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Comparisons of water quality parameters from diverse catchments during dry periods and following rain events

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ABSTRACT

In this study, 12 catchments sites located along the north coast of New South Wales in Australia were grouped into the four categories of septic, cattle, sewage treatment plant (STP) and forested sites via cluster analysis based on their land use patterns. Water samples from all these sites were collected between October 2004 and June 2006 at a regular monthly interval and within 48 h of rain events. The samples were analyzed for bacterial counts including faecal coliform and total coliform; faecal sterols including coprostanol, epicoprostanol, cholesterol, cholestanol, 24-ethylcoprostanol, campesterol, stigmasterol and β-sitosterol; and the elements including Na, Rb, Sr, Ag, Cd, Sn, Cs, Ba, Hg, Tl, Pb, Bi, U, Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, K, As, Se, P and Mo. Over the course of the sampling period, the STP site had the highest average coprostanol level of 1693 ± 567 ng/L which was significantly higher ($p < 0.05$) than the septic sites (190 ± 71 ng/L), the cattle sites (163 ± 94 ng/L) and forested sites (14 ± 4 ng/L). As expected, the forested sites had significantly lower average level of faecal coliforms (373 ± 87 cfu/100 mL) compared with the STP (1395 ± 574 cfu/100 mL), septic (1243 ± 494 cfu/100 mL) and cattle sites (535 ± 112 cfu/100 mL). The concentrations of coprostanol were not correlated with the numbers of faecal coliform bacteria when the entire data set was evaluated. The forested sites generally had the lowest average levels of elemental compositions, with significantly lower levels noted for Na, U, Mg, V, Cu, Sr, K, As, P and Mo, whereas Fe was the only element notably higher in the forested sites. Temporal and rain events analyses of the data set revealed that elevated levels of both coprostanol and faecal coliforms were not exclusive to rain events. The average coprostanol levels in rain event samples at each site were not significantly different compared with the corresponding dry event samples. Conversely, faecal coliform numbers increased by 2–4 times in rain events samples from septic, cattle and forested sites, but did not alter in the STP site. Multivariate analyses identified coprostanol and Sr as major contributing factors for the discrimination of septic, cattle, STP and forested sites for both rain and dry events samples. It was clear that each land use type of catchment could be characterized by biochemical, bacteriological and elemental parameters.

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1. Introduction

Faecal contamination of water catchments occurs from natural wildlife as well as from anthropogenic sources (Mudge and Duce, 2005). Excessive influx of faecal materials from anthropogenic sources and animal farms can pose major problems due to the potential adverse health impacts when the waters are to be used for potable, recreational and shellfish harvesting purposes (Reeves et al., 2004). Human contamination such as that derived from sewage treatment plant (STP) effluents can be regarded as a risk because of the sheer volume and the potential for entry of pathogenic organisms (Mudge et al., 1999). Faecal contamination from non-point agricultural pollution can also cause deterioration of water quality by emitting significant levels of faecal bacteria and nutrients to waterways (Gillingham and Thorrold, 2000; Ledgard et al., 1996; Monaghan et al., ~~2006~~; Scholefield et al., 1993). It is, therefore, of paramount interest to develop cost-efficient and effective means of monitoring key water quality parameters to optimize management processes with a view of maintaining adequate quality of the catchment waters. Faecal coliform and faecal sterols have been widely used for monitoring of faecal contamination in water catchments (Evenson and Strevett, 2006; Leeming et al., 1996).

Inorganic compounds in water catchments may originate from the local geology or material carried in by the tide and anthropogenic sources and they can reflect the local industrial or agricultural sources (Deely and Ferguson, 1994). The capacity for utilization of these elements by flora and fauna depends on their chemical speciation, which affects their uptake and potential toxicity. The presence of large quantities of nitrogenous and phosphorus compounds can represent excessive nutrient loading whereas some elements such as Na and K may have impact on osmoregulation of various microbes, plants and animals, whereas other metals may be directly toxic to a range of organisms. The heavy metals have the capacity to bioaccumulate in tissues and so can biomagnify in the food chain (Williams et al., 1994). It is therefore important to consider a broad range of parameters when characterizing catchment waters since these parameters link the survivability of organisms within food chains and the delivery of the final water quality characteristics.

Catchment waters represent a dynamic system of biological, chemical and physical parameters interacting with seasonal and daily weather variations and fluctuations in external loading, to yield a complex model of interactions (Dixon and Chiswell, 1996; Shrestha and Kazama, ~~2006~~). Given these considerations, it is unlikely that generalizations will be valid for all catchments waters within a region. The present study represents a selection of disparate Australian water catchments located along the north coast of New South Wales where there exists a high level of inter-annual variation in rainfall, which creates a regime of hydrologic extremes such as floods and droughts (Lake and Bond, ~~2006~~). Therefore, there exists a strong incentive to understand the catchment dynamics following rain events as well during dry periods in order to effectively comprehend water quality processes during these respective periods.

The applications of various statistical techniques such as chi-square analysis, correlations, one way analysis of variance (ANOVA), cluster analysis and discriminant analysis have helped in interpretation of complex data sets to better understand water quality by allowing the identification of major factors that influence catchments' water quality, which can further offer a valuable tool for reliable management of water systems with rapid solutions to pollution problems (Adams et al., 2001; Simeonov et al., 2004; Vega et al., 1998). In this study, a large data set was obtained from 12 different catchments sites during a 22-month monitoring program by collecting water samples for bacterial, faecal sterol and elemental analyses to address the following hypotheses:

(1) that the sites with different land use profiles would have characteristic water quality profiles reflecting land use and faecal contamination and
(2) that the samples from the various land use categories would have different water quality profiles in dry periods compared with samples taken immediately following rain events.

2. Methods

2.1. *Study areas*

Tilligerry Creek (1400 ha), Myall River (6943 ha), Manning River (735,000 ha), Morton's Creek (14,000 ha), Wallamba River (26,080 ha), Dingo Creek (55,200 ha), Coomba Park (7.6 ha), Michael Drive (90 ha), Sarah's Creek at Sarah's Crescent (2400 ha) and at Mile Road (2200 ha), Upper Wilson River (55,400 ha) and Frys Creek (1847 ha) catchments were selected within the regions located along the north coast of New South Wales in Australia on the basis of their potential land use impacts and their accessibility for routine sampling. Land use patterns of the first six catchments sites were dominated by agricultural activities (beef and dairy cattle), where animals generally outnumbered human beings and so represented the major potential source of faecal contamination in catchment waters. Coomba Park and Michael Drive were comparatively smaller urban catchments with unsewered houses and therefore represented potential contamination sources from the septic systems during periods of rain. Frys Creek was potentially impacted by STP effluent point located about 100 m upstream of the sampling location, surface run-off from a landfill located nearby and a golf course located further upstream. Sarah's Creek at Sarah's Crescent and at Mile Road and Upper Wilson River were forested catchments with virtually no human and/or agricultural activities. Water samples from the sampling locations of all of these catchment sites were collected at regular monthly intervals and within 48 h of rainfall events between October 2004 and June 2006. Water samples collected within 48 h following any rainfall events are termed as rain samples and others as dry samples in this study.

