Effect of laundry activities on in-stream concentrations of linear alkylbenzene sulfonate in a small rural South African river

A.K. Gordon, W.J. Muller, N. Gysman, S.J. Marshall, C.J. Sparham, S.M. O'Connor and M.J. Whelan

(A.K.Gordon is from the Unilever Centre for Environmental Water Quality, Institute for Water Research, Rhodes University, Grahamstown, 6140, South Africa)

Abstract

In many parts of the world clothes are washed near to or in rivers and streams. Little information is available on resulting concentrations of detergent ingredients or on any potential effects caused. In this study, the fate of a commonly used anionic surfactant, linear alkylbenzene sulphonate (LAS) was investigated in a reach of the Balfour River (Eastern Cape Province, South Africa) which was regularly used as a site for laundry activity. Samples of river water were collected upstream of the main washing site and at a number of locations downstream on several occasions in winter and summer. Sediment samples were also collected and analysed. In addition, a household survey was conducted to ascertain the amount of detergent used and the distribution of washing practices. The results of the survey suggested that the use of riverside locations for laundry activities was seasonal. Most washing tended to be done at home during the winter with riverside sites used more frequently during the summer months. The monitoring data showed that LAS concentrations in water were very variable. They were occasionally high in the immediate vicinity of the laundry site (up to 342 μ g L⁻¹) but were generally very low (< 11 μ g L⁻¹) at downstream monitoring stations, suggesting that LAS was rapidly dissipated by a combination of degradation, hydrodynamic dispersion and dilution. Concentrations in the immediate vicinity of the washing site were lower than expected on the basis of the household survey because most waste water was disposed of on the river bank rather than directly in the river. No ecological effects are expected from LAS emissions at this site.

1. Introduction

Large quantities of detergent ingredients enter the environment continuously in waste water streams or as a direct result of detergent product use in or near to surface water bodies. Consequently, the aquatic fate and effects of the most commonly used ingredients have been extensively studied. This is particularly the case for linear alkylbenzene sulfonate (LAS), the primary anionic surfactant used in laundry detergents worldwide (<u>HERA</u>, <u>2007</u>). Environmental risk assessments conducted for LAS in developed countries, where the majority of waste water is treated before it enters the natural environment, show that the risks are acceptable (i.e. that the predicted no-effect concentration (PNEC) is not likely to be exceeded by environmental concentrations of the chemical). Low LAS concentrations are attributed to high removal rates through precipitation, adsorption and biodegradation

(Fox et al., 2000), both within the sewer system (10–68% in the case of a Dutch investigation by <u>Matthijs et al.</u>, 1999) and within the waste water treatment works itself (between 70 and 99%)([McAvoy et al., 1993], [Feijtel et al., 1995], [Waters and Feijtel, 1995], [Holt et al., 1998], [McAvoy et al., 1998], [Matthijs et al., 1999] and [Holt et al., 2003]).

In urban areas of the developing world poor provision of waste water treatment means that municipal and household wastewater is discharged directly to receiving waters. For example, <u>Ding et al. (1999)</u> estimate that less than 5% of all municipal waste in Taiwan is treated by waste water treatment works, and in Brazil only 10% of the urban population have their sewage treated (<u>Eichhorn et al., 2002</u>). This means that surfactant concentrations are often high in urban water courses close to emission points, although there is evidence that concentrations decrease rapidly beyond the urban fringe (e.g. [McAvoy et al., 2003] and [Whelan et al., 2007]).

Far less is known about the fate of laundry detergents in rural areas of the developing world. In rural areas of South Africa, some homesteads and villages do not yet have piped water, necessitating the utilisation of nearby water resources. Consequently, laundry washing is sometimes undertaken alongside rural rivers, resulting in the potential for detergent ingredients to be introduced directly into the river. To date there have been no published studies reporting levels of LAS in rural South African rivers used for laundry washing. In this paper we estimate LAS concentrations in the Balfour River using information on laundry washing practices and detergent use of residents living alongside the river and compare these predictions with measured concentrations obtained from an intensive monitoring programme (water and sediment).

