To: BACWA and San Francisco Bay Regional Water Quality Control Board staff
From: David Senn and Emily Novick
Date: October 8 2013
Re: --DRAFT-- Year 1 Effluent Nutrient Data - Initial Observations

1. Introduction

At the request of BACWA and Regional Board staff, SFEI reviewed a subset of the Year 1 POTW effluent characterization data whose collection was required under the 13267 Letter[1] issued by the Regional Board in 2012.

The review was motivated by two questions that have been raised by the discharger community:

1. How will the monitoring data be used, in particular through modeling?

2. Based on the Year1 effluent characterization data, and the anticipated data uses, could some analytes be dropped during Year 2, either because they are unlikely to be used in modeling, or because they provide limited additional information given the other analytes?

To explore these questions, we analyzed effluent data from July 2012-June 2013 from the 8 largest POTWs (based on flow rate) and two additional POTWs with somewhat unique discharge requirements and advanced treatment (Napa and Sunnyvale). In addition to being among the largest contributors of nutrient loads to the Bay, these POTWs also represent a wide range of treatment processes and are geographically well-distributed throughout the region. Typical estuarine water quality model input requirements were also considered and compared with the analyte list. Finally, although evaluating data quality was not the primary purpose of this effort, we do comment in a limited way on some issues that became evident during data analysis.

This report is intended as a broad-brushstroke overview. It aims to describe general trends and identify seasonal and inter-POTW differences in effluent composition and relative importance of N and P forms that will help address the two questions above.

2. Data and Approach

Table 1 identifies the ten wastewater treatment plants that were selected. Each of these dischargers was required to sample and analyze effluent 1-2 times per month for the analytes noted in Table 2.

In evaluating the first year's effluent data, the main considerations were:

1. How consistent was effluent composition (concentrations) within individual POTWs over the course of the year?
2. How large were the inorganic vs. organic forms of N, and dissolved vs. particulate organic forms of N? How much did their proportions vary over the year?
3. How large were the particulate vs. dissolved forms of P, and the "reactive" vs. non-reactive

[1] Link to 13267 Letter

forms of dissolved P? How much did their proportions vary over the year?
4. For any parameters, do analytical and other uncertainties substantially limit the utility of the results?

To explore these issues, we evaluated the concentrations of measured analytes, and also several calculated parameters (Table 2). Since urea is not being measured in Year 2, urea data was not considered in this report.

3. Main Observations

Flows and loads of N and P are shown in the upper left panel of Figures 1-10 and 11-20, respectively. The upper right panels in Figures 1-10 and 11-20 present concentrations of N and P species, respectively. The bottom left panels in each figure present the proportion of N in organic and inorganic forms (Figures 1-10) and the proportion of P in dissolved and particulate forms (Figures 11-20). Finally, the bottom right-hand panels in Figures 1-10 and 11-20 present the concentrations of TON and DON, and the proportions of TDP present as DRP and DUP, respectively.

3.1 Typical water quality model load input requirements, and limitations of laboratory measurements

Many widely used estuarine water quality models consider multiple nutrient parameters, both in terms of external loads, and as nutrient forms in the water column or in the sediments:

1. NH_4^+ or NH_3
2. NO_3^- + NO_2^- (typically these are combined as opposed to considered separately)
3. ortho-phosphate or DRP
4. PON
5. DON
6. POP
7. DOP
8. reactive phosphorous complexed by mineral particles such as iron oxides

Some water quality models also consider a range of reactivities, or labilities, for PON, DON, POP, and DOP. The reactivities are typically not determined from monitoring data, but rather through experimentation, literature estimates, or through model calibration.

The current set of effluent characterization analytes (Table 2) are either the actual input parameter required by models, or are parameters that are needed to indirectly estimate (e.g., by subtraction) an input parameter. For example, in POTWs effluent:

PON = TON - DON = (TKN-NH_4^+) - (SKN-NH_4^+) = TKN - SKN

and

POP = TP - TDP (assuming that non-organic forms of particulate P are negligible)

and

DOP = TDP - DRP

Uncertainties about the actual chemical form being measured can be nontrivial, especially when the measured value is sensitive to sample preparation or when a parameter is actually calculated from two or more analytes. Many chemical measurements are actually “operationally-defined”, in the sense that they are the best estimate or approximation of the target chemical form. In the case of NO_3^- or NO_2^-, the measured value is likely to be a good estimate of the true concentration in the sample, because both NO_3^- and NO_2^- are 100% dissolved and responsive to the analytical reagents, and the analytical techniques are well-established. However, the value measured for TN or TP may vary depending on the sample pretreatment method used, and how completely that pretreatment liberates N or P. For so-called “dissolved” analytes that can be present in both dissolved and particle-complexed forms (e.g. P), a sample is first passed through a filter. The pore size of the filter used, and the sharpness of its cutoff, can influence what gets counted as dissolved or particulate, both because of the presence of small particles (colloids) that pass through the filter, and because the effective pore size of filters can decrease as more sample is filtered (due to filter clogging). In the end, when determining what measurements to do, there is reason to consider the accuracy and uncertainties of the measurements (and any subsequent calculations), the relative importance or sensitivity of the modeling results to a particular loading parameter, and the cost.

3.2 Flows and N & P loads

- Several POTWs exhibited strong seasonal variability in flows and/or loads, with 20-40% higher flows and loads common during wet months compared to drier months.
    - Sunnyvale loads of N and P were 3 and 1.5-2 times higher, respectively, in wet/winter months than dry weather months
    - San Jose loads of N and P were ~1.5 and 5 times higher, respectively, in wet/winter months than dry weather months.
- The load increases at some POTWs during wet winter months are likely due in large part to a combination of shorter residence time and lower temperature (resulting in lower biochemical removal efficiency), since any water that infiltrated into sewer lines and caused higher flows would have had relatively low N and P concentrations.

3.3 Nitrogen

3.3.3 Inorganic N

- As expected, dissolved inorganic nitrogen (DIN) dominated total N at all POTWs (bottom left panel in Figures 1-10).
- Also as expected, all POTWs, with the exception of Sunnyvale and Napa, exhibited a strong dominance of either NO_3^- or NH_4^+ (top right panel in Figures 1-10), with the other form being a minor constituent. During winter months, Sunnyvale effluent contained NO_3^- and NH_4^+ at comparable concentrations because of the well-documented decreased efficiency of nitrification in its effluent ponds. A mixture of NO_3^- and NH_4^+ was also observed in Napa effluent at several time points .
- In all POTWs, NO_2^- represented only a minor portion of DIN (generally <5%) (top right panel in Figures 1-10). During several sampling events in December, NO_2^- concentrations increased in San Jose effluent and comprised as much as 25% of DIN, but returned to low levels by January, and continued to be low thereafter.
- DIN concentration varied widely among POTWs. DIN was lowest at San Jose (10-15 mg L^{-1})

and Napa (10-15 mg L^{-1}), and during a few warm months at Sunnyvale (~15 mg L^{-1}). San Jose and Napa have advanced treatment for N removal, and denitrification occurs at seasonally-varying rates in Sunnyvale's effluent ponds. DIN concentrations were highest in effluent from EBMUD (35-45 mg L^{-1}, with one very low value during high flows), SFSE (generally 30-40 mg L^{-1}, with a few lower values), and South Bayside (30-45 mg L^{-1}), and were greater than rule-of-thumb estimates for DIN (20-30 mg L^{-1}) in secondary treated effluent (BACWA, 2011). The elevated values at EBMUD were expected (because of animal waste additions), but the reason for the relatively high concentrations at South Bayside and SFSE are not known. In the case of SFSE the DIN concentrations measured during 2012-2013 are consistent with earlier data included in the recent draft loading study (Novick and Senn, 2013). Even the somewhat lower levels observed at EBDA (~30 mg L^{-1}), Fairfield-Suisun (several months ≥ 30 mg L^{-1}), and Palo Alto (highly variable with several months ≥ 30 mg L^{-1}) were consistently at or above the upper end of the rule-of-thumb range for DIN.