2.2. *Water analyses*

Water samples for faecal coliform and total coliform analyses were collected in 500 mL sterile bottles and were processed

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within 48 h of collection by using a membrane filtration technique as described by APHA (1998). Appropriate volumes of water samples were filtered using 0.7 μm pore size glass fibre filters (Pall, USA) and faecal sterols (coprostanol, epicoprostanol, cholestanol, cholesterol, 24-ethylcoprostanol, campesterol, stigmasterol and β-sitosterol) extraction from filters was achieved by the diethyl ether-based soxhlet protocol followed by gas chromatography–mass spectrometry (GC–MS) analyses of faecal sterols as described previously (Leeming et al., 1996; Shah et al., 2006). For elemental analyses, water samples were collected in 500 mL APTACA® polypropylene bottles (Livingstone International, Australia). The sampling bottles were soaked in alkaline detergent solution followed by 10% HNO_3 solution, washed with deionized water and dried at room temperature prior to sample collection. Water samples (1 mL) were filtered using 0.45 μm pore size Millipore MILLEX®-HV syringe-driven filter units and then acidified with 300 μL of HNO_3 (65% v/v, Suprapur®, Merck). Final volume of 10 mL was achieved by adding fresh Milli-Q deionized water (18 MΩ cm at 25 °C) to the acidified water samples and internal standard, indium was then added to give it a final concentration of 1 ppb. All standard solutions from 10 μg/mL multi-element inductively coupled plasma mass spectrometer (ICP-MS) standards were prepared in 2% HNO_3 (Suprapur®, Merck). All standard solutions and internal standard were purchased from Choice Analytical Pvt. Ltd., NSW, Australia. All measurements for Na, Rb, Sr, Ag, Cd, Sn, Cs, Ba, Hg, Tl, Pb, Bi, U, Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, K, As, Se, P and Mo were performed using a thermo electron element 2 high-resolution ICP-MS equipped with a CETAC ASX-500 auto sampler. Details of instrumental parameters and conditions of measurements have been described elsewhere (Paul et al., 2004). Duplicate and spiked samples were analyzed at a frequency of 10% for every sequence batch. These samples were selected randomly. Less than 10% of differences for elemental measurements were recorded for duplicates and their recoveries ranged from 90% to 100%. Aqueous standards prepared in HNO_3 (2% v/v) covering the concentration range of 0–10 μg/mL were used for external calibration. Six calibration standards were employed to generate the calibration lines with each giving correlation coefficient (R^2) of a least 0.999.

3. Statistical analysis

All data were assessed for normality and were log transformed as appropriate. Chi-square, ANOVA, Duncan's multiple range test, correlation, cluster analysis and discriminant analysis were performed as appropriate using Statistica version 6.1 (Statsoft).

4. Results and discussion

4.1. *Land use similarity and grouping of catchments sites*

Cluster analysis was used to assess similarities between the sampling sites based on their land use patterns as previously described by Shrestha and Kazama (2006). This yielded a dendogram, grouping the 12 catchments sites into four statistically different clusters as shown in Fig. 1. The cluster 1 (Tilligerry Creek, Myall River, Manning River, Morton's Creek, Wallamba River and Dingo Creek) comprised sites with predominant agriculture land uses including beef and dairy cattle and minimal anthropogenic contribution and other point sources of pollution. Cluster 2 (Sarah's Creek at Sarah's Crescent and at Mile Road, and Upper Wilson River) corresponded to forested catchments sites, which received vast majority of faecal influx from wildlife. Cluster 3 (Coomba Park and Michael Drive) received pollution mainly from onsite wastewater systems, whereas cluster 4 (Frys Creek) potentially received pollution from wastewater treatment plant effluent and a landfill located upstream of the sampling location. The cluster analysis results provided an objective basis for grouping the catchments sites into the four different land use categories as suggested by Shrestha and Kazama (2006), which were used for the subsequent investigations.

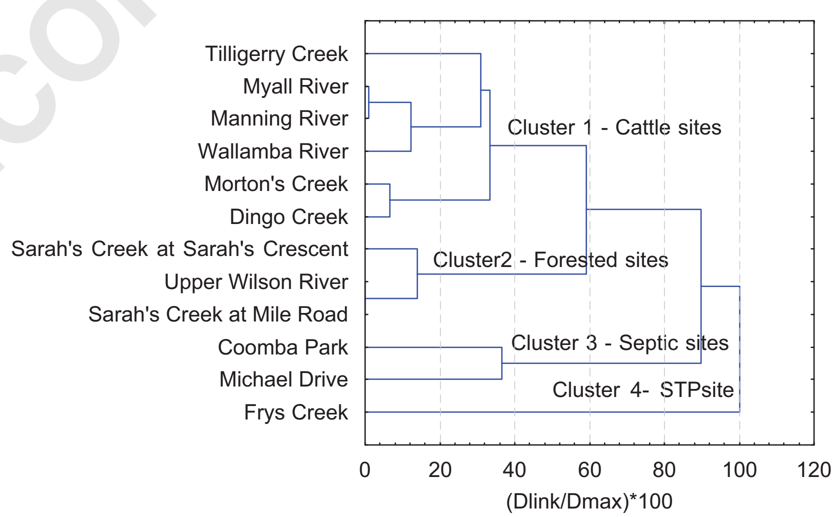

Fig. 1 – Dendogram showing four statistically different clusters of the 12 catchments sites based on their land use patterns.