The aims of the study were (1) to ascertain whether in-stream LAS concentrations could be predicted from detergent consumption data obtained from households alongside the river and (2) to determine if in-stream LAS concentrations within a typical rural South Africa river pose a risk to the aquatic biota.

2. Methods

2.1. Study area

The Balfour River is a small tributary of the Kat River, situated within the Eastern Cape Province of South Africa (Fig. 1). The river is approximately 9 km long with a catchment area of 120 km² (Hosking and Du Preez, 2002) and a mean annual discharge of 329 L s^{-1} . The river morphology is typical of low order streams: the depth is generally shallow (ranging between about 0.2 m and 1 m in riffles and pools respectively) and the bed material is coarse (boulders, gravel and sand). Land use within the catchment has not been comprehensively assessed but broadly consists of limited subsistence livestock and subsistence agriculture. Land use in the headwaters of the catchment is dominated by a mixture of indigenous forest and commercial forestry. The Balfour village is the

only settlement situated alongside the Balfour River and is composed predominantly of residential buildings, although there are also a limited number of homesteads scattered throughout the catchment.



Fig. 1. Schematic map showing monitoring sites in the Balfour River, and the four sub-villages that comprise the Balfour Village.

A number of features made this an appropriate river for the study: no other land uses or activities to which LAS input to the river could be attributed, clearly identified washing sites, a suitable reference site upstream of

washing sites, potential downstream monitoring sites, and the presence of a gauging weir nearby, which records river discharge.

2.2. Water and sediment chemistry sampling

River water and sediment was sampled on an arbitrarily chosen Wednesday and Saturday in the winter and summer of 2004, and in the autumn of 2005 at six sites, one upstream and five downstream of identified washing sites along the Balfour River (Fig. 1). The objective was to sample when LAS input to the river was highest and lowest in order to determine the full range of potential concentrations in-stream. Wednesday and Saturday were chosen as suitable days for sampling after a preliminary investigation suggested more laundry washing occurred over the weekend and less in the middle of the week. On each sampling day, 1 L grab samples of river water were collected in pre-washed glass Schott bottles hourly between 8 am and 5 pm. In addition, three one-off sediment samples (approximately 120 g per sample) were collected in glass jars from each site.

The sample bottles and jars were pre-washed in 10% HCl, rinsed in deionised water and left to dry. Once dry they were rinsed with 50–100 mL methanol, and again rinsed in deionised water and dried. For sample preservation, 30 mL of 37–40% formaldehyde (i.e. 3% v/v formalin) was placed in the Schott bottles (e.g. <u>Eichhorn et al.</u>, <u>2002</u>). These were then sealed and packed for transport to the field. Sediment samples were obtained by taking three grab samples per site of in-stream river sediment to a depth of 5 cm. Excess water was allowed to drain out for 1 min. Sediment was transferred to the glass jars and preserved with 10% formalin (enough volume was added to immerse the sediment). Methanol-washed aluminium foil was placed over the mouth of the jar and then fastened with the lid in order to prevent sample contamination. After sampling, and while still in the field, samples were kept on ice. In the laboratory, water and sediment samples were kept at approximately 4 °C until transport in polystyrene boxes with dry ice to the Safety and Environmental Assurance Centre (SEAC), Unilever Colworth, United Kingdom, for analysis of LAS.

2.3. Extraction of water samples

Typically 500 mL of river water was mixed with 25 mL of methanol before loading onto a methanol-conditioned C_{18} 1 g / 6 mL Isolute solid phase cartridge (Kinesis, Bolnhurst, UK). After drying for 1 h under vacuum the solid phase cartridges were eluted with methanol (approximately 20 mL). The eluent was taken to dryness under nitrogen and resuspended in 1 mL of methanol.

2.4. Extraction of sediment samples

Overlying water was removed before oven drying at 80 °C for 16 h. The dry sediment (10 g, large stones and grit not included) was extracted by sonication with methanol at 50 °C in a Decon FS 200b Ultrasonic bath (240 V,

3 A, 50 Hz)(Decon Ultrasonics Ltd, Hove, Sussex, UK). Three 10 min extractions (50 mL and 2×40 mL) were carried out with the sediment separated from the extract by means of a centrifugation step. The combined extract was normally concentrated to 2 mL.

