Appendix D

PCB Equipment Blank Analysis

Appendix D – PCB Equipment Blank Analysis

As discussed in Section 5.5.1 of the report, one ISCO® autosampler equipment blank was collected during the study. This is the same equipment used at the Green River Kanaskat-Palmer site. An ISCO autosampler equipment blank was also collected for the previous Green River surface water study (King County 2014a). Polychlorinated biphenyls (PCBs) were detected in both equipment blanks; total PCB concentrations were within the range of several samples collected at Kanaskat-Palmer, as well as some samples collected downstream of this location during the previous study. The following discussion explores the potential bias the autosampler equipment may have on PCB results. To do this, PCB congener profiles were compared for the autosampler equipment blanks, environmental samples collected with autosamplers and without autosamplers (e.g., composite grabs). For all figures and subsequent analysis, only detected PCB concentrations are presented.[1]

Figure D-1 presents congener profiles for the two autosampler equipment blanks and King County Environmental Laboratory (KCEL) reverse-osmosis (RO) water[2]. Evaluation of the congener profiles indicates that three congeners (with their coelutions) were strongly associated with blank samples collected with the autosamplers. These congener groups were: 44 (coelutes with 47 and 65), 45 (coelutes with 51) and 68[3]. Together, these congeners comprise between 69% and 89% of the total PCBs in the equipment blanks collected for the two studies (Figure D-1), with total PCB concentrations at 155 and 197 pg/L, respectively.

The purpose of the equipment blank samples was to represent the potential contamination that could occur from collecting environmental samples with autosampler equipment. In addition to the sampler equipment, the RO water used as the blank sample media can also be a source of PCBs. The KCEL RO water was analyzed in 2009 for a separate study (King County 2013f). Figure D-1 shows the three congener groups of concern for the equipment blank (44c, 45c and 68) are not present in high concentrations in RO water analyzed in 2009 (King County 2013f). These results indicate the source of these congeners is more likely associated with the autosampler equipment rather than RO water. PCB congener 11 was present in the equipment blank collected in 2012 and the RO water at similar concentrations, suggesting the presence of this congener in equipment blanks, as well as a few others observed at low levels, are more likely associated with the lab RO water.

While KCEL RO water has only been analyzed once for PCBs, autosampler equipment blanks have been analyzed for two other County projects (King County 2011a, King County 2013f). In each case, the same three congener groups made up the largest percentage of

---

[1] Full citations for references in this appendix can be found in Section 8 of the main report.

[2] Reverse-osmosis (RO) water is used by the King County Environmental Lab (KCEL) as equipment blank media. The PCB congener results for RO water help identify which congeners detected in the equipment blank may be sourced from the RO water versus the equipment itself.

[3] From here on, congeners that coelute with other congeners will be identified by the lowest IUPAC number of the group followed by a "c". For example, congener 44 coelutes with congeners 47 and 65; this group will be identified as 44c. The term "congener group" is used to refer to a group of coeluting congeners. Coeluting congeners are analyzed together; therefore, the resulting concentrations reflect the sum of the congener group. Refer to Figure 1 to identify specific coeluting congeners.

total PCB concentrations[4] in these samples. This further supports the likely presence of these congener groups from the autosampler equipment and the possibility of high bias of these congeners in environmental samples. Additional analyses of KCEL RO water are recommended to better characterize RO water impacts on equipment blank results.

For congener group 45c, concentrations were often greater in the equipment blank than the environmental samples; a similar pattern was observed for congener 44c. Congener 68 was generally detected at higher concentrations in environmental samples than in the equipment blank samples. These three congener groups comprised the majority (≥70 %) of the total PCB concentration for all but two Kanaskat-Palmer samples. In comparison, these congener groups only comprised a majority of the total PCBs in two Upper Green samples, which were not collected with the autosampler. Concentrations of the most abundant PCB congeners in these samples are presented in Figures D-2 (baseflow) and D-3 (storm events). Samples are identified by sample ID number (L#####-#) or as a field replicate [L#####-# (rep)].

The previous surface water sampling effort in the Green River Watershed included collection of dry baseflow and storm samples collected with autosamplers at two Green River locations (Flaming Geyser and Foster Links) and four major tributaries (Newaukum Creek, Soos Creek, Mill Creek and the Black River) (King County 2014a). Average concentrations of the most abundant PCB congeners detected in these samples and the two autosampler equipment blanks are presented in Figures D-4 (baseflow) and D-5 (storm events). While congeners 44c, 45c and 68 were detected in the baseflow samples other congeners comprise the majority of total PCBs on average at several sites. During storm events, the PCB congener pattern is quite similar between the equipment blanks and the environmental samples; however, the average concentrations of congeners 44c and 68 are more than five times higher in the environmental samples. These results indicate the potential equipment blank contamination associated with these congeners does not fully account for the concentrations detected in the environmental samples. Overall, these results indicate the PCB concentrations reported in the previous Green River study are less biased than most of the Kanaskat-Palmer samples, where concentrations were much closer to equipment blank concentrations.

