines (Alberta Environment, 1999). Five metals (Cr, Cu, Zn, Al, and Fe) had higher concentrations than their maximum values recommended by the American criteria (USEPA, 2006). Contents of two metals (Ni and Pb) exceeded their toxicant levels defined by the European standards (European Commission, 2006).

Contents of toxic metals in the effluent from BF were, in

Table 3 Concentrations and reductions of toxic metals in WF, EB, and BF

Element	Concentration (μg/L)			Reduction (%)	
	WF	EB	BF	WF-EB	WF-BF
Mo	25.1	21.7	8.3	13.5	66.9
Cr	30.2	18.2	11.4	39.7	62.2
Ni	36.3	27.3	29.9	24.8	17.6
Pb	39.0	34.0	19.0	12.8	51.3
Cu	238.0	153.0	39.1	35.7	83.6
Zn	273.0	199.0	208.0	27.1	23.8
Al	4,060.0	2,490.0	1,200.0	38.7	70.4
Fe	6,760.0	4,500.0	1,760.0	33.4	73.9

WF: wash water of tunnel electrostatic filters; EB: the effluents from the empty bag; BF: the effluent from the bag filled in with the sorbent combination.

Table 2 Statistically significant differences between the mean concentrations of toxic metals in the background samples (TW and E) and the effluents from the columns filled in with the organic sorbent media (A, Pm, Po, M, and Po-M)

Element	Mean concentration (μg/L)						
	TW	A	Pm	Po	M	Po-M	E
Mo	18.9	15.9	*12.8*	*12.8*	***5.4***	***7.2***	16.4
Cr	38.8	3.1**	3.4*	3.3*	3.2*	2.8**	5.6
Cu	72.4	10.3	8.2*	12.1	14.1	8.8	17.9
Zn	661.3	83.5*	131.5	354.4	99.8	67.9*	158.2
Al	9,135.7	344.4*	220.1*	378.8*	431.1	204.3*	1,057.0
Fe	10,853.3	957.7***	1,370.6**	1,275.7***	905.4***	633.3***	3,263.3

* $P < 0.05$ (significant); ** $P < 0.01$ (highly significant); *** $P < 0.001$ (extremely significant); left side symbol: significant difference to TW; right side symbol: significant difference to E.

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general, lower than those in the effluent from EB (Table 3). There were, however, two metals (Ni and Zn) that leached out from the sorbent combination and thus had slightly higher concentrations. In these two cases, the reductions of Ni and Zn concentrations were relatively low in comparison with other metals. The highest reduction levels, achieved during the treatment of WF by the sorbents, were quite impressive, as for one day test, and reached 83.6% of Cu, 73.9% of Fe, and 70.4% of Al (Table 3).

3 Conclusions

The obtained results from the column experiment showed that the sorbent combination Po-M was the most suitable and efficient in the treatment of TW. The suitability could be attributed to the fact that none of the measured toxic metals leached out from the combination (as it was found for Mo, Cu, and Zn in the effluents from other sorbents). The treatment efficiency was generally evaluated based on the levels of concentrations and reductions of toxic metals. In this context, concentrations of four metals (Cr, Zn, Al, and Fe) in Po-M effluents were statistically significantly lower compared with the respective concentrations in the background samples (TW and E). Besides, the sorbent combination Po-M efficiently reduced the concentrations of all measured toxic metals to the values that were compliant with the European standards, the American criteria, and the Canadian guidelines for priority toxic pollutants in surface waters and for the protection of aquatic life in freshwater.

The bag experiment was perhaps too short to provide the efficient treatment for WF. However, the obtained results could give an overall idea about the application of the organic sorbents and the use of filtration bags for the treatment of this type of wash water. In this respect, it was found that BF reduced more effectively the concentrations of toxic metals (except Ni and Zn that leached out from the sorbents) compared with EB. The reduction levels were high and therefore also impressive, as for one day test.

Further investigations and detailed studies are required, because the wash water runoff from road tunnels represents a comprehensive spectrum of traffic pollution that can cause serious ecological problems. Hence, the treatment of tunnel wash waters is supposed to become a standard procedure, in particular, in mountainous countries with spectacular road network such as Norway, having approximately 800 km of tunnels.

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