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4.2. *Water quality parameters of all sites groups*

The samples from all sites throughout the entire 22-month sampling period were initially assessed by comparing the average values for each of the bacterial, faecal sterol and elemental parameters for each of the land use category groups, as summarized in Table 1. Fig. 2 shows the comparisons for coprostanol and faecal coliform counts with standard error and deviation levels. These data indicated that the variance can be quite high for certain parameters, particularly at the human impacted sites, but it was clear that the different land use sites could be differentiated on the basis of these water quality parameters. The average coprostanol level measured at the STP impacted site, 1693±567 ng/L, was significantly higher than all the other sites, including the septic impacted sites ($p<0.05$) and the forested sites had the lowest levels of this sterol. The cattle and septic impacted sites had statistically similar average levels of coprostanol. The STP and septic impacted sites had comparable average levels of faecal coliforms and together with cattle sites, were significantly higher in these counts compared with the forested sites. The forested sites generally had the lowest

Table 1 – Comparison of faecal sterols (ng/L) (average±standard error), coliform bacteria (cfu/100 mL) (average±standard error) and elemental compositions (ppb/ppm) (average±standard error) of the four primary catchments categories

Variable		All (rain+dry events) samples			
		Septic sites ($n=38$)	Cattle sites ($n=172$)	STP sites ($n=23$)	Forested sites ($n=63$)
Faecal sterols (ng/L)	Coprostanol	190 ± 71^{b}	163 ± 94^{a}	1693 ± 567^{c}	14 ± 4^{a}
	Epicoprostanol	15 ± 7^{a}	3.8 ± 0.88^{ab}	45 ± 11^{c}	0.99 ± 0.57^{b}
	Cholesterol	7110 ± 3648^{b}	551 ± 193^{a}	2810 ± 1138^{c}	670 ± 90^{a}
	Cholestanol	370 ± 152^{b}	39 ± 5^{a}	226 ± 53^{c}	36 ± 7^{a}
	24-Ethylcopro stanol	134 ± 56^{ab}	70 ± 13^{ac}	69 ± 13^{b}	29 ± 4^{c}
	Campesterol	395 ± 109^{a}	80 ± 10^{b}	190 ± 40^{a}	71 ± 9^{b}
	Stigmasterol	603 ± 153^{a}	187 ± 33^{b}	424 ± 113^{a}	280 ± 60^{b}
	Sitosterol	1696 ± 495^{a}	406 ± 49^{b}	866 ± 211^{a}	516 ± 66^{b}
cfu/100 mL	Faecal coliform	1243 ± 494^{a}	535 ± 112^{a}	1395 ± 574^{a}	373 ± 87^{b}
	Total coliform	188620 ± 175414^{a}	3154 ± 735^{b}	7779 ± 2543^{a}	1947 ± 469^{b}
Elements (ppb) (* denotes values in ppm)	Na*	501 ± 441^{ab}	223 ± 102^{bc}	145 ± 28^{a}	152 ± 50^{c}
	Rb	4 ± 2^{b}	5 ± 0.9^{b}	13 ± 2^{a}	3 ± 0.5^{b}
	Sr	291 ± 184^{a}	360 ± 53^{c}	86 ± 11^{a}	135 ± 41^{b}
	Ag	0.2 ± 0.2	0.3 ± 0.2	0.04 ± 0.01	0.02 ± 0.006
	Cd	0.03 ± 0.01	0.2 ± 0.1	0.02 ± 0.006	0.32 ± 0.29
	Sn	2 ± 2	5 ± 5	0.2 ± 0.09	0.1 ± 0.03
	Cs	0.06 ± 0.008	0.06 ± 0.012	0.08 ± 0.013	0.06 ± 0.012
	Ba	30 ± 3	21 ± 1	20 ± 2	29 ± 5
	Hg	7 ± 4	5 ± 1	6 ± 5	5 ± 2
	Tl	0.1 ± 0.09	0.1 ± 0.04	0.1 ± 0.07	0.1 ± 0.06
	Pb	12 ± 12	7 ± 3	0.4 ± 0.1	0.7 ± 0.2
	Bi	0.05 ± 0.02	0.1 ± 0.04	0.1 ± 0.05	0.07 ± 0.02
	U	0.3 ± 0.1^{a}	0.5 ± 0.4^{abc}	0.03 ± 0.008^{bc}	0.03 ± 0.006^{c}
	Mg*	28 ± 22^{b}	34 ± 8^{a}	7 ± 0.8^{b}	17 ± 5^{b}
	V	1 ± 0.2^{a}	0.6 ± 0.04^{b}	0.6 ± 0.06^{b}	0.9 ± 0.1^{b}
	Cr	1 ± 0.5	3 ± 1.2	0.6 ± 0.3	0.9 ± 0.1
	Mn	85 ± 46	50 ± 7	37 ± 9	120 ± 36
	Fe	711 ± 172^{b}	318 ± 30^{c}	149 ± 33^{a}	978 ± 230^{bc}
	Co	0.5 ± 0.1^{b}	0.3 ± 0.07^{a}	0.2 ± 0.04^{ab}	0.3 ± 0.09^{ab}
	Ni	1 ± 0.4	16 ± 10	1 ± 0.76	5 ± 3
	Cu	2 ± 0.6^{a}	0.9 ± 0.2^{b}	1 ± 0.5^{a}	0.6 ± 0.1^{b}
	Zn	27 ± 16	19 ± 4	8 ± 5	10 ± 3
	K*	10 ± 8^{b}	14 ± 3^{b}	13 ± 2^{a}	7 ± 2^{b}
	As	3 ± 0.9^{a}	1 ± 0.4^{b}	1 ± 0.3^{b}	1 ± 0.1^{b}
	Se	4 ± 1	8 ± 1	3 ± 1	5 ± 1
	P	479 ± 246^{b}	163 ± 112^{c}	$44\pm16b^{c}$	8 ± 4^{a}
	Mo	1 ± 0.2^{a}	1 ± 0.5^{ab}	0.5 ± 0.1^{ab}	0.09 ± 0.02^{b}

Differences between the septic, cattle, STP and forested sites groups for all samples were carried out with respect to enlisted variables using one way ANOVA. The significance level was taken at $p<0.05$. Different site groups identified as statistically different are denoted by different letters as determined by the pairwise Duncan's multiple range test.