2.5. Liquid chromatography/mass spectrometry

Final extracts from the water and sediment samples were analysed using liquid chromatography/mass spectrometry as described in <u>Whelan et al. (2007)</u>. The detection limit of the method was typically 1 μ g L⁻¹ and 100 μ g kg⁻¹ for LAS in water and sediment respectively. Measured LAS concentrations were analysed using the STATISTICATM version 7 statistical package. The data were checked for normality and homogeneity of variance, and as a consequence then subjected to the nonparametric Kruskal–Wallis ANOVA (analysis of variance) and median test.

2.6. Obtaining data on laundry washing practices and detergent usage

Two types of interview methods were conducted in order to obtain data regarding the frequency, periodicity and location of laundry washing, and the type and quantity of laundry detergent used by rural villagers. The first method was an unstructured community workshop organised within the Balfour village, and the second method was a semi-structured interview of 40 targeted individual households within the village.

2.7. Calculating potential in-stream LAS concentrations

The potential in-stream LAS concentration was calculated from the detergent usage estimates, for risk assessment purposes. Although there were a number of laundry washing sites along the Balfour River, the predicted in-stream LAS concentrations were determined for the lowermost washing site (Fig. 1), assuming all washing occurred at this site. The predicted in-stream LAS concentrations (C_0 , mg L⁻¹) were calculated from:

$$C_0 = \frac{L_{\rm P}}{Q}$$

where Q is discharge (L s⁻¹) and L_P is average input of LAS to the river (mg s⁻¹), which in turn is determined by L_D (total LAS input, mg) over the period (P) in which laundry is typically performed (assumed to be 4 h):

$$L_{\rm p} = \frac{L_{\rm D}}{P \cdot 3600} \cdot F$$

(1)

2)

where *F* is the proportion of LAS used which actually enters the river. The input of LAS to the river during nearstream laundry washing (L_D) was estimated using detergent consumption data obtained from individual household interviews for the Balfour Village. The LAS component of the daily detergent input was calculated by determining the proportion of LAS in the various detergent products and the activity of the LAS used to manufacture these products. An initial assumption was made that 100% of the LAS component entered the river (i.e. F = 1). However, a significant fraction of laundry is washed on the river bank rather than in the river itself, so this assumption is very conservative. A lower estimate of F = 0.3 was considered to be more realistic, whilst still being conservative. An attempt was also made to estimate *F* by back calculating from the observed LAS concentration (C_{OBS} , $\mu g L^{-1}$) in the Balfour stream at site 2. Combining Eqs. (1) and (2) and rearranging we get:

$$F = \frac{C_{OBS} \cdot Q \cdot P \cdot 3600}{L_D}$$

3)

in which L_D is expressed in mg d⁻¹. River discharge data (from 1972 to 2005) were obtained from the Department of Water Affairs and Forestry, measured by the flow gauge weir Q9H019 situated within the Balfour River at 32°33′05″ S and 26°40′17″ E (Fig. 1). In order to reflect the seasonality in river discharge, mean monthly flow data were utilised to calculate seasonal in-stream LAS concentrations. LAS concentrations at downstream sites were not calculated because of the difficulties of defining the upstream boundary conditions (characterized by highly variable temporal loading) and subsequent advection, dispersion and degradation.

3. Results

3.1. LAS concentrations measured in the Balfour

Laboratory quality control analyses showed good average recoveries of LAS spiked at 10 μ g L⁻¹ in MilliQ Ultrapure water in the laboratory averaging 87% (n = 28). Average recovery for 10 μ g L⁻¹ LAS laboratory-spiked river water was 101% (n = 10). Average recoveries for laboratory-spiked river sediment at 1000 μ g kg⁻¹ and 200 μ g kg⁻¹ LAS averaged 92% and 88% respectively (n = 4 for both analyses). River water was also field-spiked as part of the quality control procedure in order to ensure adequate preservation. Spiked river water showed an average LAS recovery of 107% for a 1000 μ g L⁻¹ spike and 91% for a 10 μ g L⁻¹ LAS spike (n = 9 and n = 10 respectively).