3.3.4 Organic N, and Particulate vs. Dissolved Organic N

- TON ranged between 10-20% of TN at most POTWs. Fairfield-Suisun and Palo Alto were exceptions, where TON was ≤ 5% of TN. At Sunnyvale, the TON proportion appeared to vary seasonally, comprising nearly 20% in warm months and ~10% in winter months.
- Both TON and DON are calculated parameters (TKN - NH_4^+ and SKN - NH_4^+, respectively). In cases when most of the DIN is present as NH_4^+, the calculated TON and DON values represent small difference between between two relatively large numbers, each of which has analytical uncertainty and sample-related uncertainty (if measurements were conducted on different samples). For that reason, of all the analytes, TON and DON might be expected to have the largest relative uncertainty (e.g., standard deviation / mean). This uncertainty needs to be taken into account when comparing the magnitudes of TON and DON in a given sample, and when considering the variability in their concentrations over time.
- Of all the N forms, TON and DON exhibited the greatest relative variability (Figures 1-10, bottom right panel). Much of this variability likely owes to them being calculated by difference (see bullet above). Note also, though, that the y-axis scales for the TON and DON graphs.
- In general, TON concentrations were comparable to or less than rule-of thumb concentrations for plants that do not nitrify effluent (~5 mg L^{-1}). Overall, TON for the POTWs investigated in this report fell between 2-5 mg L^{-1}, with a few being consistently lower than 2 mg L^{-1} (Fairfield-Suisun, Palo Alto, San Jose), and EBMUD frequently exceeding 5 mg L^{-1}.
- Despite the variability and uncertainty, TON was generally greater than DON, as would be expected if particulate organic nitrogen (PON) was present. At some POTWs PON represented as much as 50% of TON, and was on the order of 1-3 mg L^{-1}. While 50% is a relatively large proportion of TON, PON nonetheless remained a small percentage of TN (<5-10%). At POTWs that perform filtration, PON should be even smaller. On average, PON does appear to be lower in San Jose effluent than at several of the other large POTWs (e.g., EBMUD, CCCSD, EBDA). However, San Jose also has lower TN due to biological nitrogen removal, and the observed lower PON may be due to both N removal and filtration.

3.3 Phosphorous

3.3.1 Total Phosphorous

- In general, TP showed considerable inter-monthly or seasonal variability within individual POTWs (e.g., ±50% or more; upper right panel in Figures 11-20). EBDA was an exception, where TP was still variable but over a relatively narrow range (±20%).
- While at most POTWs TP variations were not obviously systematic or seasonal, pronounced seasonality was evident at Fairfield-Suisun, San Jose (10-fold higher concentrations in winter than summer), Sunnyvale, and Palo Alto.
- TP concentrations differed substantially among POTWs. Lowest values were measured at CCCSD (<1.5 mg L^{-1}) and Napa (<1.5 mg L^{-1}), and during warm-weather months at San Jose (<0.5 mg L^{-1}). Highest concentrations were seen at Sunnyvale (up to 6-8 mg L^{-1}), Fairfield-Suisun (up to 4-5 mg L^{-1}), Palo Alto (up to 4-5 mg L^{-1}), and EBMUD (up to 4-5 mg L^{-1}). With the exception of Sunnyvale during some months, the observed concentrations were comparable to or considerably lower than rule-of-thumb TP concentrations for secondary treatment (4-6 mg L^{-1}).

3.3.2 Dissolved vs. Particulate P

- In general, >80% of TP was measured in the dissolved phase across most POTWs (bottom right panels in Figures 11-20). At some POTWS, TP was >95% in the dissolved phase. Some POTWs (Fairfield-Suisun, Palo Alto, Sunnyvale, and occasionally San Jose). The proportion of dissolved P occasionally dipped as low as 60% at CCCSD; the relatively larger swings may be due in part to its already low TP.
- Apparent analytical or reporting issues with SFSE and Napa P data make it difficult to interpret their reported levels.

3.3.3 Reactive vs. unreactive dissolved P

- The proportions of reactive (DRP) vs. unreactive (DUP) dissolved phosphorous were highly variable among POTWs. For example, >90-95% of TDP was present as DRP in effluent from Palo Alto and Sunnyvale. At other POTWs (e.g., CCCSD and EBMUD), DRP ranged from 60-90% of TDP.
- Like DON and PON, DUP is a calculated value and a small difference between two relatively large values. DRP in many cases was comparable to TDP; in some cases the values were likely indistinguishable given their individual analytical uncertainties (this is evident from the number of DRP proportions that exceed 1). In other cases, there seems to be a clear systematic difference between TDP and TRP (e.g., EBMUD, CCCSD, EBDA).

4. Recommendations

- Overall, the nutrient-related analytes (i.e. Table 2) defined in the 13267 letter are a reasonable list for characterizing effluent the Year 1 program and for continued measurement in Year 2, both with respect to limited amount of historic data on effluent composition and likely data usages.

- Based on a preliminary analysis of effluent characterization and load data from Year 1, an additional year of effluent characterization, based on this list of parameters, appears justified. Seasonal variability in composition and loads, inter-POTW variability, and analytical uncertainty were all substantial enough in Year 1 that an additional year of data collection would help better define N and P loads and the abundance of major and minor nutrient forms. The need for additional data is particularly true considering that, at a number of POTWs, little historic data was available prior to the current monitoring effort on most forms of P, organic N, and speciation of inorganic N.
- Calculated PON represents a fairly small percentage of TN. For that reason, it may seem that distinguishing between TON, PON, and DON is unnecessary, and that one parameter (i.e., SKN) could be dropped from the analyte list. However, PON has a different fate than DIN and DON once entering receiving waters; PON will tend to settle and accumulate in sediments. Before a decision can be made about whether a parameter like SKN can be dropped from the analyte list, the relative importance of PON and its fate needs to be considered. For example, assume: on an annual basis only 10% of DIN that enters the Bay is converted into phytoplankton biomass; some percentage of that newly produced phytoplankton biomass (e.g., 50%, probably a high number) settles and accumulates in the Bay sediments (the remainder is recycled in the water column or transported out of the Bay as phytoplankton biomass); in this example, the 5-10% of TN that leaves POTWs in the form of PON would be comparable in magnitude to settling phytoplanktonas a PON source to the Bay's sediments. For this reason, alongside the uncertainty in the concentrations (in part due to the short time-series and data quality issues), continuing to measure both TKN and SKN seems justified.
- Of all the parameters, 2-3 may warrant further discussion as to whether they are high value and essential, or could potentially be dropped. That decision might be better made after an additional year of data. The cost of doing these measurements needs to be considered relative to the potential gains in terms of the data (or lack there of) would be used.
    - Given the analytical uncertainty and close correspondence between TDP and TRP, it may be reasonable to argue that only one of these parameters needs to be measured.
    - A case could also be made that NO_2^- is not necessary. However NO_2^- is probably among the least expensive measurements (and depending on the measurement technique is obtained anyway during NO_3^- analysis (if measured by ion chromatography)), and may provide useful diagnostic information about treatment plant operation.
    - A case might also be made that the analytical uncertainties are large enough that PON and DON can not be realistically distinguished. More detailed analysis of current data (and QA/QC data, such as replicates, analytical precision, etc.) would be needed to make the case that SKN might be a candidate for dropping.
- A coordinated data QA/QC plan is needed. Over the first year of sampling (July 2012 - June 2013) individuals from the BACWA Permits Committee and Regional Board staff reviewed data on a quarterly basis, and again at the close of the year. Those data checks proved

essential for catching errors either in reporting or laboratory analyses. Nonetheless, there appear to be some remaining issues. Detailed QA/QC of the data was not among this reports goals. Some immediate action may be needed based on apparent data quality issues with some POTWs reported data, so that any analytical issues can be addressed early in Year 2 to ensure usable data for some problematic parameters. A first step along would be a coordinated review of Year 1 data.

- In addition, an on-going data analysis plan needs to be established, and become of regular monitoring program data analysis and reporting. This plan also needs to consider eventual data usage.