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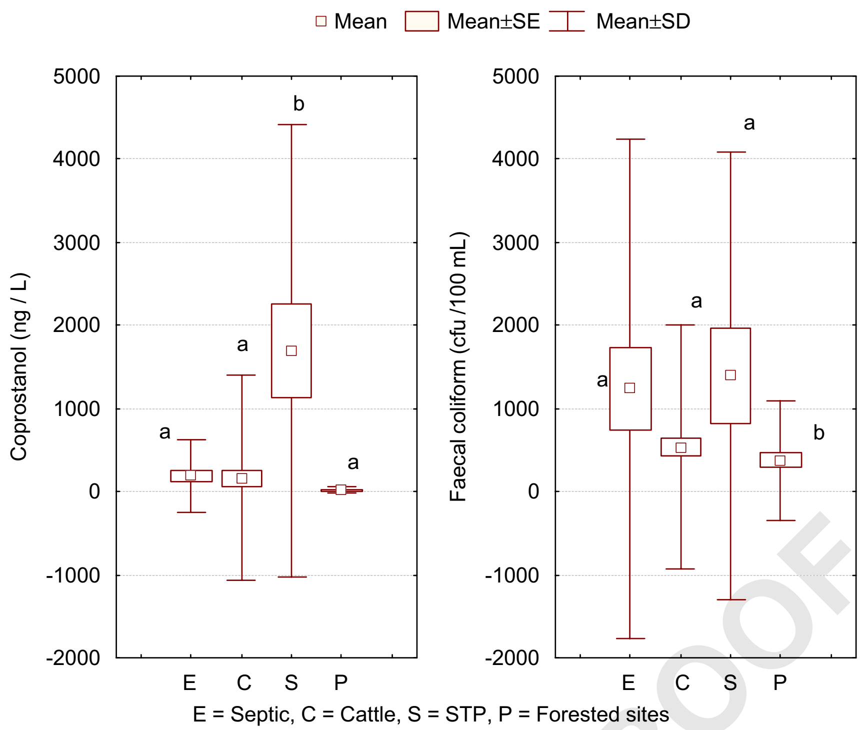

Fig. 2 – Coprostanol (ng/L) and faecal coliform (cfu/100 mL) levels in septic, cattle and STP impacted and forested sites. Sites significantly different with respect to coprostanol and faecal coliform are denoted by different letters as assessed by Duncan's multiple range test taken at $p<0.05$.

average levels of elemental compositions compared with other sites, with significantly lower levels noted for Na, U, Mg, V, Cu, Sr, K, As, P and Mo, whereas Fe was the only element notably higher in the forested sites. The significantly higher levels of phosphorus in the human and cattle impacted sites may be indicative of nutrient loading. It would appear from these data that higher levels of human impact were reflected by correspondingly high levels of coprostanol and faecal coliform counts, but cattle-impacted areas were also similar to these septic sites profiles. Regression analyses of coprostanol and faecal coliform data for the rain events samples of all the four sites groups showed very poor correlation between these parameters. There were no further correlations between these parameters for the dry event samples of the cattle and septic sites. There were, however, correlations between both these parameters in the dry events samples of the forested ($R^2 = 0.39$) and STP sites ($R^2 = 0.99$) which were significant at $p<0.05$. Both these factors from the entire data set including dry and rain event samples of all the sites groups showed no notable correlation between them ($R^2<0.001$).

Rain events have been shown to contribute substantially to bacterial loading and nutrient contamination by surface run-off contributions (Lin and Kao, 2003; Lipp et al., 2001). Therefore, a preliminary review of the rainfall, faecal coliform and coprostanol data for all sites and all events were assessed by comparing ranked rainfall data with overlying faecal coliform and coprostanol data as shown in Fig. 3. Examination of the bacterial numbers in relation to the ranked rainfall events revealed that there were numerous samples showing high numbers of faecal coliform when there were no rainfalls. This finding was consistent with Young and Thackston (1999) who observed high bacterial counts during both wet as well as dry weathers that caused violations of river water quality standards. The corollary is therefore that the monitoring should be performed on a regular basis at key sites for the purpose of managing bacterial loads (Long and Plummer, 2004). Out of 166 total rainfall events samples, there were 95 samples with faecal coliform numbers >150 cfu/100 mL, which was a significantly higher frequency compared with the 48 high count samples observed out of 170 total dry events samples ($p<0.05$). These bacterial levels represented the ANZECC guideline limit of 150 cfu/100 mL of faecal coliform for primary recreational contact limit (ANZECC, 2000). The results indicated that there was a higher chance of observing significant increase in faecal coliform counts in samples taken following rainfalls, but these loads were not limited to rain events alone. In contrast, an evaluation of coprostanol levels in relation to the ranked rainfall events revealed that there were very low levels of this sterol during dry periods (152 out of 282 samples) where the coprostanol range was 0–50 ng/L. The low-level rain events (0–5 mm) were associated with the release of some relatively high levels of coprostanol, but the higher rainfall events yielded only sporadic levels of the sterol. This might be explained by the build up of sterol material during dry periods, which could be released during the first rain events. However, it was deemed unlikely that these low levels of rainfall would contribute to surface run-off contributions and there may be other mechanisms operating which affect sampling levels, which have not yet been

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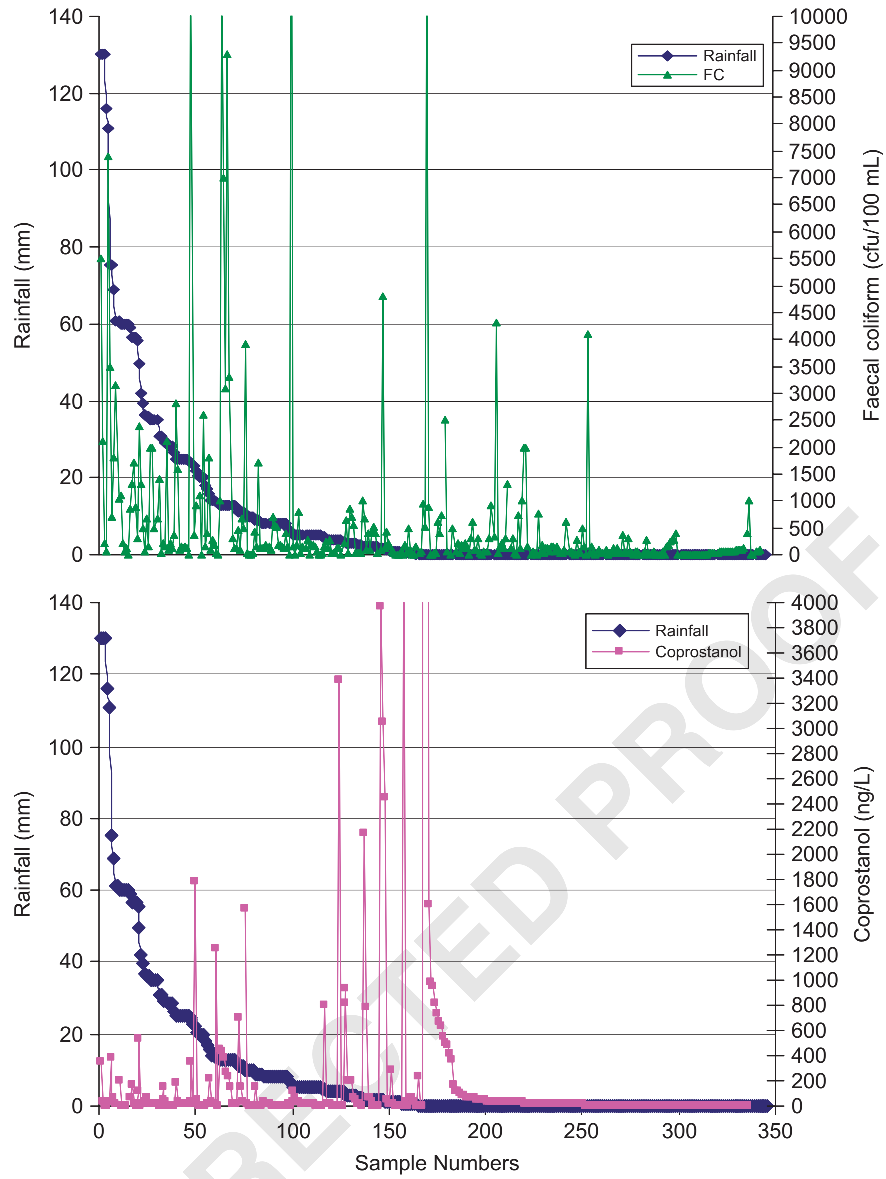