Measured LAS concentrations organised by site, day of the week, time of sampling and season are summarised in <u>Fig. 2</u>. The change in average LAS concentration (all data) with distance downstream of the lowermost washing site is shown in <u>Fig. 3</u>. Although LAS was detected at the reference site (site 1), concentrations were consistently below 4 μ g L⁻¹ (<u>Fig. 2</u> and <u>Fig. 3</u>). At site 2, the first sampling site below the laundry washing sites, considerably higher concentrations of LAS were observed during summer, with a peak concentration of 342 μ g L⁻¹ measured

at 10 h00 on Saturday (Fig. 2C and D). LAS concentrations at sampling sites 3–6, further downstream, were much lower (Fig. 2E–L; Fig. 3), with the highest concentration measured being 11 µg L⁻¹ at site 3 on Saturday during summer at 16 h00 (Fig. 2E). The mean LAS concentration measured at site 2 was considerably higher, although not significantly different (Kruskal–Wallis; $p \ge 0.05$) from concentrations at sampling sites further downstream (Table 1). The lack of statistical significance in the differences between concentrations at the different downstream sites was largely a consequence of the range in concentrations measured. Measured instream LAS concentrations at all six sites were significantly higher on Saturday (particularly in summer) compared to Wednesday (Kruskal–Wallis; $p \le 0.05$). It was also evident that measured LAS concentrations were significantly higher during summer sampling compared to autumn and winter samplings (Kruskal–Wallis; $p \le 0.05$) (Table 1). At site 2 the highest concentrations of LAS were measured in the morning, although concentrations in summer did increase again in the late afternoon compared to concentrations measured at midday (Fig. 2C and D). At sampling sites further downstream there was no distinct pattern in terms of the timing of peak LAS concentrations (Fig. 2E–L).



Fig. 2. A–L. LAS measured at sampling sites 1–6 on a Saturday and Wednesday in winter, summer and autumn. Note: log *y*-axis in panels C and D.



Fig. 3. Average LAS concentrations in the Balfour River (all data). Error bars show the 95th and 5th percentile concentrations.

Table 1.

Variable	Mean LAS (μ g L ⁻¹)	Standard deviation	N
Site 1	2	1	28
Site 2	21	65	28
Site 3	3	2	27
Site 4	3	2	27
Site 5	3	2	27
Site 6	2	1	27
Saturday	8	38	86
Wednesday	2	3	78
Autumn	2	2	60
Winter	2	2	44
Summer	12	45	60

Mean LAS concentrations measured per site, day and season sampled.

The highest concentration of LAS measured in river sediment was $186 \ \mu g \ kg^{-1}$ at site 3 on Saturday during summer, with samples from remaining sites below the detection limit (100 $\ \mu g \ kg^{-1}$). Samples obtained four days later on Wednesday were all below the detection limit. During the winter sampling, elevated concentrations of LAS (between 101 and 176 $\ \mu g \ kg^{-1}$) were measured in sediment from sites 2 to 4 on Saturday and sites 2–5 on Wednesday. Samples from all sites on both Saturday and Wednesday in August were below the detection limit.

3.2. Balfour community profile

Twelve community representatives from various community structures (sub-village committees and street committees) attended the community workshop interview, providing information for the profile of Balfour Village. The Balfour Village consists of four sub-villages: Phase 4 (30 households); Mandela Park (164 households); Chris Hani (151 households) and Phola Park (113 households) (<u>Fig. 1</u>). Phase 4 is the only sub-village on the west bank of the Balfour River and has not been provided with communal taps. Mandela Park lies opposite Phase 4 and is supplied with a few communal taps. Chris Hani lies alongside the river to the south of Mandela Park and is also only supplied with a few communal taps. Residents of these three sub-villages are generally poorer than those from Phola Park and thus possess few rainwater tanks. Consequently they rely extensively on river water for consumption, cooking and laundry washing. In contrast, Phola Park is situated approximately 1 km from the river and has been provided with more communal taps than the other sub-villages. The taps also work more frequently than the other sub-villages, although residents do collect water from the river if necessary. Thus, it was decided to exclude the Phola Park from the individual household interviews when determining washing practices and in-stream LAS predictions and instead concentrate on the remaining sub-villages alongside the river.