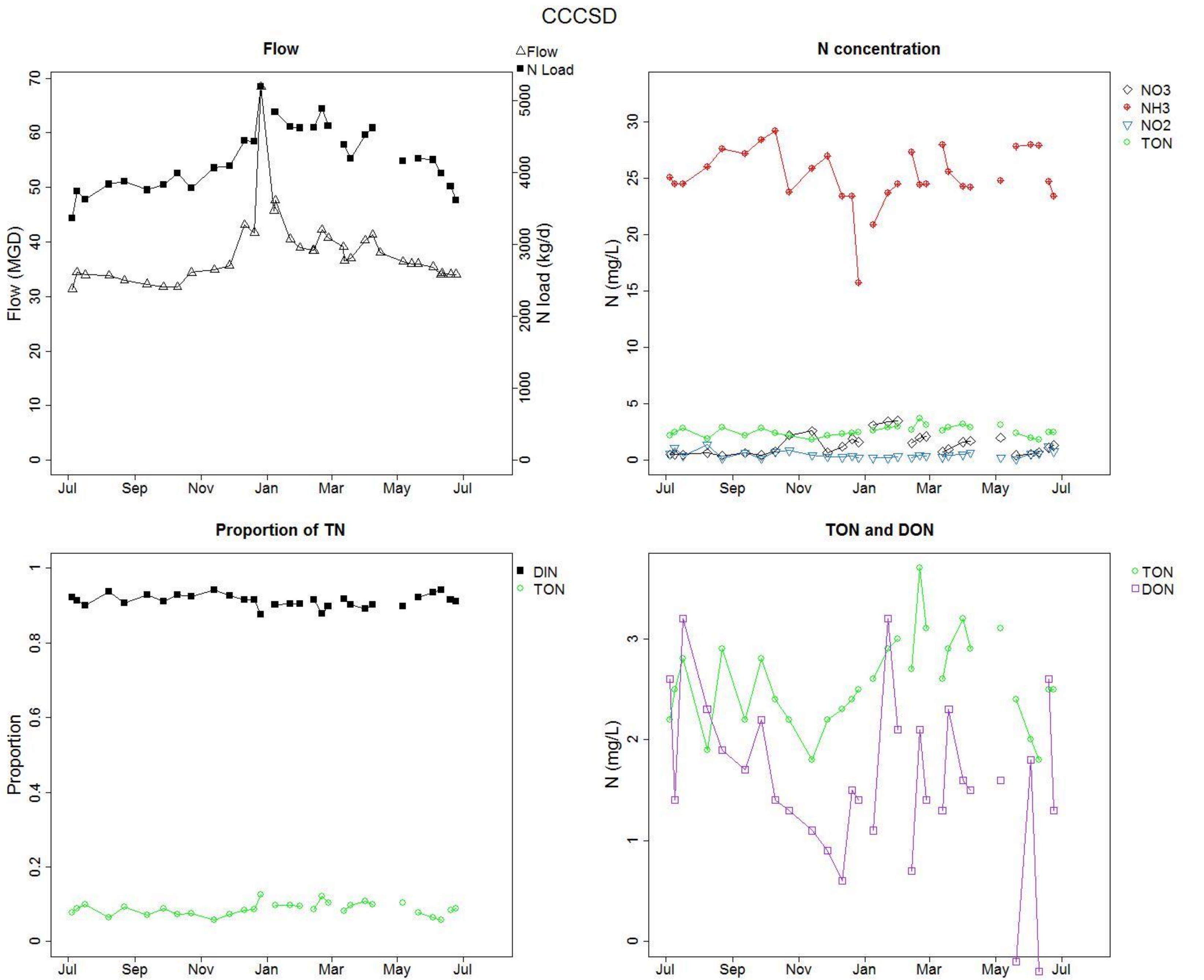
Table 1 POTWs considered in this report.

POTW	Average Flow (MGD)
Central Contra Costa Sanitation District (CCCSD)	38
EBDA	63
EBMUD	60
Fairfield-Suisun	14
Napa	11
Palo Alto	21
San Jose	93
San Francisco Southeast (SFSE)	58
South Bayside	13
Sunnyvale	11

Table 2 Analytes and calculated concentrations

Parameter	Measured or calculated	Calculation
NO_3^- - nitrate	measured	
NO_2^- - nitrite	measured	
NH_4^+ - ammonium	measured	
TKN - Total Kjeldahl Nitrogen	measured	
SKN - Soluble Kjeldahl Nitrogen	measured	
TN = Total Nitrogen	calculated	TN = TKN + NO3 + NO2
TDN = Total Dissolved Nitrogen	calculated	TDN = SKN + NO3 + NO2
TON - Total organic N (TON), the total amount of organically-complexed N in the sample, including both particulate and dissolved forms,	calculated	TON = TKN - NH_4^+
DON - Dissolved organic nitrogen (DON), he amount of organically-complexed nitrogen that passes through a specified filter pore size (often 0.4 µm),	calculated	DON = SKN - NH_4^+
PON - particulate organic nitrogen	calculated	PON = TON - DON
TP - total phosphorous	measured	
TDP - total dissolved phosphorous	measured	
DRP - dissolved reactive phosphorous	measured	
TPP - total particulate phosphorous, which would include particualte organic phosphorous (POP) + any mineral-complexed P, which would be expected to be small.	calculated	TPP = TP - TDP
DUR - dissolved non-reactive phosphorous, an approximation for dissolved organic P (DOP)	calculated	DUR = TDP - DRP

N



CCCSD
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
Jul
Sep
Nov
Jan
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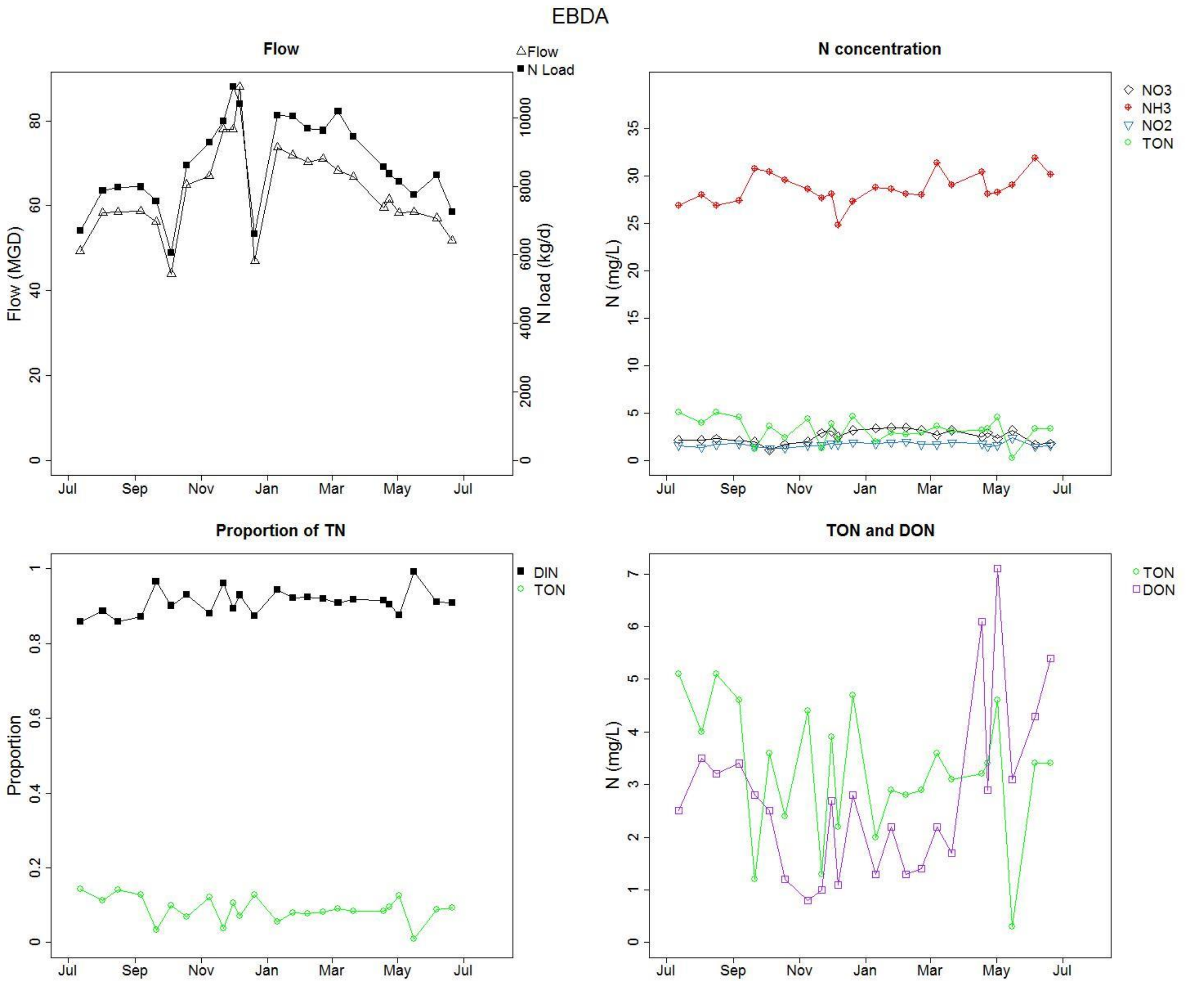
May
Jul