Single grab samples have also been collected in the Green River, at Fort Dent (river mile 11)[5], as part of the Lower Duwamish Waterway Remedial Investigation (Windward 2010). This site is just upstream of the Foster Links location (river mile 10) sampled during the Green River Watershed water study (King County 2014a). These grab samples were collected by submerging the laboratory supplied sample bottle approximately 1-ft below the water surface; thus, no auto or grab sampling equipment was used. Figures D-6 (baseflow) and D-7 (storm events) illustrate the difference in congener pattern between the samples collected with autosamplers (Foster Links in 2010-11) and those collected as

[4] The specific congener results for these other equipment blanks can be found in the referenced reports; they are not presented in this appendix.
[5] River mile designations are based on river mile 0 being at the southern end of Harbor Island; consistent with LDW site river mile designations.

single grabs (Fort Dent in 2007-08).[6] Congener 68 was never detected at Fort Dent and congener groups 44c and 45c were infrequently detected, with overall average detected concentrations of 21.8 and 3.14 pg/L, respectively. Congener groups 44c and 45c comprised 5% or less of the total PCB concentrations in 17 of 18 Fort Dent samples, but on average comprised 40% of the total PCB concentrations at the Foster Links location. While samples from these two sites are not directly comparable for several reasons[7], these data provide additional evidence that autosampler results for congener groups 44c, 45c and 68 are likely biased high due to equipment blank contamination.

In 2012, King County conducted a comparison of sampling methods to determine if samples collected with an autosampler from a single point were representative of samples collected from a cross section of the Green River (King County 2014a). The samples were collected simultaneously, once during dry baseflow and once during a storm event at Foster Links location. The PCB congener profiles for both sample types are presented in Figures D-8 (baseflow) and D-9 (storm events). Congener concentrations in samples collected during storm events were comparable between both collection methods, with the exception of congeners 44c, 45c and 68, which were detected at substantially higher concentrations in the autosampler sample. In the baseflow samples, a number of additional congener groups were also dissimilar between the two methods; higher concentrations and a greater frequency of detection were observed in the sample collected by the autosampler. This comparison between sampling methods includes both spatial and sampling equipment differences; the autosampler collected aliquots from a single location, whereas each composite grab consisted of samples collected at multiple points along a cross-section of the river. This confounding factor inhibits a direct comparison of sampling equipment and the potential to determine the degree of bias introduced by autosampler equipment. Even so, the storm event samples provide additional evidence that the three congener groups tend to be biased high based on equipment blank samples.

In conclusion, there is a need to better characterize the influence of autosampler equipment contamination on PCB environmental sample results. This is particularly important when environmental concentrations are relatively low (within the range of equipment blank concentrations) (e.g., in the Kanaskat-Palmer samples). The environmentally-relevant total PCB concentrations and consistent PCB congener pattern in equipment blanks suggests PCB results in samples collected with autosamplers are biased high for congeners 44c, 45c and 68. However, there is uncertainty around the degree of bias. Future sampling efforts could include a more direct comparison between composite grabs and autosampler collection methods. Additional analysis of PCBs in KCEL RO water and blanks for isolated Teflon and silicon tubing could also be conducted to better understand equipment blank results.

---

[6] At Fort Dent, a storm sample was a targeted event with at least 0.25-in. rainfall over 24 hours, with a minimum of 24 hours antecedent dry period. The other sampling events presented in Figure D-6, were conducted during routine monthly monitoring and may or may not correspond to storm events.
[7] These samples were collected in different years, at slightly different locations, under different flow conditions and with different collection methods (single grab versus 24 hour composite).