3.3. Washing practices

Laundry washing is generally undertaken by respondents once (35%) or twice a week (43%), with 18% of respondents undertaking washing three times a week. More washing occurs over, and either side of the weekend (except on Sunday when no washing is undertaken). The most popular days are Saturday (27%), Monday (20%), Friday (19%) and Wednesday (16%). Duration of washing activity generally varies between 1 and 4 h and is usually undertaken in the morning. Monthly powdered laundry detergent usage per household was determined to be 1.5 kg. Taking into consideration the quantity of LAS in each detergent brand used, the activity of the LAS, and the number of households in the three villages alongside the Balfour River (345), the total monthly LAS consumption by the communities living alongside the Balfour was determined to be 58.6 kg. Differences in the quantity of laundry detergent used during different seasons were not determined.

The location of laundry washing varies seasonally. During summer, 25% of respondents undertake washing at the river, and 75% at home. During winter, however, only 8% of respondents wash at the river, and 92% wash at home. Consequently, there is potential for more LAS to enter the river during the summer months than the winter months.

When at the river, the fate of the discarded washing water is dependent on the position of the washing site. If the washing site is directly beside the river, the discarded wash liquor may enter the river when it is poured on the ground. However, if the washing site is positioned some way from the river (usually because there is no

comfortable place available beside the river), the discarded liquor often drains into the ground before reaching the river. If washing is undertaken at the homestead the wash liquor is discarded on (and usually infiltrates) the ground. All the above information and data were used in predicting potential in-stream LAS concentrations in the Balfour River.

3.4. Predicted in-stream LAS concentrations

Potential in-stream LAS concentrations at site 2 based on the washing practice survey, assuming F = 1 and F = 0.3, are shown in Fig. 4 for different days of the week and different months of the year. The predictions reflect the periodic nature of near-stream laundry practices and the seasonality of river flow (Fig. 5). The predicted peak concentrations varied from day to day depending on the number of washers using the river bank. The highest concentration each week was predicted to be on a Saturday reflecting the results of the laundry washing survey. In-stream LAS peak concentrations on other days of the week were predicted to be considerably lower. Potential in-stream LAS concentrations were predicted to be highest in July, August, and October. Even under the unrealistic assumption of F = 1 (i.e. all discarded laundry liquor is poured directly into the river) predicted peak LAS concentrations only exceed the LAS PNEC of 245 µg L⁻¹ proposed by Dyer et al. (2003) on certain days in July, August and October (Fig. 4B). Under the assumption of F = 0.3, predicted peak LAS concentrations never exceed the PNEC (Fig. 4B).



Fig. 4. Potential peak concentration of LAS expected within the Balfour River each day of each month assuming (A) 100% LAS input to the river (F = 1) and (B) 30% LAS input to the river (F = 0.3). Note: the predicted no-effect concentration (PNEC) for LAS was derived by Dyer et al. (2003).



Fig. 5. Average median monthly flow rates $(m^3 s^{-1})$ measured at the Balfour River Weir (April 1972–Aug 2005).

Values of *F* based on the observed concentration data at site 2 and corresponding load estimates for day of week and season (Eq. (3)) had a mean value of 0.11, a median of 0.018 and a 95th percentile value of 0.37. Overall, adopting a value for *F* of 0.3 is probably a reasonable worst case assumption for this site, although on one occasion at site 2 the peak measured concentration (at 342 μ g L⁻¹) exceeded the predicted concentration, suggesting that locally high concentrations are experienced intermittently.

4. Discussion and conclusions

The good LAS recoveries measured in field-spiked river water suggest that the methods used for sample preservation, storage and transportation to the United Kingdom were effective. Furthermore, the good LAS recovery rates observed for laboratory-spiked water and sediment samples indicate that the sample preparation and LAS analysis methods were of high standard.