Fig. 3 – Rainfall, faecal coliform and coprostanol data for all catchments sites and all events. The data were assessed by comparing ranked rainfall data with overlying faecal coliform and coprostanol loadings.

identified. It was clear that coprostanol levels were not directly linked to the volume of rainfall deposition, although dilution by water volume may have an impact. This graph also provides a basis for dividing the samples for each site into rain and dry events samples for further investigation.

4.3. *Rain and dry events samples*

The samples from the various site categories were first divided into rain and dry events samples. The STP site notably had the highest coprostanol levels under both dry and wet conditions. However, there were no significant differences between the coprostanol concentrations in the septic and cattle-impacted sites in either wet or dry conditions. The mean faecal coliform numbers for all sites (including the forested sites), either following a rain event or during a dry period, were higher than the ANZECC (2000) guidelines limit of 150 cfu/100 mL. The highest faecal coliform counts were observed at either the STP and/or the septic sites. Even though high numbers of faecal coliforms were observed at the forested sites, the coprostanol levels were 1–2 orders of magnitude lower than the other sites. The septic sites contained significantly higher levels of most of the elemental compositions, whereas the STP site contained the highest levels of K and Rb and cattle sites had significantly higher levels of Sr than the forested sites in both dry and rain events samples. It was, therefore, concluded that the catchments types could be characterized by the profiles of faecal sterols,

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coliform bacteria and elemental parameters in either wet or dry conditions.

Analyses were then undertaken to compare the various parameters at each site under the rain and dry conditions. There were significant differences between rain and dry events samples of the cattle and forested sites with respect to faecal sterols, coliforms and several elements (see Table 2). Coprostanol concentrations along with total coliform numbers were significantly higher in dry events samples than rain events samples of the cattle sites. It was interesting to note that in the cattle sites dry events samples there was higher variance in both coprostanol and faecal coliform levels. Several elements were significantly higher in dry events samples of the cattle sites. While coprostanol concentrations were not significantly different between rain and dry events samples of the septic and forested sites, faecal coliform numbers were 2–3 times higher in rain events samples of both the sites. There were no significant differences between rain and dry events samples of the STP site with respect to any of the parameters.

Water quality parameters of rain and dry events samples were further evaluated through discriminant analysis. Discriminant analysis was separately performed on log-transformed data of rain and dry events samples after dividing the whole data set into the four sites groups of septic, cattle, STP and forested categories. Four discriminant analyses were performed using (i) all the variables (sterols, coliforms and elemental compositions), (ii) sterols and bacterial counts, (iii) sterols and (iv) elements, to differentiate between the various land uses sites under rain and dry conditions. The associated statistics, the primary variables contributing to the resolution and the post-hoc classification of samples have been summarized in Table 3. For rain samples, the standard discriminant analysis mode using all variables assigned overall 98% of the cases correctly into the four sites groups of septic, cattle, forested and STP, while using the sterols and coliforms, sterols alone and elemental compositions alone; the standard discriminant analysis yielded the corresponding classification matrices assigning overall 66%, 54% and 89% of the cases correctly into the four sites groups of septic, cattle, forested and STP (see Table 3). As shown in Table 3, the forward discriminant analysis results suggested that coprostanol, V and Sr were the three primary parameters to discriminate between the four sites groups, which also means that these parameters accounted for most of the expected sites differences in the rain events samples. It should be noted that coprostanol was also the most significant discriminant factor when sterols with coliforms and sterols alone were used as discriminant parameters by forward discriminant analysis mode. For dry events samples, the standard discriminant analysis using all the variables also gave excellent separation of cases from the four land use sites with 100% of the cases correctly classified by post-hoc analysis (see Table 3). As shown in Table 3, the forward discriminant analysis results indicated that coprostanol, sitosterol and Sr were the three primary parameters to discriminate between the four groups in the dry events samples. Therefore, under both wet and dry conditions, coprostanol was an important factor in differentiating between water qualities from the four different types of catchments. Canonical plots of rain and dry events samples as obtained by standard discriminant analysis using all variables are given in Fig. 4.

As shown in Table 3, dry events samples were more correctly assigned than rain events samples into the four sites groups, which could easily be explained by more fluctuation in rain events samples because of variability of different parameters discharging into waterways during rainfalls that may have deposited over the dry periods. Regardless of this, it is interesting that coprostanol and Sr were the major discriminant factors for both rain and dry events samples. In both rain and dry events samples, the use of all variables in the standard discriminant analysis yielded the best results for differentiating the sites and the elemental analyses yielded a better capacity for distinguishing the sites than the faecal sterol and bacterial factors. The elemental profiles would be expected to reflect inputs from local geology, wildlife, agriculture, weather patterns and other human activities. Since many of the sites within these groups represented different geographical locations, it was proposed that the elemental compositions were at least in part, reflective of land use activities. Coliforms were not highlighted as major discriminant factors when all variables were considered.