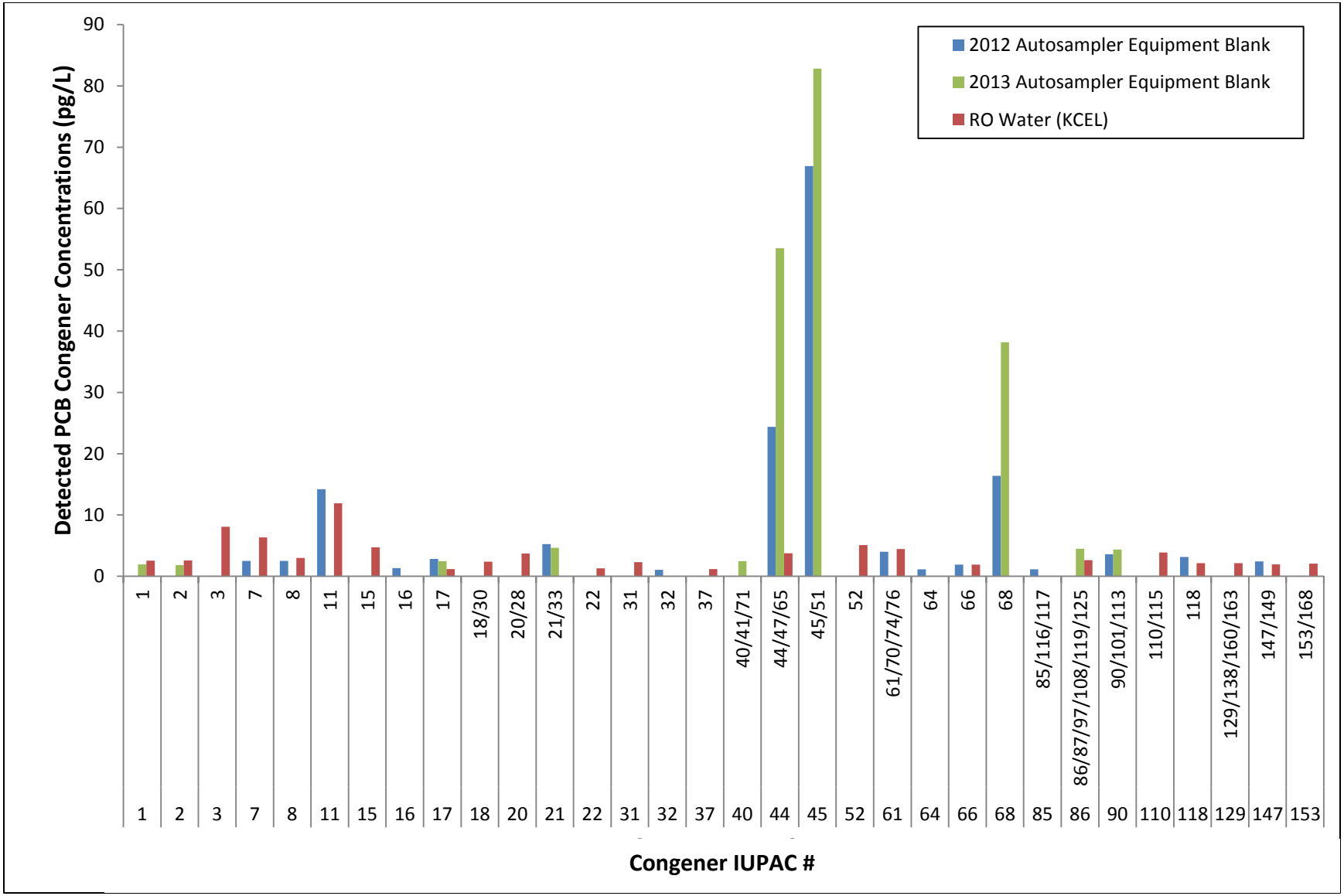

Figure D-1. ISCO© autosampler equipment blanks and KCEL RO water PCB congener profiles.

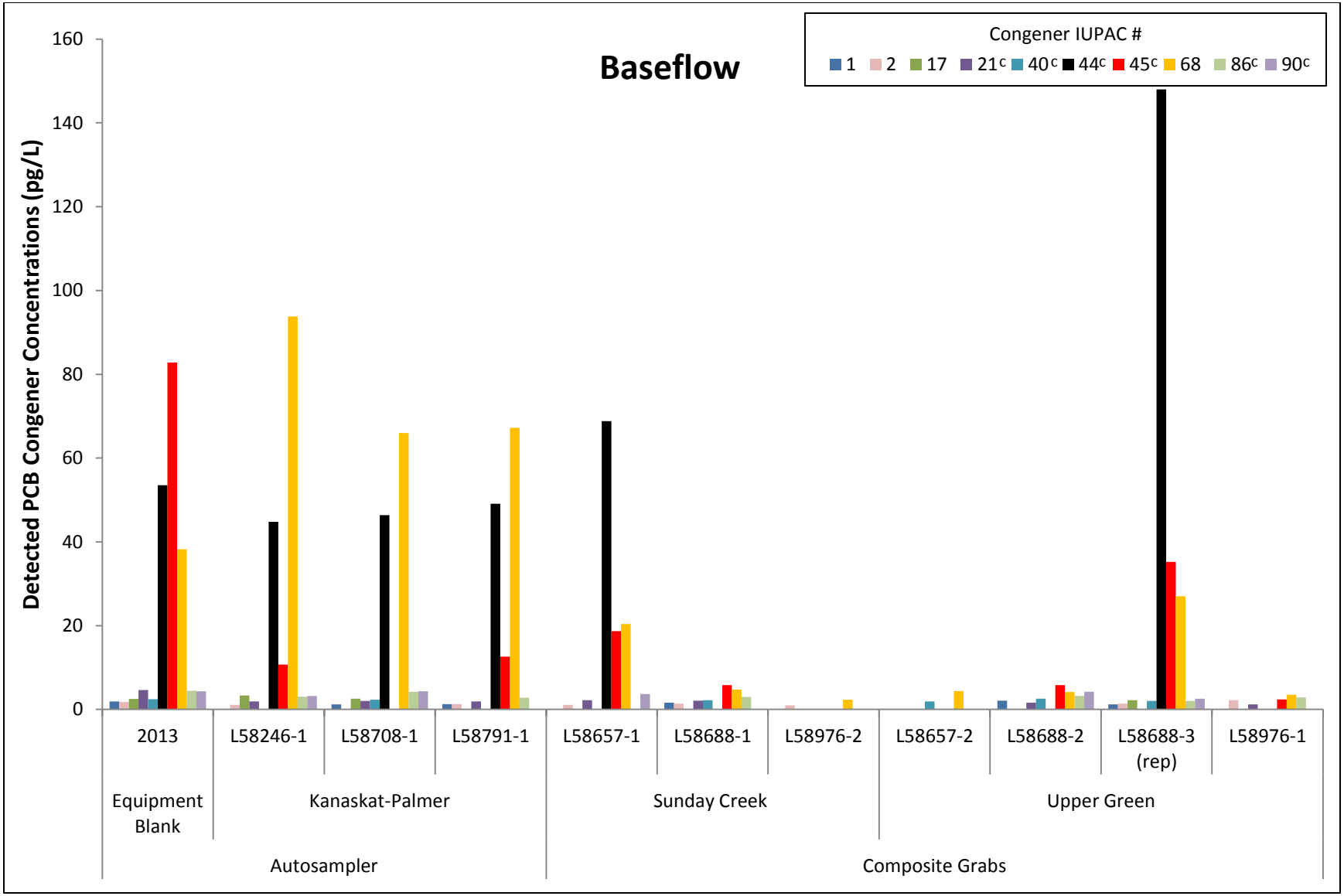

Figure D-2. Concentrations of the most abundant PCB congeners in the 2013 ISCO autosampler equipment blank compared to those in baseflow samples at Kanaskat-Palmer, Sunday Creek and Upper Green (current report).