Figure 1

N


EBDA
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
Jul
Sep
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Jan
Mar
May
Jul

Figure 2

N

EBMUD

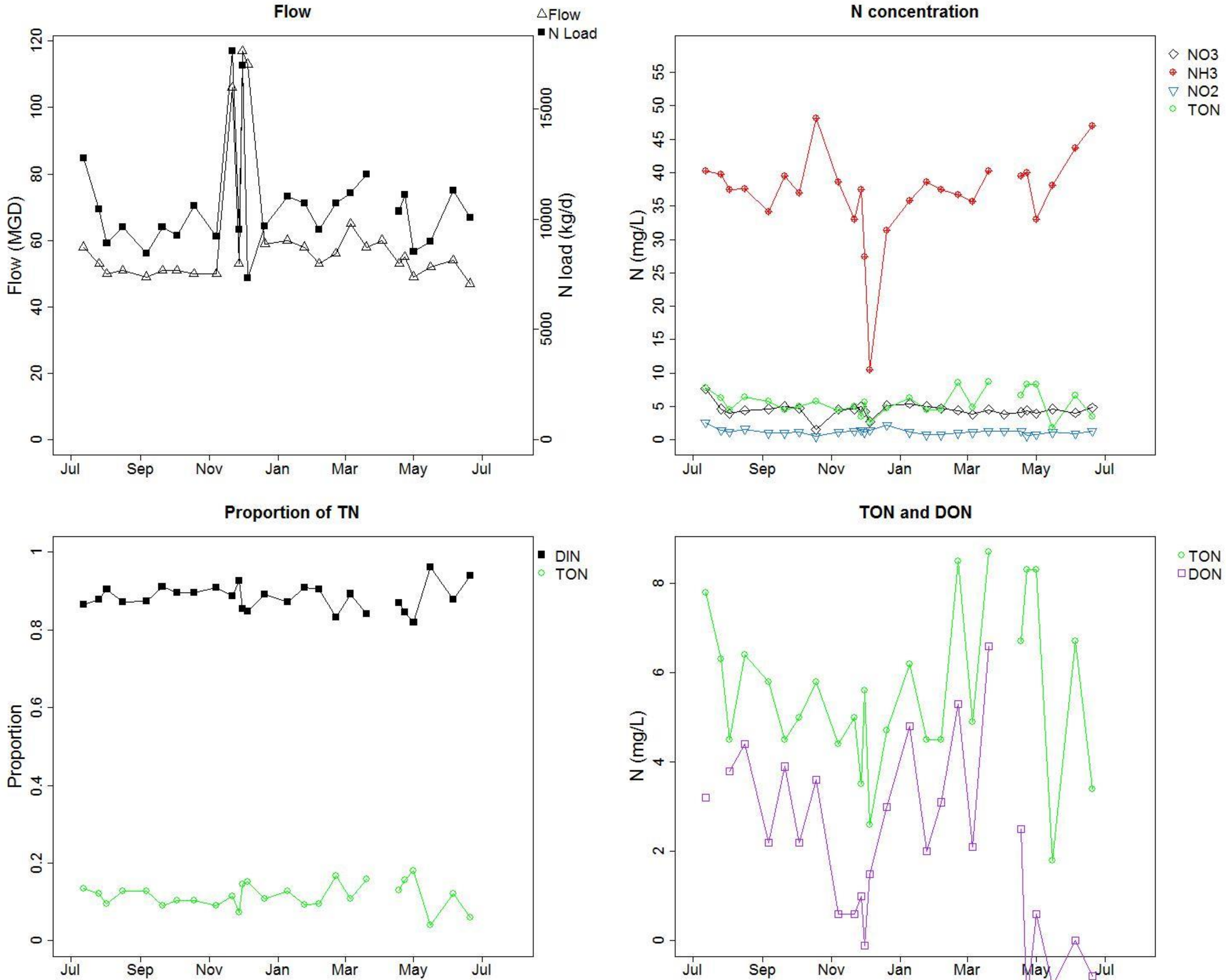
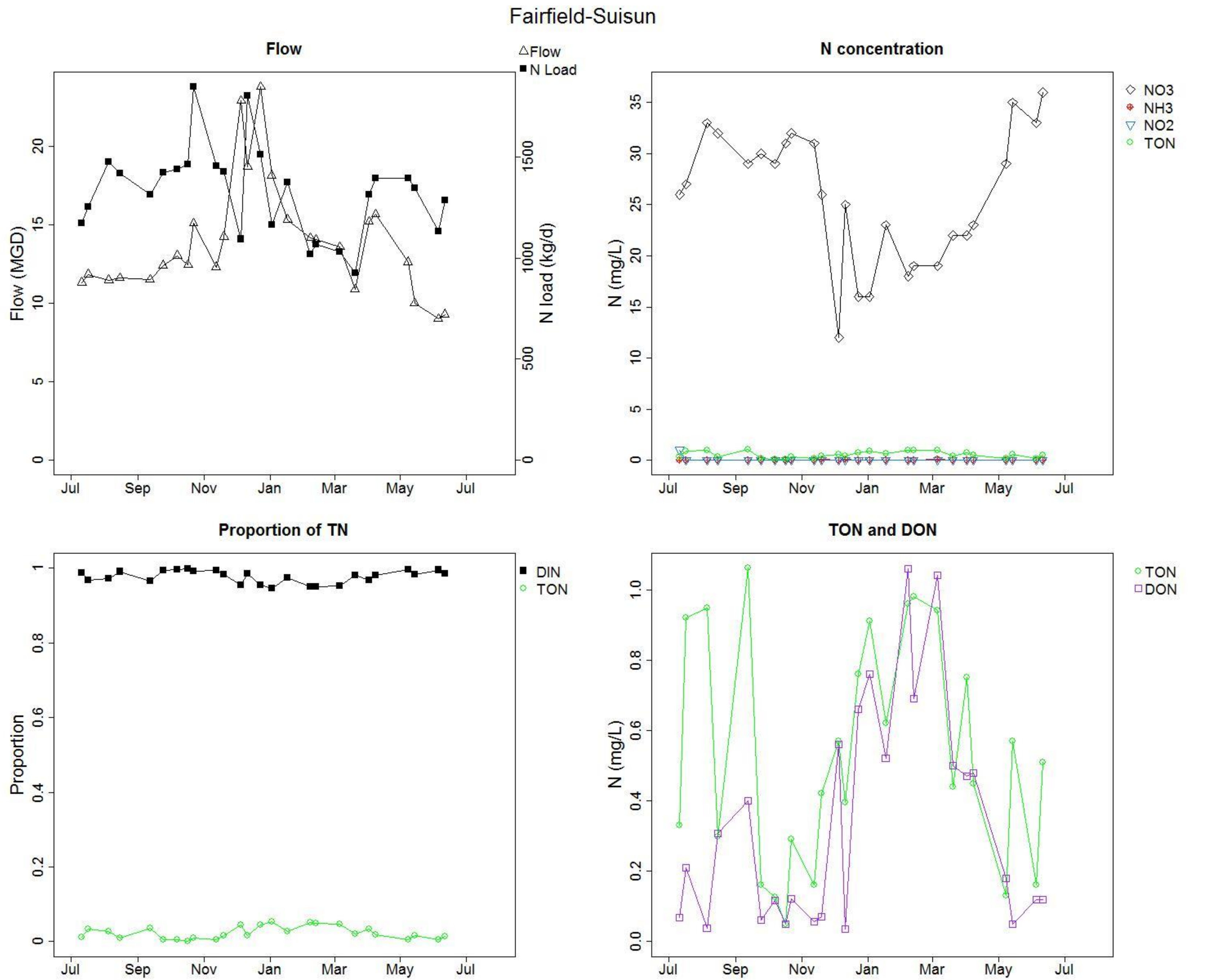