As identified by discriminant analysis, box and whisker plots of selected parameters showing their trends of rain and dry events samples in the four sites groups are given in Fig. 5. The average coprostanol concentrations were the highest in the STP and lowest in the forested sites in both rain and dry events samples. The septic sites contained higher average levels of coprostanol than the cattle sites in rain events samples, while the cattle sites had higher levels of coprostanol in dry samples. The average Sr levels were the highest in septic sites in rain samples, but they were the lowest in the septic sites in dry samples. In both rain and dry events samples, the cattle sites contained higher levels of Sr than the STP and forested sites. The STP site contained the lowest levels of Sr in rain events samples. While no parameters exhibited any significant correlation with coprostanol at $p<0.05$; campesterol ($R=0.47$), cholesterol ($R=0.75$), Na ($R=0.75$), Rb ($R=0.99$), Cd ($R=0.98$), Cs ($R=0.94$), Tl ($R=0.85$), Bi ($R=0.85$), U ($R=0.93$), Mg ($R=0.99$), Mn ($R=0.71$), Fe ($R=-0.39$), K ($R=0.98$), As ($R=0.78$), Se ($R=0.79$) and Mo ($R=0.80$) showed statistical correlations with Sr which were significant at $p<0.05$.

This demonstrated the significance of using discriminant analysis combined with box and whisker plots for the evaluation of temporal changes in the water quality. The discriminant analysis of temporal data allowed evaluation of the differences between different land use areas during dry periods and rain events and also identification of the parameters that had the main contribution to such differences; while box and whisker plots facilitated the graphical visualization of variation patterns. The analyses revealed the potential importance of elements in evaluating water quality parameters. Some of the elements identified as either significantly different between locations or during dry and wet periods, represented important nutrient growth factors such as Fe, K, P; while others represented potential heavy metal contaminants. Their origins may be reflective of anthropogenic sources and/or natural geological and nutri-

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Table 2 – Comparison of faecal sterols (ng/L) (average ± standard error), coliform bacteria (cfu/100 mL) (average ± standard error) and elemental compositions (ppb/ppm) (average ± standard error) of rain and dry events samples at each separate primary catchments category

Variable		Septic sites		Cattle sites		STP site		Forested sites	
		Dry samples ($n=18$)	Rain samples ($n=20$)	Dry samples ($n=89$)	Rain samples ($n=83$)	Dry samples ($n=8$)	Rain samples ($n=15$)	Dry samples ($n=32$)	Rain samples ($n=31$)
Faecal sterols (ng/L)	Coprostanol	175±67	203±124	203±177	119±43^{b}	2238±1521	1402±376	6±1	23±10
	Epicoprostanol	12±5	17±13	0.65±0.3	7±1^{b}	30±16	53±15	0	2±1^{b}
	Cholesterol	11209±7322	3421±2138	559±188	543±72	4510±3219	1904±433	681±132	659±123
	Cholestanol	307±121	427±272	25±6	54±9^{b}	222±106	229±62	42±14	29±5
	24-Ethylcoprostanol	99±30	166±104	20±3	123±27^{b}	67±33	70±12	28±7	31±6
	Campesterol	414±120	378±179	62±15	99±12^{b}	239±105	164±27	72±13	71±14
	Stigmasterol	720±236	499±203	164±57	211±33^{b}	377±140	449±160	332±112	226±39
	Sitosterol	2240±851	1207±546	276±42	545±90^{b}	1056±539	648±167	506±107	526±79
cfu/100 mL	Faecal coliform	488±267	1885±870^{b}	195±51	900±220^{b}	1788±1464	1170±409	245±90	506±150^{b}
	Total coliform	428482±413298	11880±4190	3518±1232	2758±753^{b}	8594±6680	7372±2144	2073±688	1799±636
Elements (ppb) (* denotes values in ppm)	Na*	72±12	885±836	166±41	285±210	152±59	142±33	132±48	172±90
	Rb	1±0.2	6±4	6±1	4±1	15±4	12±2	3±0.6	3±0.8
	Sr	86±14	466±339	483±88	219±48^{b}	97±24	79±11	133±55	136±62
	Ag	0.02±0.01	0.4±0.36	0.5±0.5	0.1±0.09	0.04±0.02	0.03±0.02	0.02±0.007	0.1±0.01
	Cd	0.02±0.007	0.05±0.02	0.3±0.2	0.01±0.006^{b}	0.02±0.01	0.02±0.008	0.6±0.6	0.02±0.009
	Sn	0.1±0.07	3±3	9±9	1±0.9	0.2±0.1	0.2±0.1	0.1±0.04	0.1±0.06
	Cs	0.04±0.007	0.07±0.01	0.08±0.02	0.05±0.01	0.08±0.02	0.09±0.01	0.07±0.01	0.06±0.02
	Ba	34±4	26±4	22±1	19±1	20±3	20±3	34±10	24±4
	Hg	0.8±0.1	13±7	5±2	5±2	1±0.6	10±9	10±5	1±0.1
	Tl	0.006±0.006	0.2±0.16	0.2±0.06	0.1±0.04	0.005±0.005	0.1±0.1	0.1±0.08	0.2±0.1
	Pb	0.9±0.31	23±22	8±5	6±6^{b}	0.7±0.3	0.3±0.1	0.4±0.1	1±0.3^{b}
	Bi	0.05±0.04	0.05±0.03	0.1±0.02	0.1±0.09	0.02±0.009	0.1±0.08	0.04±0.01	0.1±0.04
	U	0.2±0.05	0.5±0.2	1±0.8	0.1±0.04	0.03±0.007	0.4±0.01	0.03±0.006	0.04±0.01
	Mg*	5±0.6	48±43	49±13	17±6^{b}	7±2	6±1	17±8	16±8
	V	1±0.4	1±0.2	0.5±0.07	0.6±0.05	0.6±0.1	0.6±0.1	1±0.2	1±0.3
	Cr	2±1	0.5±0.1	3±2	3±1	0.7±0.5	0.6±0.5	1±0.3	0.6±0.2
	Mn	146±99	32±15	62±11	35±9^{b}	27±3	44±15	152±67	58±27
	Fe	572±80	828±313	311±42	326±44	139±48	155±46	842±143	1118±445
	Co	0.5±0.2	0.5±0.2	0.3±0.1	0.3±0.09	0.2±0.03	0.3±0.07	0.4±0.1	0.3±0.08
	Ni	2±0.8	0.6±0.3	21±19	10±4	1±0.8	1±1	8±6	1±0.8
	Cu	3±1	1±0.3	1±0.3	0.7±0.4^{b}	1±0.4	2±0.8	0.2±0.08	1±0.3
	Zn	51±34	7±5	32±8	4±2^{b}	14±13	6±5	10±5	9±5
	K*	2±0.6	18±15	17±4	10±5	17±3	11±2	8±3	6±3
	As	4±2	1±0.4	2±0.8	1±0.1	1±0.8	1±0.2	1±0.1	1±0.3
	Se	7±3	2±0.6	10±2	4±0.9^{b}	5±3	3±1	5±1	5±1
	P	873±444	30±8	241±209	74±23	13±6	63±26	3±1	15±9
	Mo	1±0.5	0.8±0.2	0.6±0.1	3±1	0.4±0.1	0.6±0.3	0.8±0.01	0.1±0.04

Differences between dry and rain events samples of the septic, cattle, STP and forested sites categories were carried out with respect to enlisted variables using one way ANOVA. The significance level was taken at $p<0.05$. Rain samples identified as statistically different to dry samples are denoted by ^{b}, as determined by the pairwise Duncan's multiple range test.