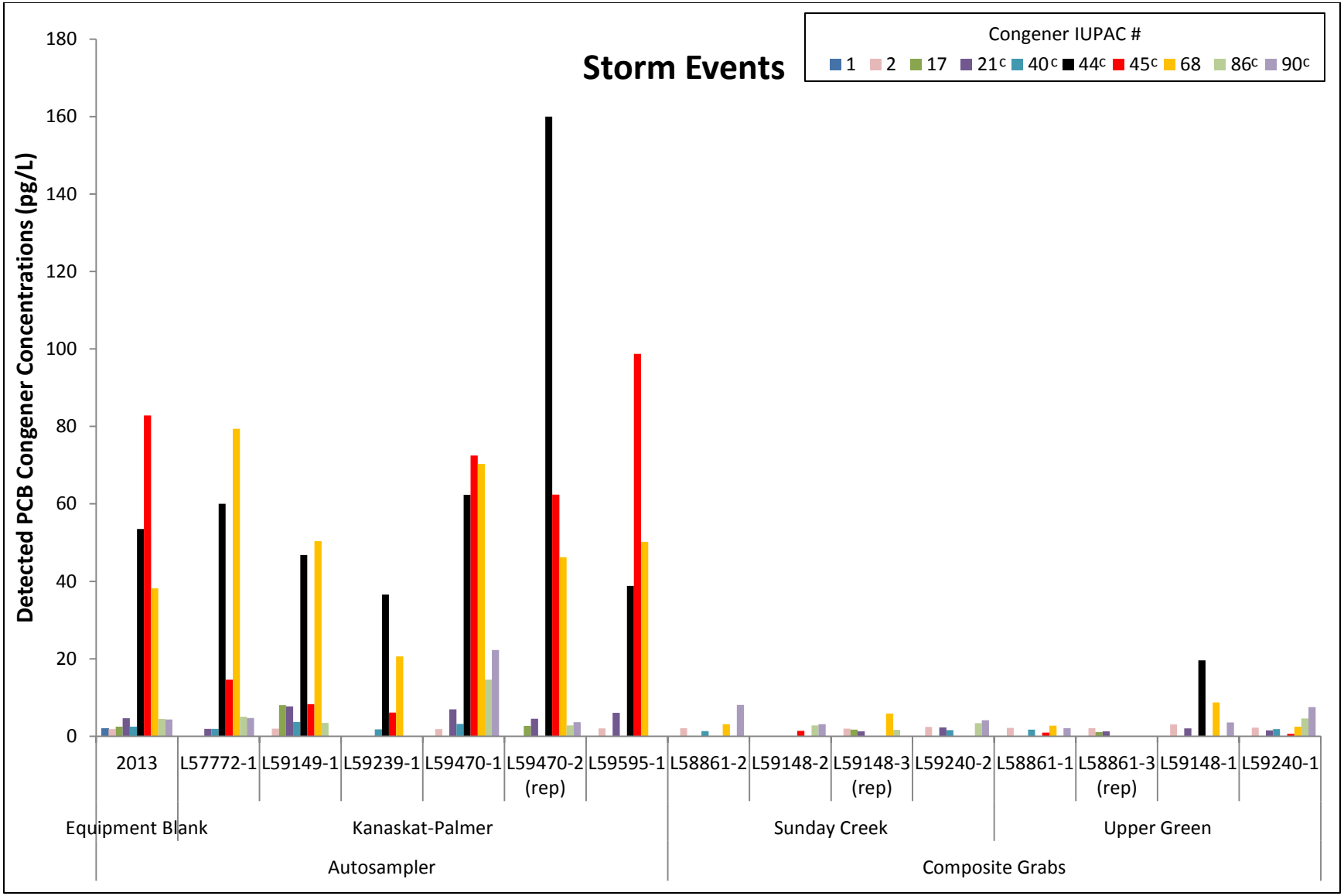

Figure D-3. Concentrations of the most abundant PCB congeners in the 2013 ISCO autosampler equipment blank compared to those in storm event samples at Kanaskat-Palmer, Sunday Creek and Upper Green (current report).