Figure 3

N


Fairfield-Suisun
Flow
△Flow
■ N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
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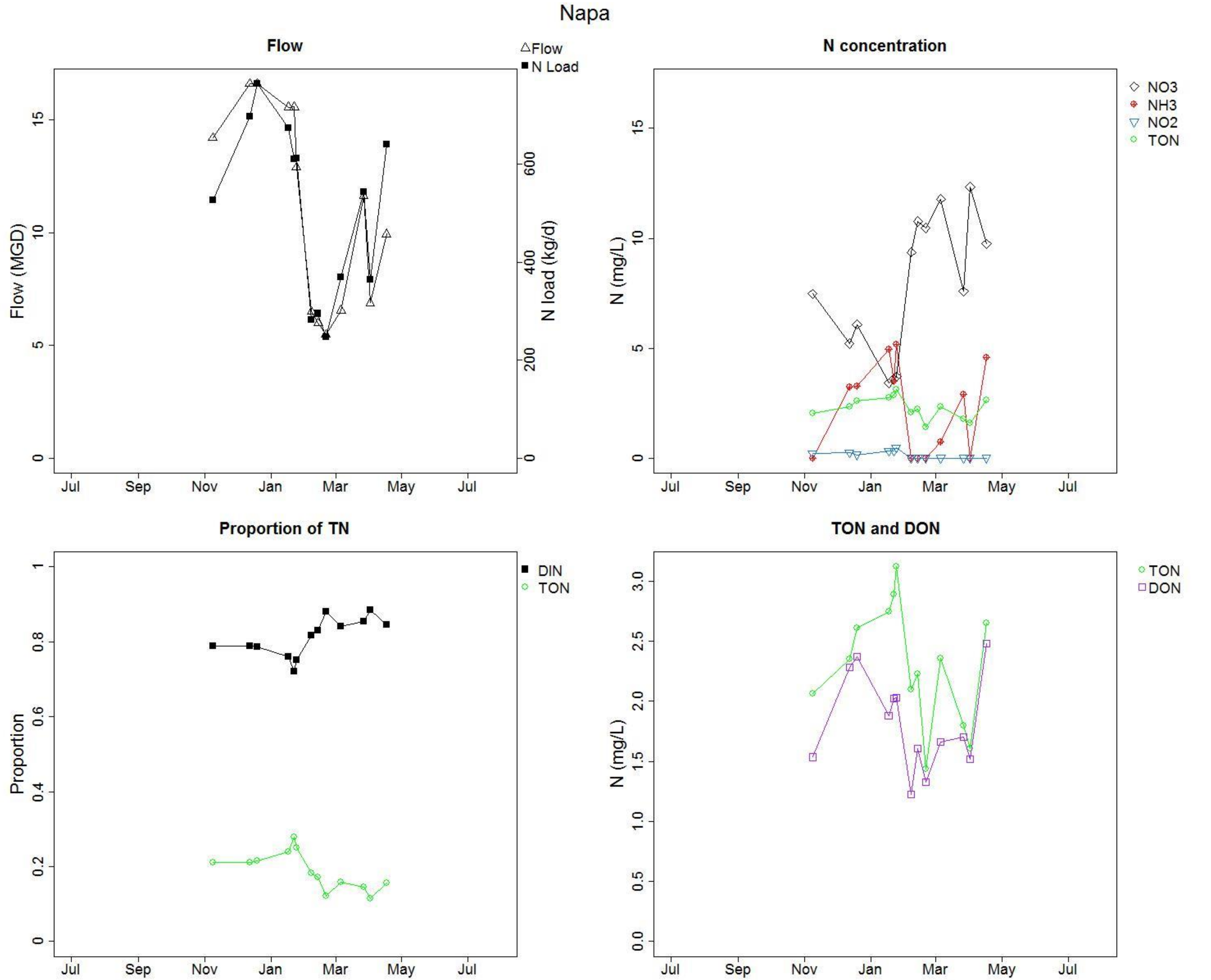
May
Jul

Figure 4

N



Napa
Flow
Flow (MGD)
N load (kg/d)
△Flow
■ N Load
N concentration
N (mg/L)
NO3
NH3
NO2
TON
Proportion of TN
Proportion
DIN
TON
TON and DON
N (mg/L)
TON
DON
Jul
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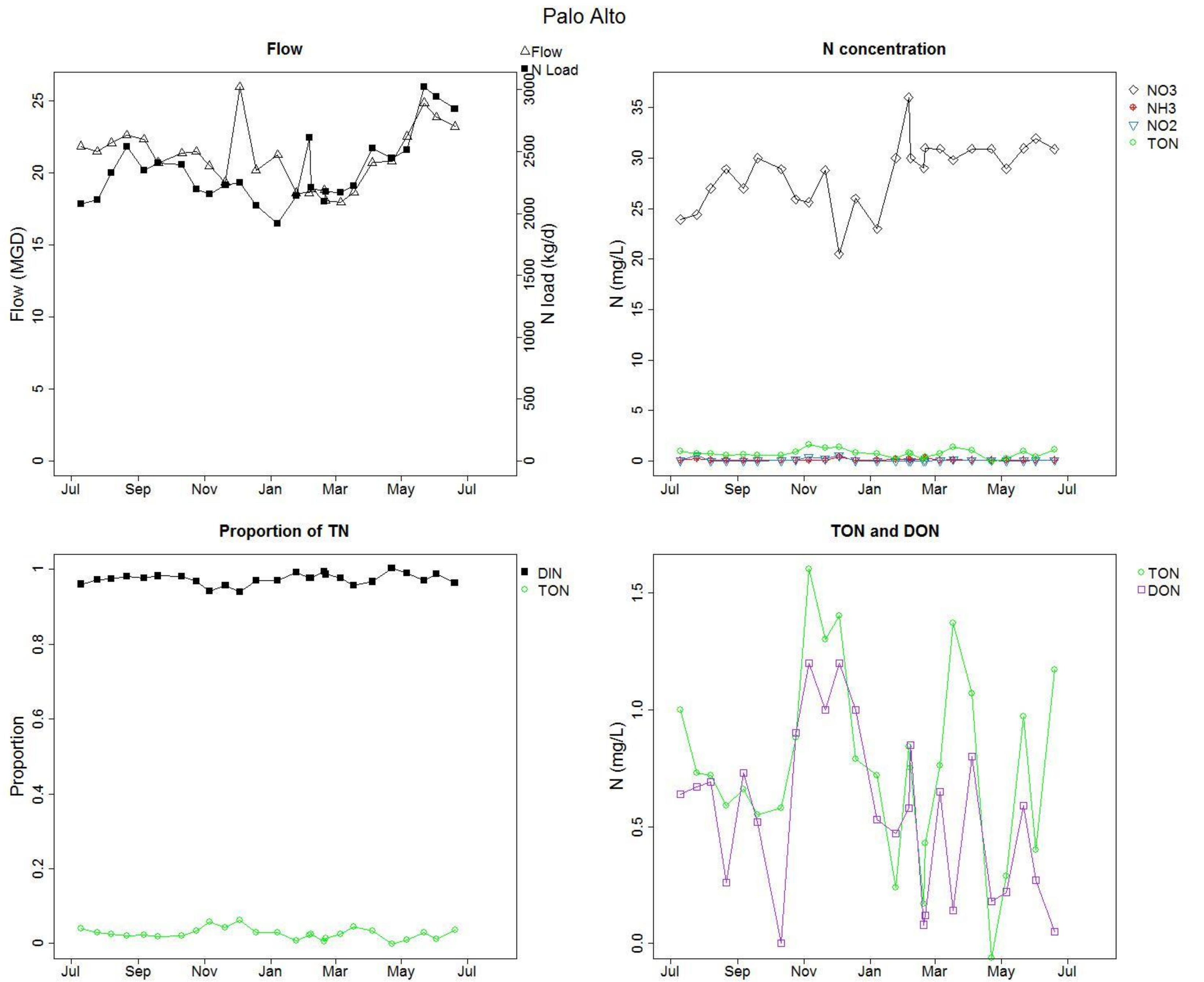
Mar
May
Jul