Table 3 – Statistical parameters of discriminant analysis

Discriminant analysis		Rain samples				Dry samples			
		All variables ($n = 102$)	Sterols+FC+TC ($n = 122$)	Sterols ($n = 133$)	Elements ($n = 118$)	All variables ($n = 88$)	Sterols+FC+TC ($n = 99$)	Sterols ($n = 109$)	Elements ($n = 130$)
Wilks' lambda		0.01	0.2	0.32	0.03	0.005	0.17	0.29	0.04
p		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
F		5.62	7.58	7.06	6.67	6.23	6.84	6.24	6.55
Three primary variables contributing to discrimination		coprostanol	coprostanol	coprostanol	Rb	coprostanol	sitosterol	cholestanol	Sr
		V	total coliform	24-ethylcoprostanol	U	sitosterol	coprostanol	coprostanol	Rb
		Sr	faecal coliform	sitosterol	Sr	Sr	epicoprostanol	epicoprostanol	Na
% observed correct classification	septic	100	53	12	85	100	63	50	81
	cattle	100	93	92	100	100	95	96	99
	STP	91	64	73	82	100	71	62	86
	forested	100	53	38	87	100	62	25	93
	overall	98	66	54	89	100	73	58	90

Discriminant analysis on rain and dry samples were carried out to characterize them into the septic, cattle, STP and forested sites using different sets of variables.

ent-cycling processes (Simeonov et al., 2003). These elements may exert significant impact on survivability of bacterial contaminants and members of the various aquatic ecosystems.

From the ongoing discussion, a valuable insight into the temporal variation patterns of several chemical, biochemical and bacterial parameters reflecting catchments water quality during dry periods and rainfalls was achieved. The interpretation of the compiled data showed importance of measurement of these water quality parameters during both dry and rain periods. It also portrayed dynamic nature of water catchments where various parameters were generally not exclusive to any areas or rainfalls. Thus, land-based sources are important contributors to pollution of catchments waters and seasonal changes can cause significant variations on water quality parameters. Therefore, there is a strong need for better control of management practices for mitigating land use impacts on the catchments waters. Furthermore, the impacts and effects of land use patterns and seasonal pollution on fauna, flora, humans and the receiving environment in general need to be carefully assessed for the use in the development of realistic control strategies (Kouassi et al., 1995). Further research leading into studying the survival and correlation patterns of key biomarkers like coprostanol and faecal coliform will be very useful for the management of catchments waters to monitor and measure faecal contamination as well as to characterize contributing sources of faecal contamination (Leeming and Nichols, 1996).

These results thus indicated that levels of bacterial, organic and inorganic components of aquatic ecosystems can occur under both wet and dry conditions and that different land use activities were associated with alterations in contamination profiles. Forested sites have bacterial and chemical loads representing nutrient cycling and wildlife contributions, which require better understanding for appropriate interpretation and management. It appears that human septic impacted sites were certainly characterized by periodically high levels of coprostanol and faecal coliforms, especially after rain events. However, this was not the case for the STP site investigated, which remained relatively stable in its contamination profile and seemed to actually improve in quality following rain. It was thus concluded that effective management of key aquatic systems would require systematic and extended monitoring to establish the water quality parameters relevant for that site and to determine reasonable operating levels for key indicators in the contexts of seasonal variations and influences of rainfall events in situ.

5. Conclusions

(1) The sites with different land use profiles had characteristic water quality profiles reflecting land use and faecal contamination. Average levels of coprostanol were the highest in the STP site and the lowest in the forested sites. Average faecal coliform numbers were lower in forested sites than human and agriculture impacted sites, but were still higher than regulatory acceptable limits for primary recreational contact.