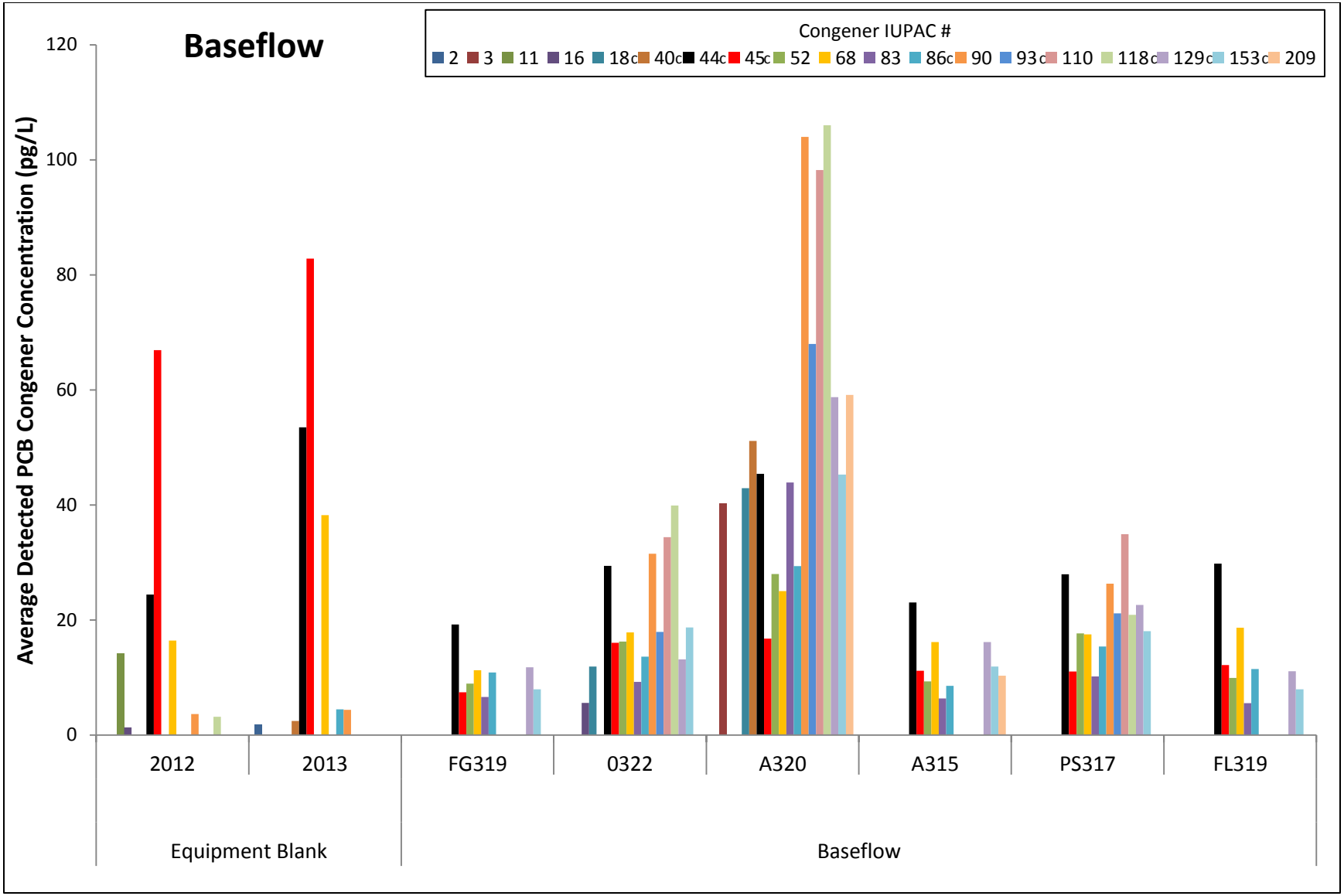

Figure D-4. Concentrations of the most abundant PCB congeners in the 2012 and 2013 ISCO autosampler equipment blanks compared to those in baseflow samples collected for the Green River Watershed Study (King County 2014).

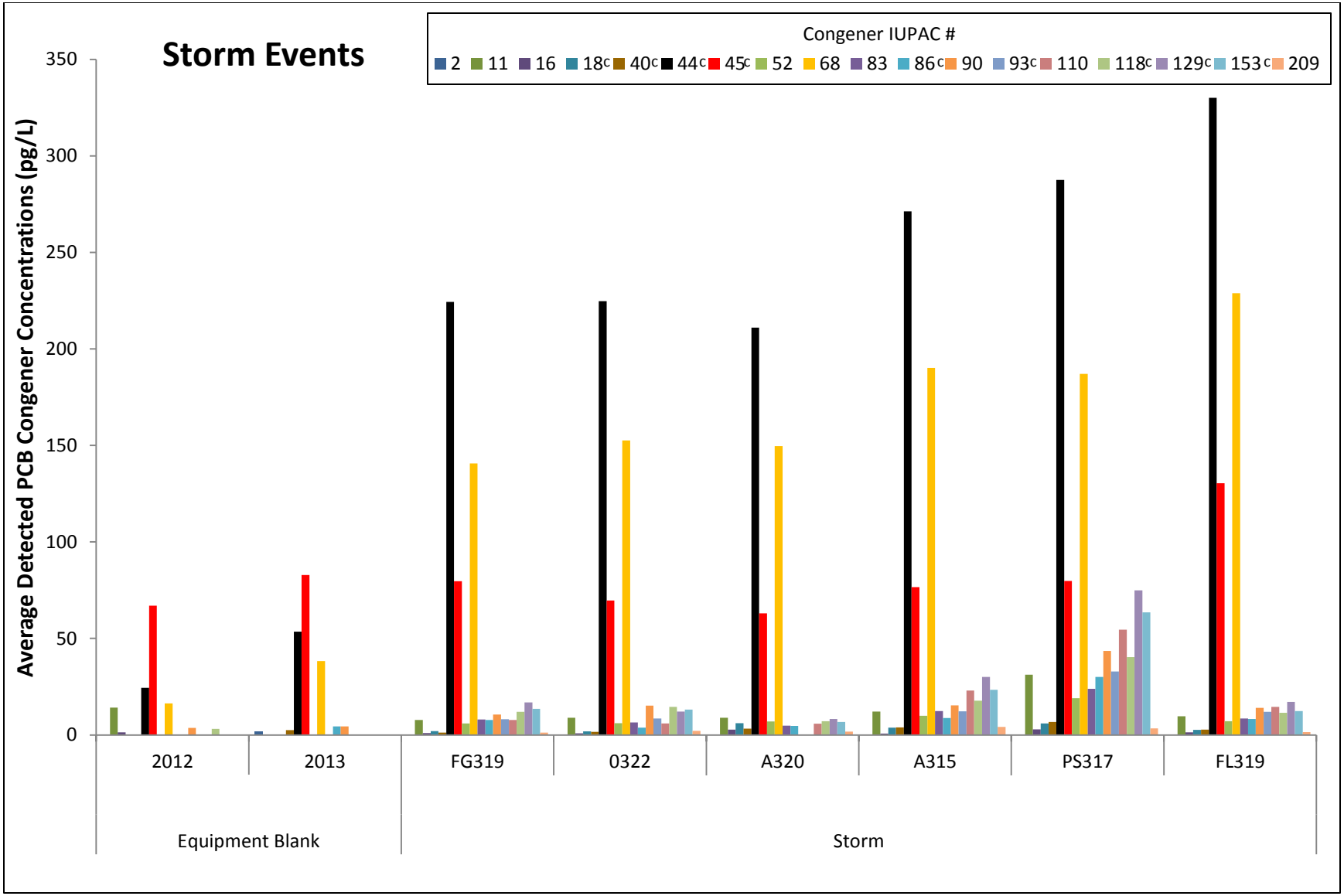

Figure D-5. Concentrations of the most abundant PCB congeners in the 2012 and 2013 ISCO autosampler equipment blanks compared to those in storm event samples collected for the Green River Watershed Study (King County 2014).