Site 1 was chosen as a reference site, with no apparent evidence of laundry washing occurring along the banks upstream. No LAS was measured within sediments at this site over the three seasons sampled. However, very low in-stream LAS concentrations were measured at this site, suggesting some washing activity upstream. Most of these concentrations were just above the detection limit and consequently the ecological impact of LAS at this site will be inconsequential because they are so far below the LAS PNEC.

The apparent variability of LAS concentrations observed in sediment suggests that LAS concentrations in sediment are transient, although high spatial variability could also be an important explanatory factor. The higher concentrations observed during winter could be related to the lower river flows experienced at this time, possibly resulting in increased particulate deposition (and a deposition of finer sediment size fractions) with associated sorbed-phase LAS. In contrast, the lack of LAS within sediment samples during summer (except for the one measurement of 186 μ g kg⁻¹ at site 3 on Saturday when there was unseasonably low flow) could be a result of higher flows within the river at this time of year resulting in higher rates of sediment entrainment and lower deposition rates. It is also possible that lower water temperatures in winter (average 13 °C) compared with summer (average 22 °C) reduce LAS degradation rates in sediment PNEC of 8100 μ g kg⁻¹ from available toxicity test data. This value is considerably higher than the LAS concentrations measured in Balfour River sediments, suggesting little anticipated effect on sediment dwelling organisms within this river.

The highest pelagic LAS concentrations were measured at site 2, the closest sampling site to areas where laundry washing took place. Considerably lower concentrations were measured at site 3, just 49 m downstream from site 2. This was most clearly seen on Saturday during the summer sampling when 342 μ g LAS L⁻¹ was measured at site 2, but only a maximum of 11 μ g L⁻¹ was measured at site 3. The pattern of LAS concentrations with distance downstream (Fig. 3) reflects an intermittent emission of wash water to the river (characterised by high concentration variability at site 2) followed by relatively rapid mixing and a high degree of hydrodynamic dispersion. Hydrodynamic dispersion is particularly important in "spill" scenarios (e.g. Gandolfi et al., 2001), where solute plumes will spread out relatively quickly, reducing peak solute concentrations significantly, even in the absence of loss mechanisms (such as sorption or degradation). In the case of LAS, degradation is likely to enhance the effects of dispersion in reducing concentrations and some LAS may also have been advected or diffused into the sediment. Fox et al. (2000) reported a first order rate constant of 0.3 h^{-1} for a stream in Yorkshire, UK with similar channel morphology to the Balfour River. This corresponds with a half life of about 2.3 h. The removal was attributed to primary biodegradation and the deposition of suspended matter onto which the LAS had adsorbed. Similar reductions in LAS with increasing distance downstream from a LAS input have been observed by McAvoy et al. (2003). Such rapid degradation would have a significant effect on concentration changes in the monitored reach. Other workers including Whelan et al. (1999); Eichhorn et al. (2002), and Whelan et al. (2007) have observed lower rate constants – probably because of deeper water and a lower contact with bed and bank sediments.

Significantly higher in-stream LAS concentrations were measured on Saturday compared to Wednesday. This was particularly evident during summer reflecting more laundry washing on Friday and Saturday compared to midweek. Higher in-stream LAS concentrations on Saturday corroborate information provided by residents of Balfour Village, which indicated that Saturday was the most preferable day to wash laundry. Predicted in-stream

LAS concentrations were based on the information from the washing practices survey and, hence, were also estimated to be highest on Saturdays.

The measured in-stream LAS concentrations were significantly higher during the summer sampling campaign compared to concentrations measured in autumn and winter. The higher concentrations on summer Saturdays can be attributed to a combination of high laundry activity and lower flows than expected for this time of the year. Although hydrological data (Fig. 5) from the gauging station on the Balfour River suggests that lowest flows normally occur during the winter months (June–September) and highest flows during the summer months (December–March), the daily flow rate measured on the Saturday sampled in summer 2004 was much lower (0.05 m³ s⁻¹) than would normally have been expected for that time of year (Table 2). A rain storm on the following Tuesday caused the higher flow of $0.72 \text{ m}^3 \text{ s}^{-1}$ measured on Wednesday. This flow rate was more reflective of the expected summer flow rates, and partially explains the much lower LAS concentrations measured on Wednesday. Flow rates measured during the winter 2004 and autumn 2005 sampling campaigns corresponded with the average median flows expected during this season (Table 2). Thus it appears that low flow conditions during winter are associated with lower in-stream LAS concentrations compared with similar flow conditions during the summer months (when they occur) because the potential for LAS input is much higher in summer.