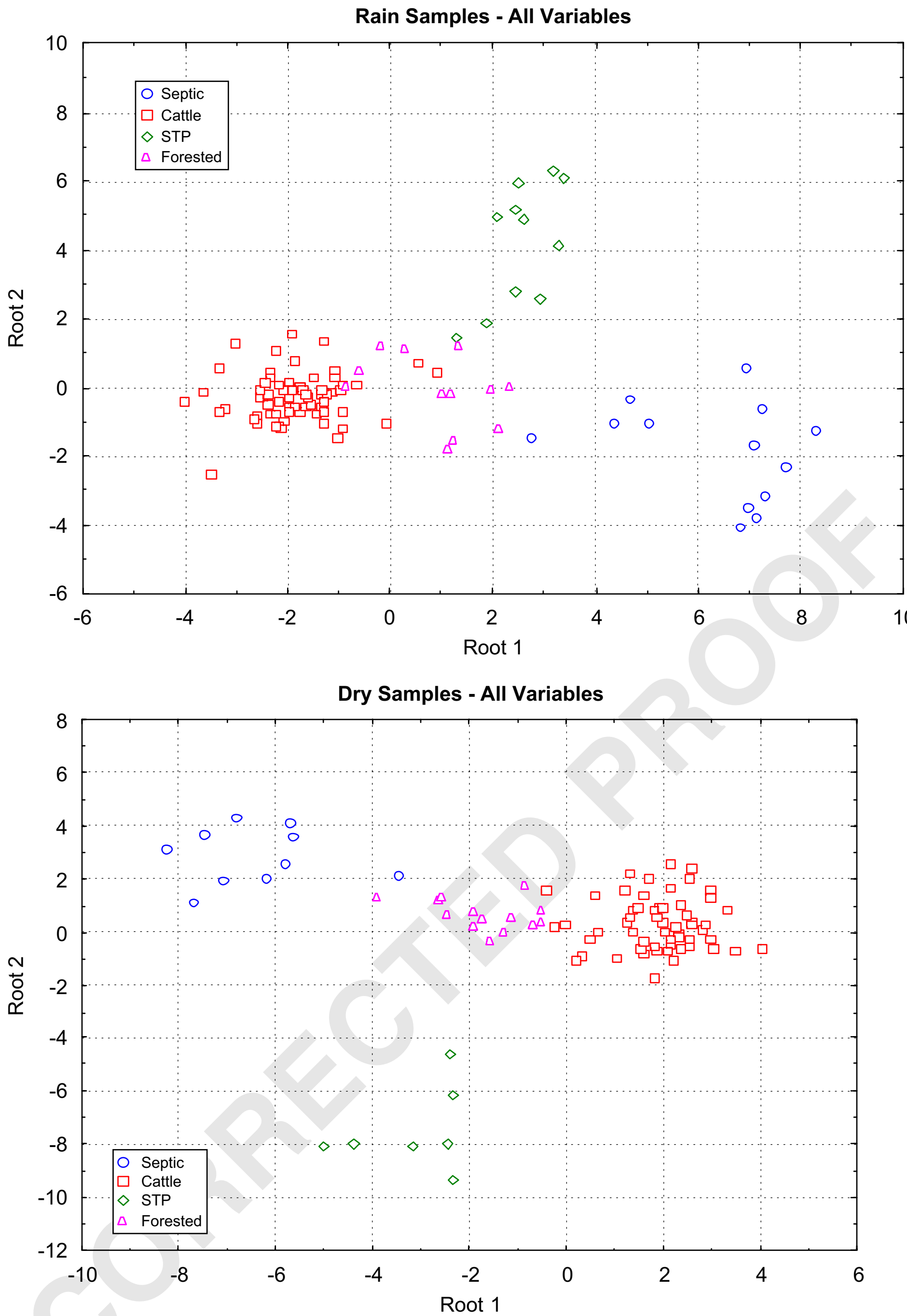

Fig. 4 – Canonical plots of rain ($n = 102$) and dry ($n = 88$) samples. Discrimination analysis on dry and rain samples was carried out using all variables (sterols, coliforms and elemental compositions) to characterize them into the septic, cattle and STP impacted and forested sites.

(2) The samples from the various land use categories generally had different water quality profiles in dry periods compared with samples taken following rain events. Elevated levels of both coprostanol and faecal coliforms were however not exclusive to rain events and were observed during dry periods as well.

(3) Discriminant analysis revealed that coprostanol and Sr were the major common factors contributing to discrimination of the septic, cattle, STP and forested sites for both rain and dry samples.

(4) Elemental profiles of water samples were more characteristic of the four land use types of catchments sites than the profiles of sterols and coliform bacteria allowing better differentiation of the catchments. Sr and Rb were the

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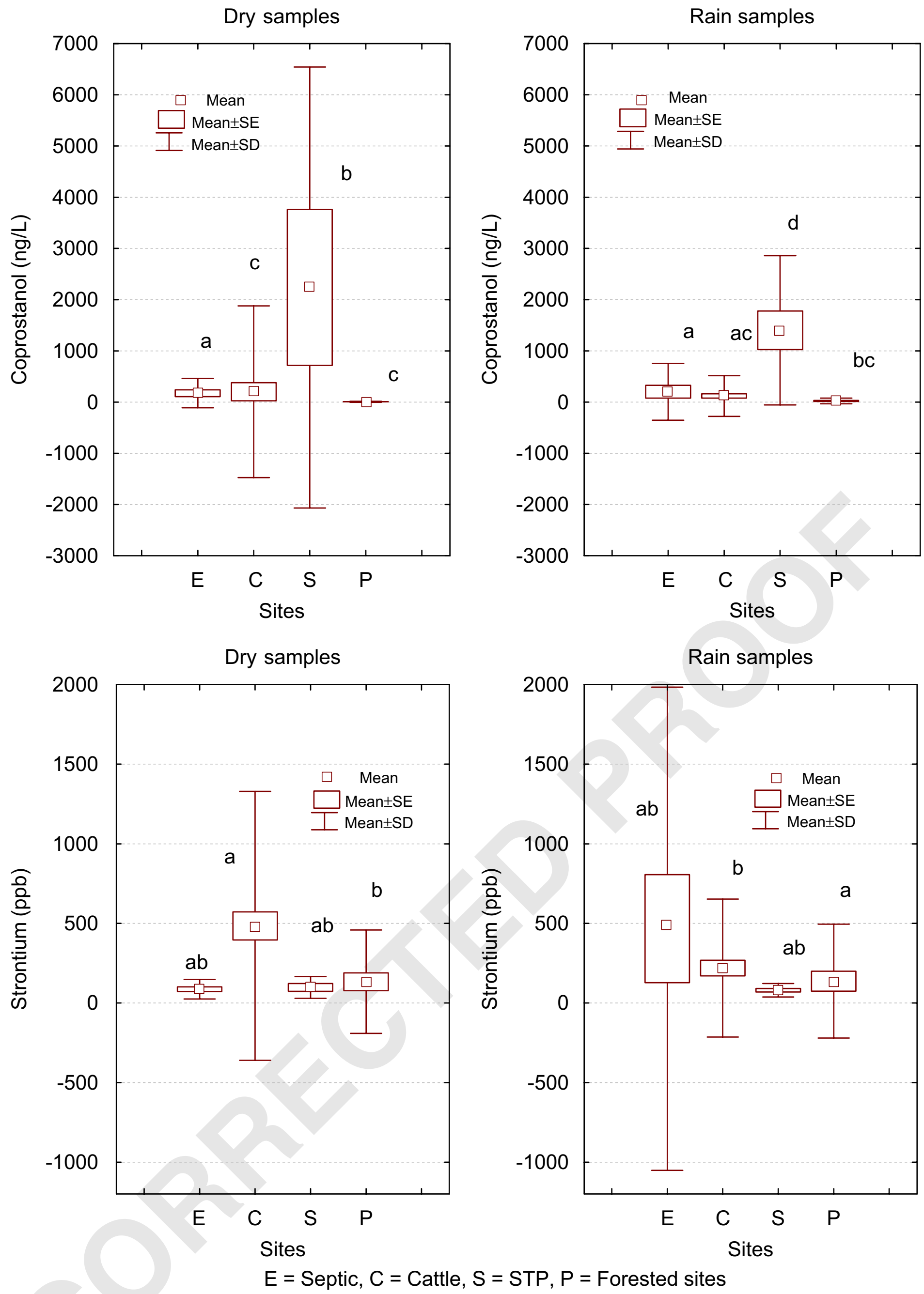

Fig. 5 – Sites differences with respect to coprostanol (ng/L) and Sr (ppb) concentrations in dry ($n = 147$) and rain ($n = 149$) events samples. Sites significantly different with respect to coprostanol and Sr are denoted by different letters as assessed by Duncan's multiple range test taken at $p < 0.05$.

major common elements contributing to discrimination of the different land use sites for both rain and dry samples when only elemental profiles were considered.

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