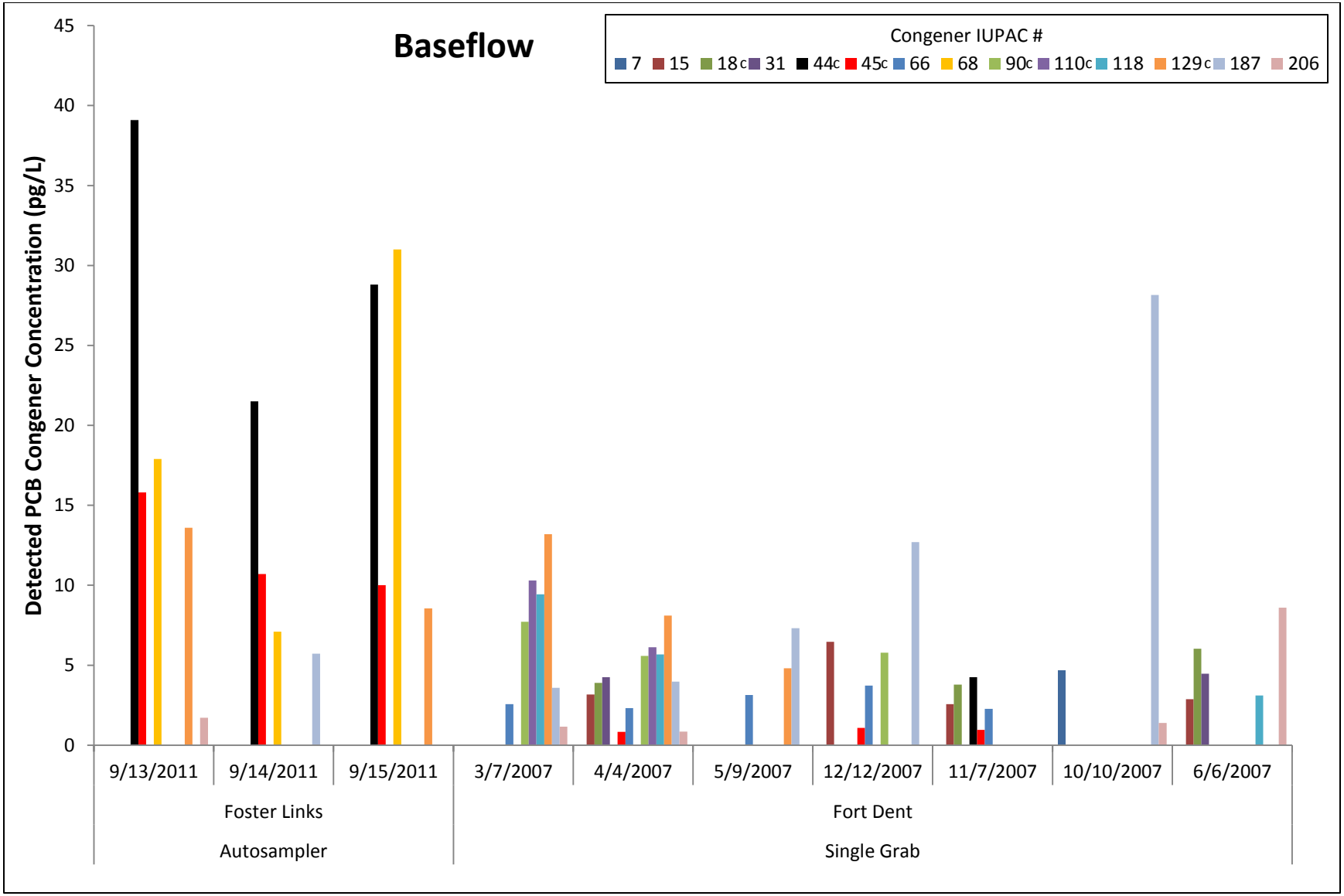

Figure D-6. Concentrations of the most abundant PCB congeners in baseflow samples collected in the Green River at Foster Links (King County 2014) and Fort Dent (Windward 2010). (Fort Dent sampling events presented were conducted during routine monthly monitoring and may or may not correspond to storm events).