Figure 5

N


Palo Alto
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
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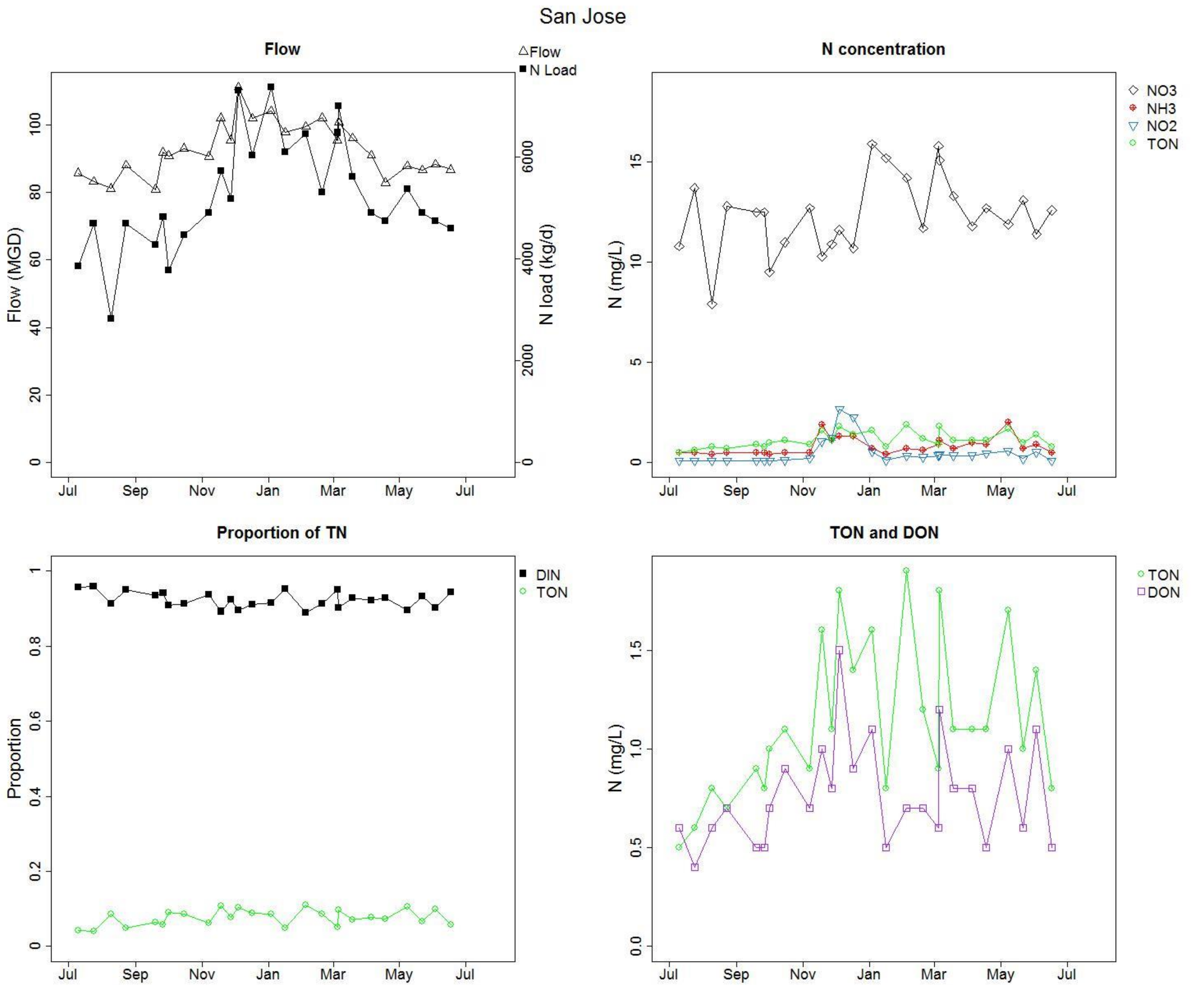
May
Jul

Figure 6

N


San Jose
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
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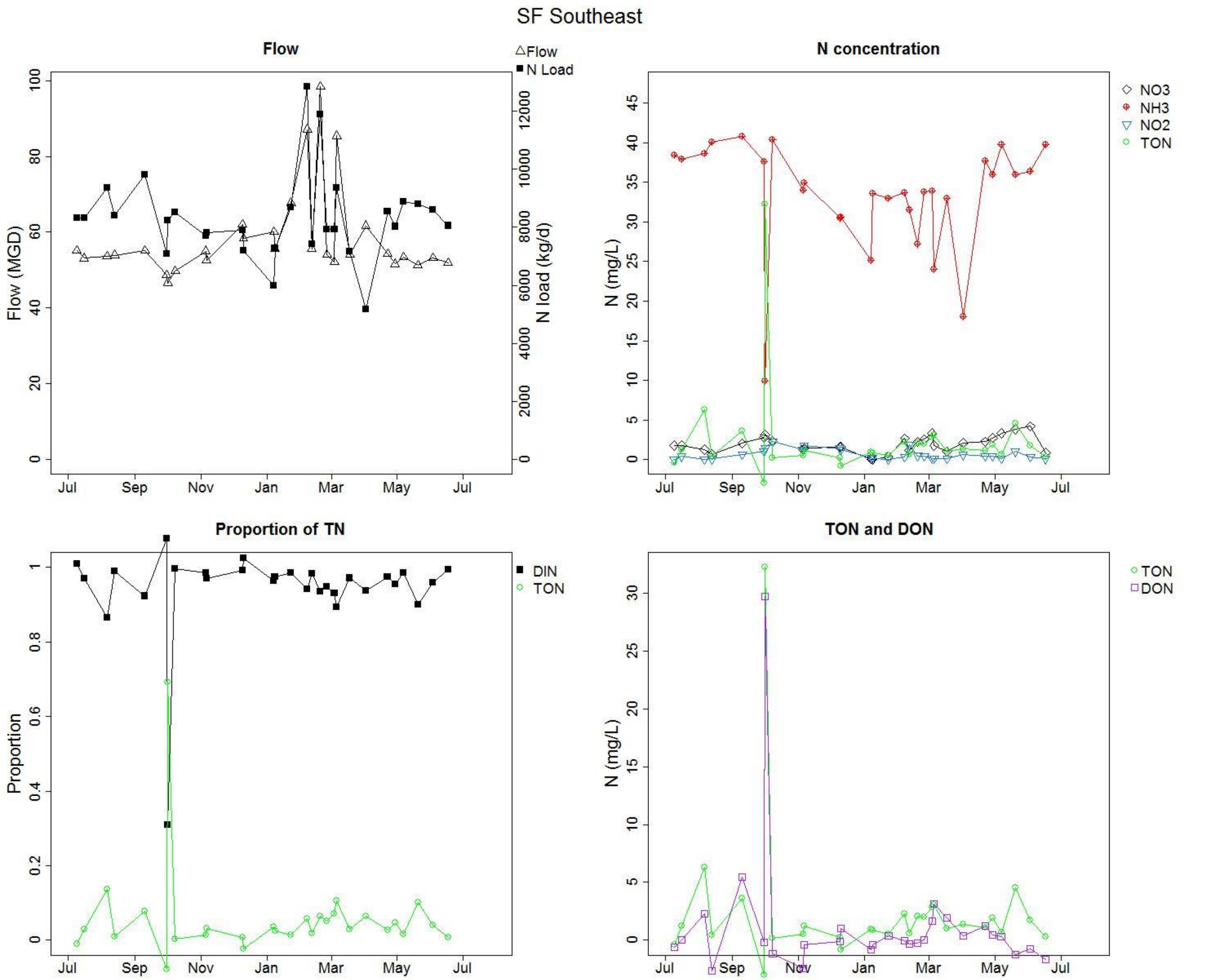
May
Jul