Table 2.

Sampling season	Date	Flow rate $(m^3 s^{-1})$
Winter 2004	Saturday 31/7/2004	0.08
Winter 2004	Wednesday 4/8/2004	0.05
Summer 2004	Saturday 4/12/2004	0.05
Summer 2004	Wednesday 8/12/2004	0.72
Autumn 2005	Saturday 30/4/2005	0.23
Autumn 2005	Wednesday 4/5/2005	0.27

Average daily flow rates $(m^3 s^{-1})$ for river water sampling occasions.

In-stream LAS concentrations predicted from the washing surveys suggested that the winter and spring months were likely to result in the highest in-stream LAS concentrations due to the low flow at this time. However this was not reflected in the measured in-stream LAS concentrations. Possible explanations for this discrepancy are that a lower percentage of potential washers than determined from the survey (8%) may have actually washed clothing beside the river, or perhaps laundry washing was undertaken further from the river resulting in less discarded laundry liquor reaching the river in winter than initially assumed. Calculated values of the fraction of estimated LAS used which enters the Balfour River (F), based on the observed concentration data (Eq. (3)),

suggest that only a small fraction of laundry liquor (< 10%) is discarded close enough to the river to allow it to make a significant contribution to in-stream LAS concentrations.

Highest concentrations of LAS at site 2 were measured in the morning, with concentrations in summer increasing again in the late afternoon compared with concentrations measured at midday. The survey of Balfour residents revealed that laundry washing most often took place when climatic conditions beside the river were most comfortable. During summer, temperatures can be uncomfortably high, so the washing takes place during the early morning or may be left until late afternoon. Further downstream, there is no distinct temporal pattern for the highest measured LAS concentrations.

There are no South African water quality guidelines derived for LAS. However, the Australian and New Zealand Guidelines for fresh water quality (<u>ANZECC and ARMCANZ, 2000</u>) specify a value of 280 μ g L⁻¹ for fresh waters. This was derived based on international chronic toxicity data and the BurrliOZ statistical distribution with 95% species protection (PC95). This concentration is similar to the LAS no-observed-effect concentration of 268 μ g L⁻¹ derived by Belanger et al. (2002) using a comprehensive model stream ecosystem study with a range of aquatic invertebrates and the PNEC of 245 μ g L⁻¹ derived by Dyer et al. (2003) from a species sensitivity distribution. The peak LAS concentration of 342 μ g L⁻¹ measured at site 2 would have exceeded these effect thresholds, suggesting possible sublethal effects on resident aquatic organisms. However, the mean LAS concentration measured at site 2 was considerably lower at $21 \pm 65 \ \mu g \ L^{-1}$ (± standard deviation). Mean LAS concentration at sites further downstream ranged between 2 and 3 μ g L⁻¹, suggesting very limited risk to aquatic organisms. Consequently, it appears that higher LAS concentrations with the potential to cause sublethal ecological effects are likely to occur only very occasionally in parts of the Balfour River, close to laundry washing sites, for short periods of time and for a limited distance downstream. The assumption of 100% detergent discharge directly to the river resulted in a significant over-prediction of in-stream LAS concentrations based on detergent usage and washing practice information from nearby residents. The most likely explanation for this over-prediction is that a significant fraction of the laundry liquor discarded on the river bank infiltrates the soil rather than running into the river. At the Balfour River site, the transfer of LAS is estimated to be < 10% of the LAS used depending on the season.

Acknowledgements

We are grateful to the South African Department of Water Affairs and Forestry for supplying river discharge data, to staff and students of the Institute for Water Research for field assistance, and to Unilever for funding.

References

ANZECC and ARMCANZ (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand). National water quality management strategy, Australian and New Zealand Guidelines for fresh and marine water quality. Canberra, Australia; 2000.