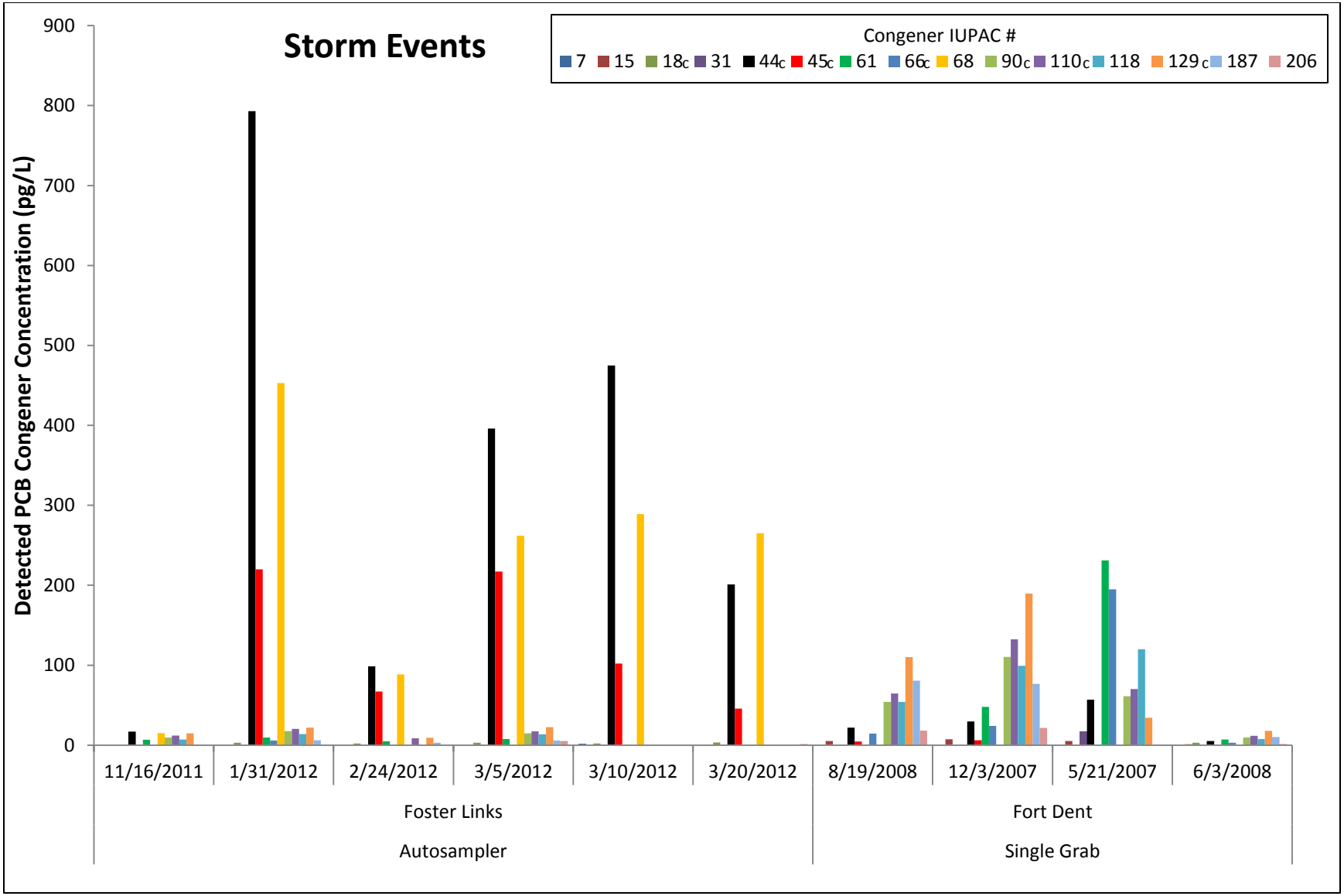

Figure D-7. Concentrations of the most abundant PCB congeners in storm event samples collected in the Green River at Foster Links (King County 2014) and Fort Dent (Windward 2010).