Figure 7

N


SF Southeast
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
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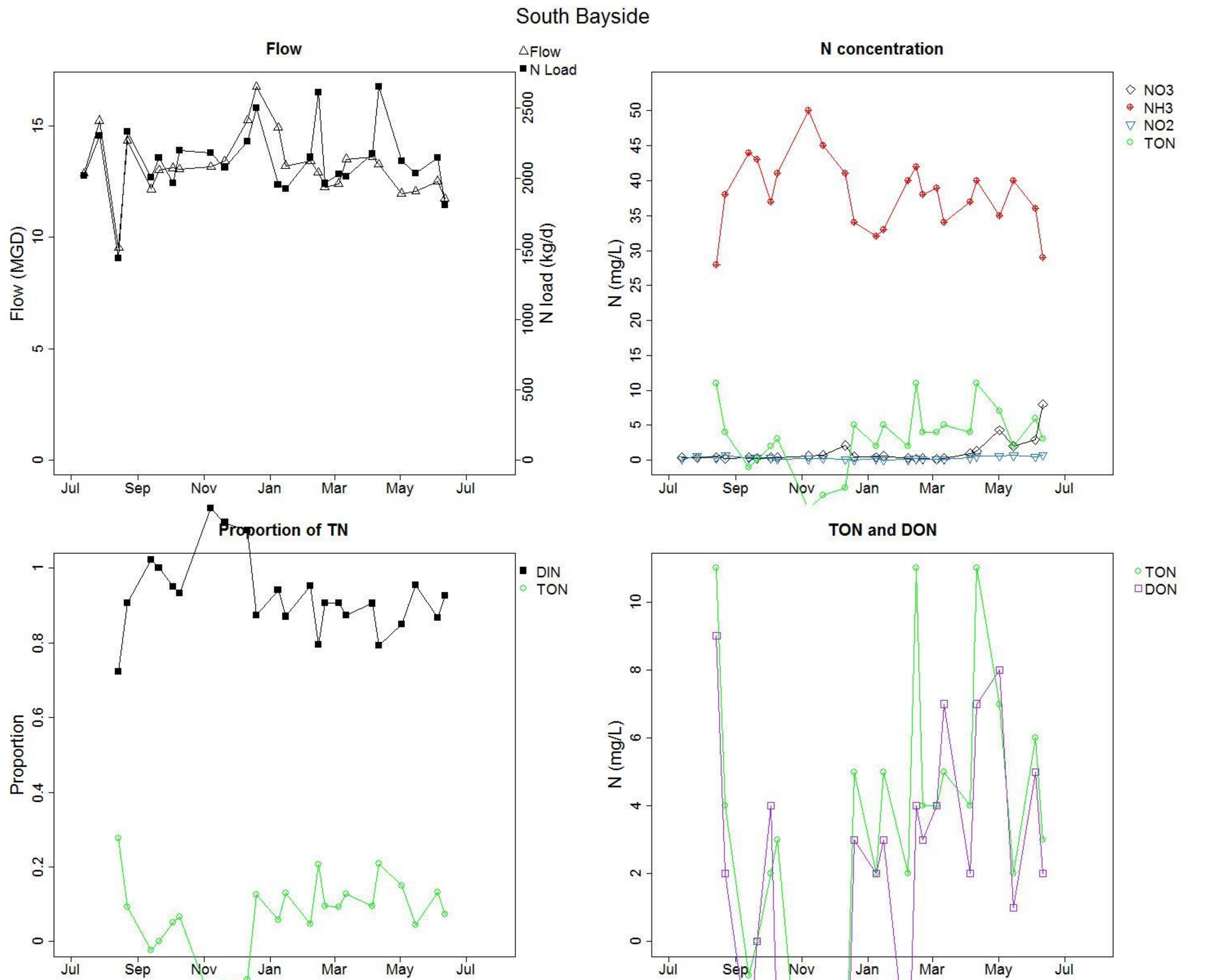
Jul

Figure 8

N


South Bayside
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
Jul
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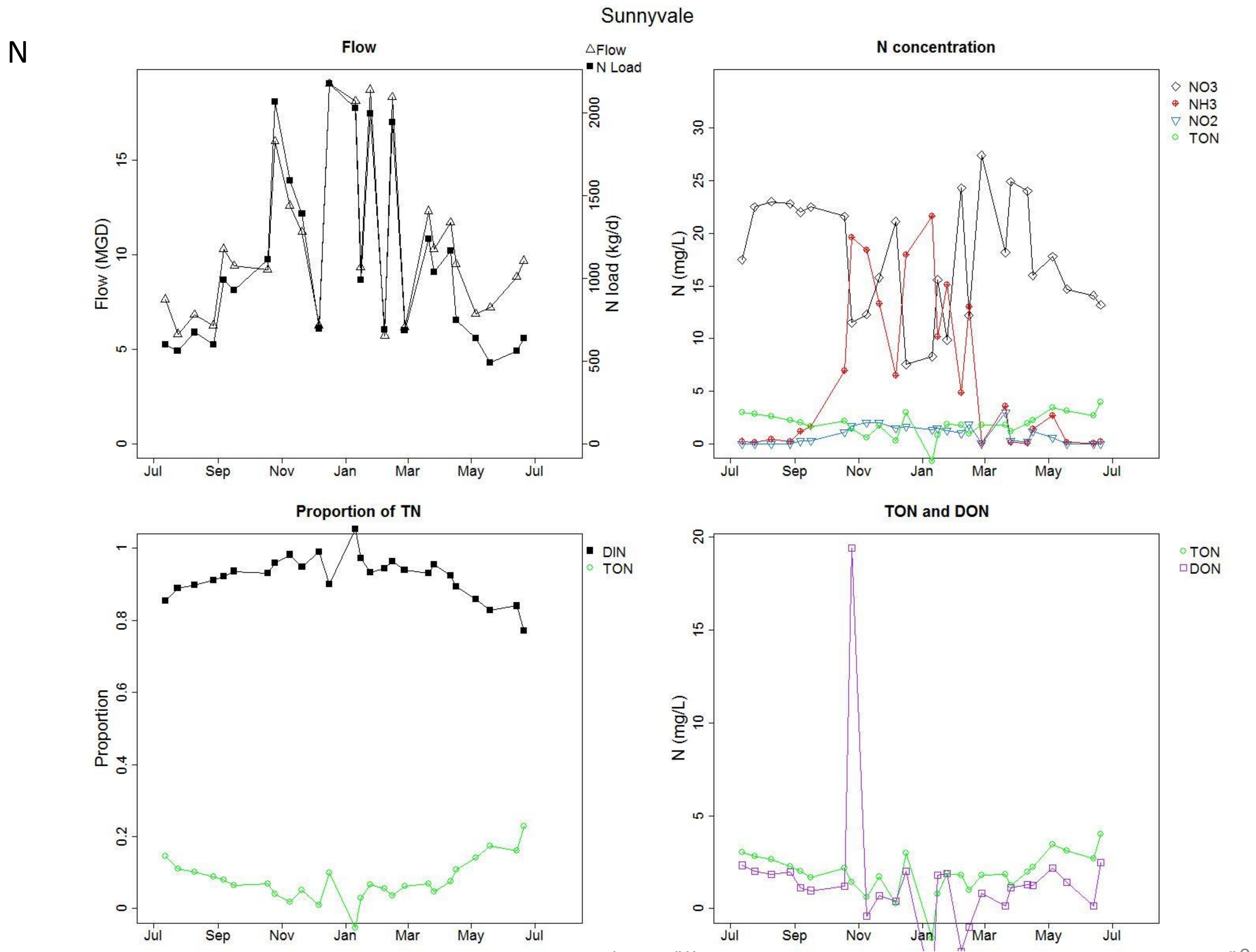
May
Jul