Belanger SE, Bowling JW, Lee DM, LeBlanc EM, Kerr KM, McAvoy DC, et al. Integration of aquatic fate and ecological responses to linear alkyl benzene sulfonate (LAS) in model stream ecosystems. Ecotoxicol Environ Saf 2002;52:150–71.

DingWH, Tzing SH, Lo JH. Occurrence and concentrations of aromatic surfactants and their degradation products in river water of Taiwan. Chemosphere 1999;38:2597–606.

Dyer SD, Peng C, McAvoy DC, Fendinger NJ, Masscheleyn P, Castillo LV, et al. The influences of untreated wastewater to the aquatic communities in the Balatuin River, The Philippines. Chemosphere 2003;52:43–53.

Eichhorn P, Rodrigues SV, Baumann W, Knepper TP. Incomplete degradation of linear alkylbenzene sulfonate in Brazilian surface waters and pursuit of their polar metabolites in drinking waters. Sci Total Environ 2002;284:123–34

Feijtel TCJ, Matthijs E, Rottiers A, Rijs GBJ, Kiewiet A, De Nijs A. AIS/CESIO Environmental SurfactantMonitoring Programme. Part 1: LASmonitoring study in "deMeern" sewage treatment plant and receiving river "leidsche Rijn". Chemosphere 1995;30:1053–66.

Fox KK, Holt M, Daniel M, Buckland H, Guymer I. Removal of linear alkylbenzene sulfonate from a small Yorkshire stream. Sci Total Environ 2000;251:265–75.

Gandolfi C, Facchi A, Whelan MJ. On the relative role of hydrodynamic dispersion in river water quality and its implication for model calibration. Water Resour Res 2001;37:2365–75.

Hera (Health and Environmental Health Assessment Secretariat). Linear alkylbenzene sulfonate. Version 3. Belgium: Brussels; 2007. 81pp.

Holt MS, Fox KK, Burford M, Daniel M, Buckland H. UK monitoring study on the removal of linear alkylbenzene sulfonate in trickling filter type sewage treatment plants. Contribution to GREAT-ER project # 2. Sci Total Environ 1998;210/211:255–69.

Holt MS, Fox KK, Daniel M, Buckland H. Linear alkylbenzene sulfonate and boron monitoring in four catchments in the UK contribution to GREAT-ER # 11. Sci Total Environ 2003;314–316:271–88.

Hosking SG, Du Preez M. Valuing water gains in the Eastern Cape's Working for Water Programme. Water SA 2002;28:23–8.

Matthijs E, Holt MS, Kiewiet A, Rijs GBJ. Environmental monitoring for linear alkylbenzene sulfonate, alcohol ethoxylate, alcohol sulfate, and soap. Environ Toxicol Chem 1999;18:2634–44.

McAvoy DC, Eckhoff WS, Rapaport RA. Fate of linear alkylbenzene sulfonate in the environment. Environ Toxicol Chem 1993;12:977–87.

McAvoy DC, Dyer S, Fendiger NJ, Eckhoff WS, Lawrence DL, Begley WM. Removal of alcohol ethoxylates, alkyl ethoxylate sulfates, and linear alkylbenzene sulfonates in wastewater treatment. Environ Toxicol Chem 1998;17:1705–11.

McAvoy DC, Masscheleyn P, Peng C, Morrall SW, Casilla AB, Lim JMU, et al. Risk Assessment approach for untreated wastewater using the QUAL2E water quality model. Chemosphere 2003;52:55–66.

Waters J, Feijtel TCJ. AIS/CESIO Environmental Surfactant Monitoring Programme: outcome of five national pilot studies on linear alkylbenzene sulphonate (LAS). Chemosphere 1995;30:1939–56.

Whelan MJ, Gandolfi C, Bischetti GB. A simple stochastic model of point source solute transport in rivers based on gauging station data with implications for sampling requirements. Water Res 1999;33:3171–81.

Whelan MJ, Van Egmond R, Guymer I, Lacoursiere JO, Vought LMB, Finnegan C, et al. The behaviour of linear alkyl benzene sulphonate under direct discharge conditions in Vientiane, Lao PDR. Water Res 2007;41:4730–40.