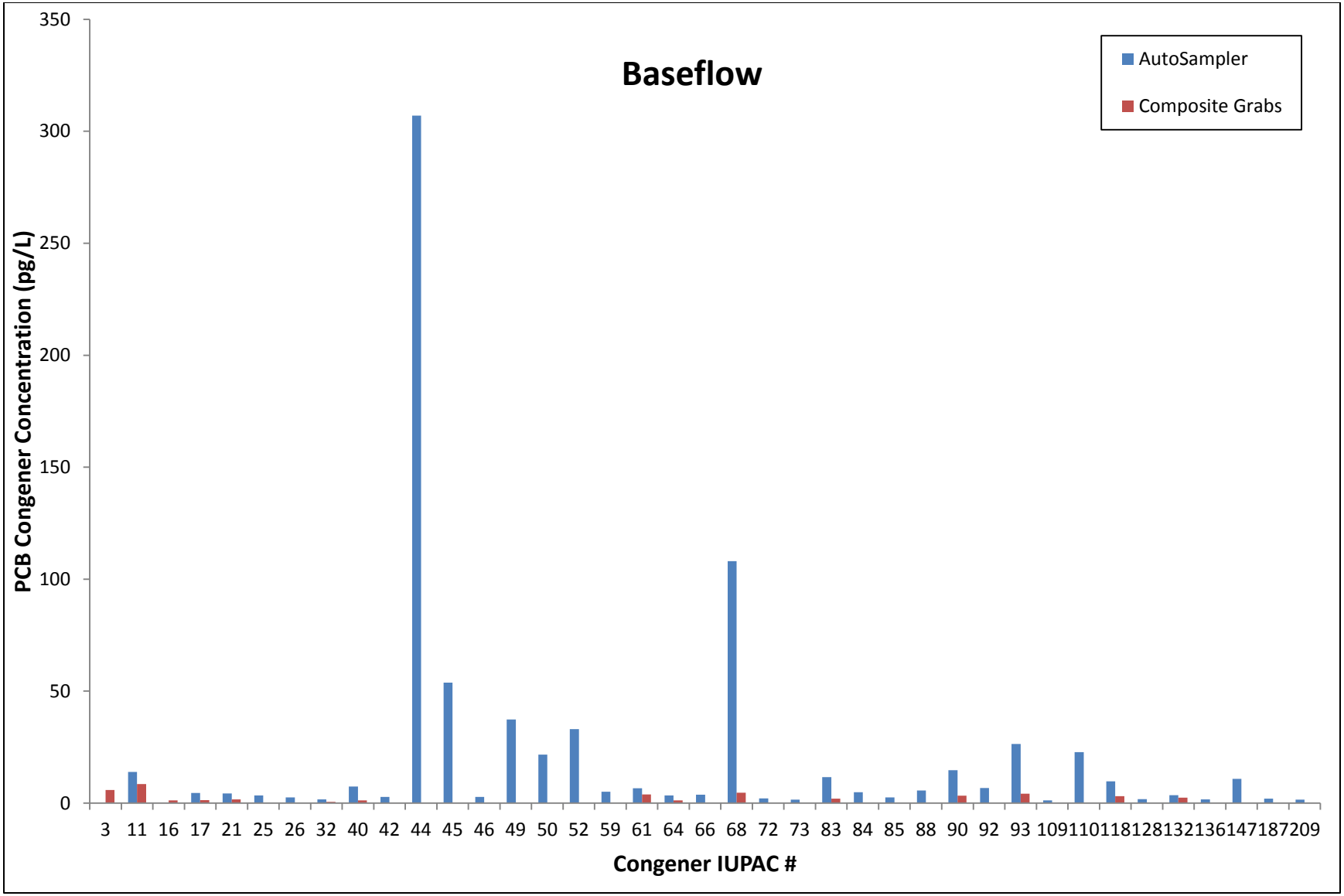

Figure D-8. PCB congener profiles for method comparison baseflow samples: ISCO® autosampler composite and cross-sectional composite grabs (King County 2014). (Congeners that coelute with other congeners are identified by the lowest IUPAC number of the group. Figure D-1 presents specific coeluting congeners).

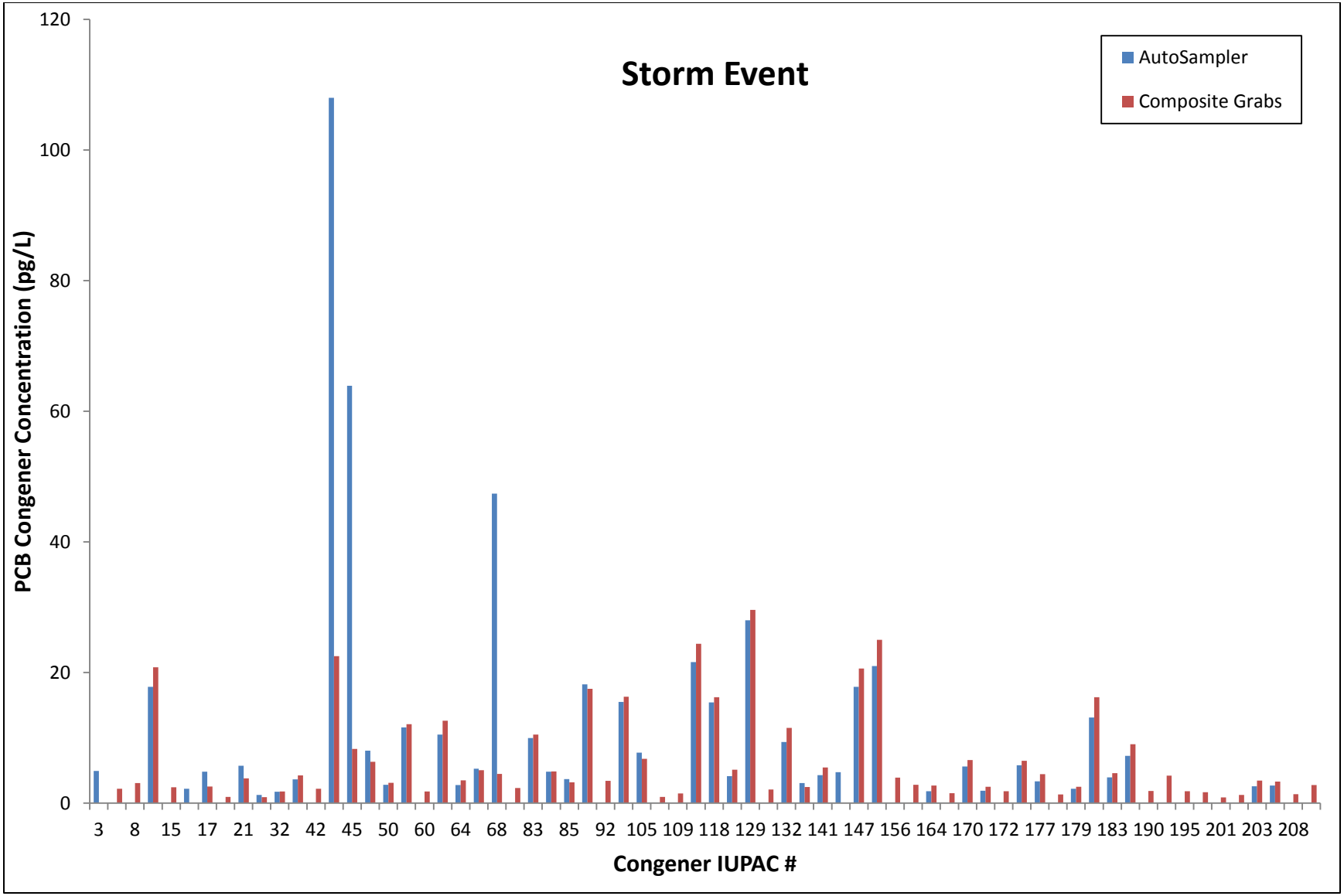

Figure D-9. PCB congener profiles for method comparison storm event samples: ISCO® autosampler composite and cross-sectional composite grabs (King County 2014). (Congeners that coelute with other congeners are identified by the lowest IUPAC number of the group. Figure D-1 presents specific coeluting congeners.