Figure 9



N
Sunnyvale
Flow
Flow
N Load
Flow (MGD)
N load (kg/d)
N concentration
NO3
NH3
NO2
TON
N (mg/L)
Proportion of TN
DIN
TON
Proportion
TON and DON
TON
DON
N (mg/L)
Jul
Sep
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Jul

Figure 10

P

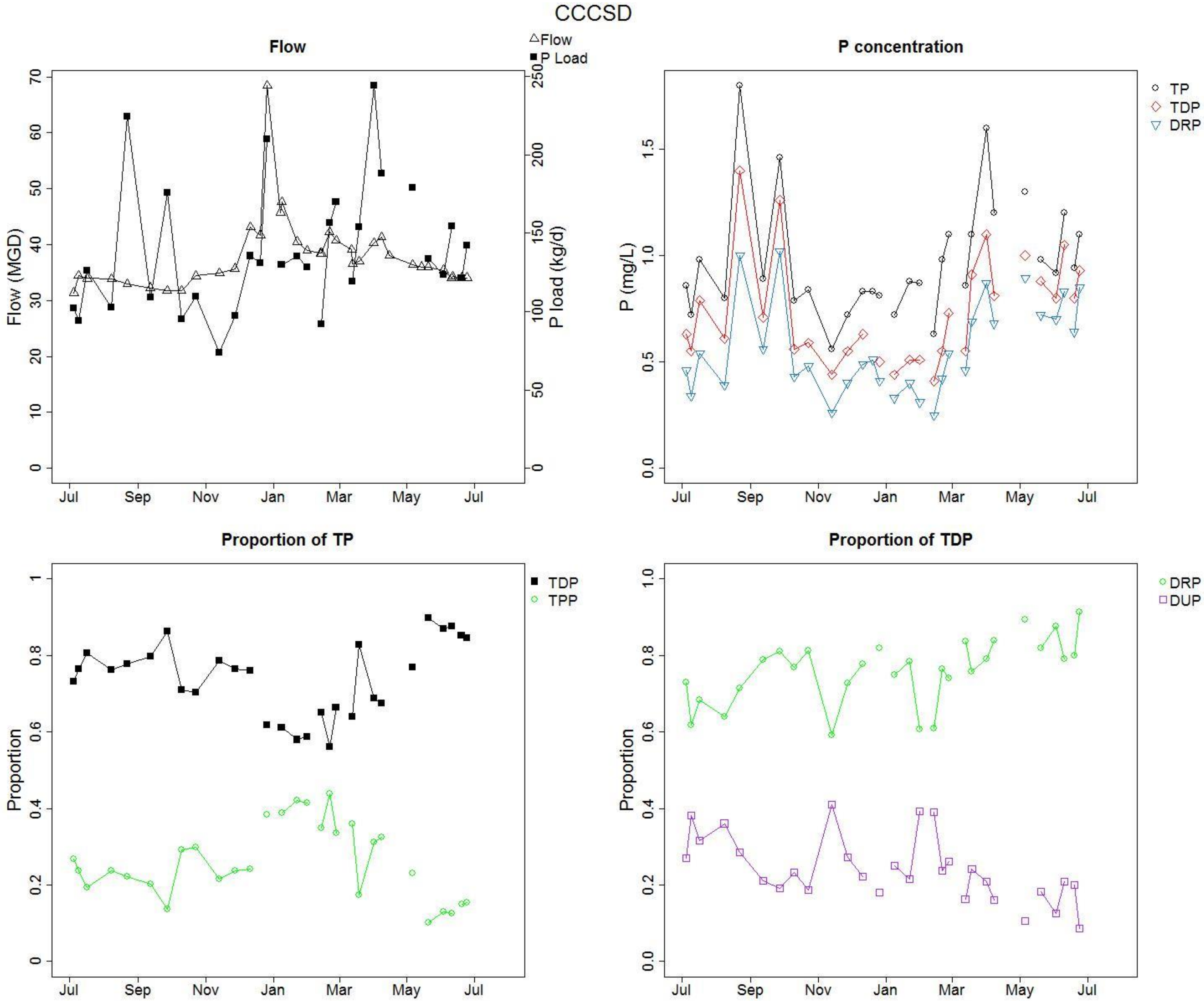
CCCSD
Flow
Flow
P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
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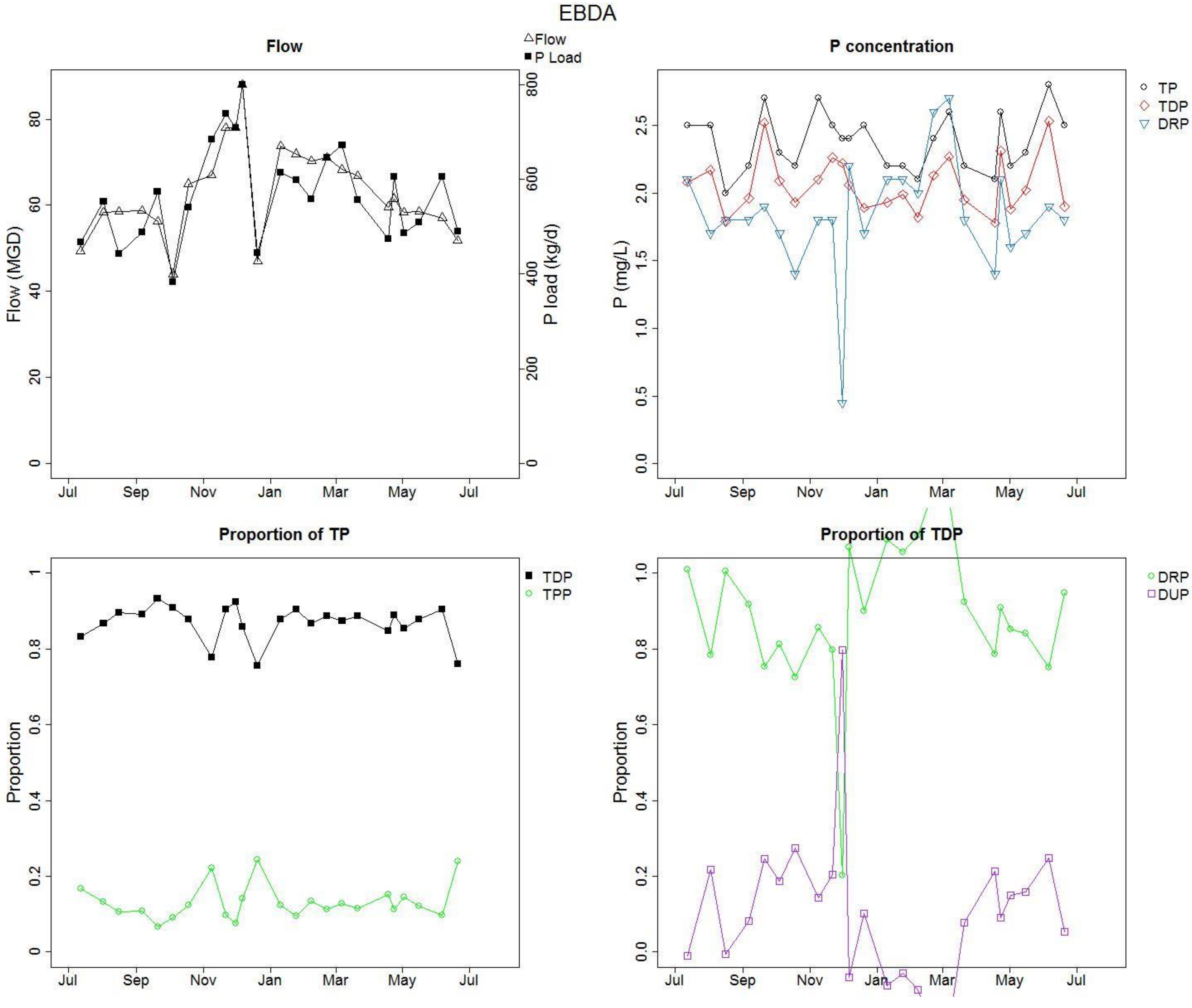
Figure 11

P


EBDA
Flow
Flow
P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
Sep
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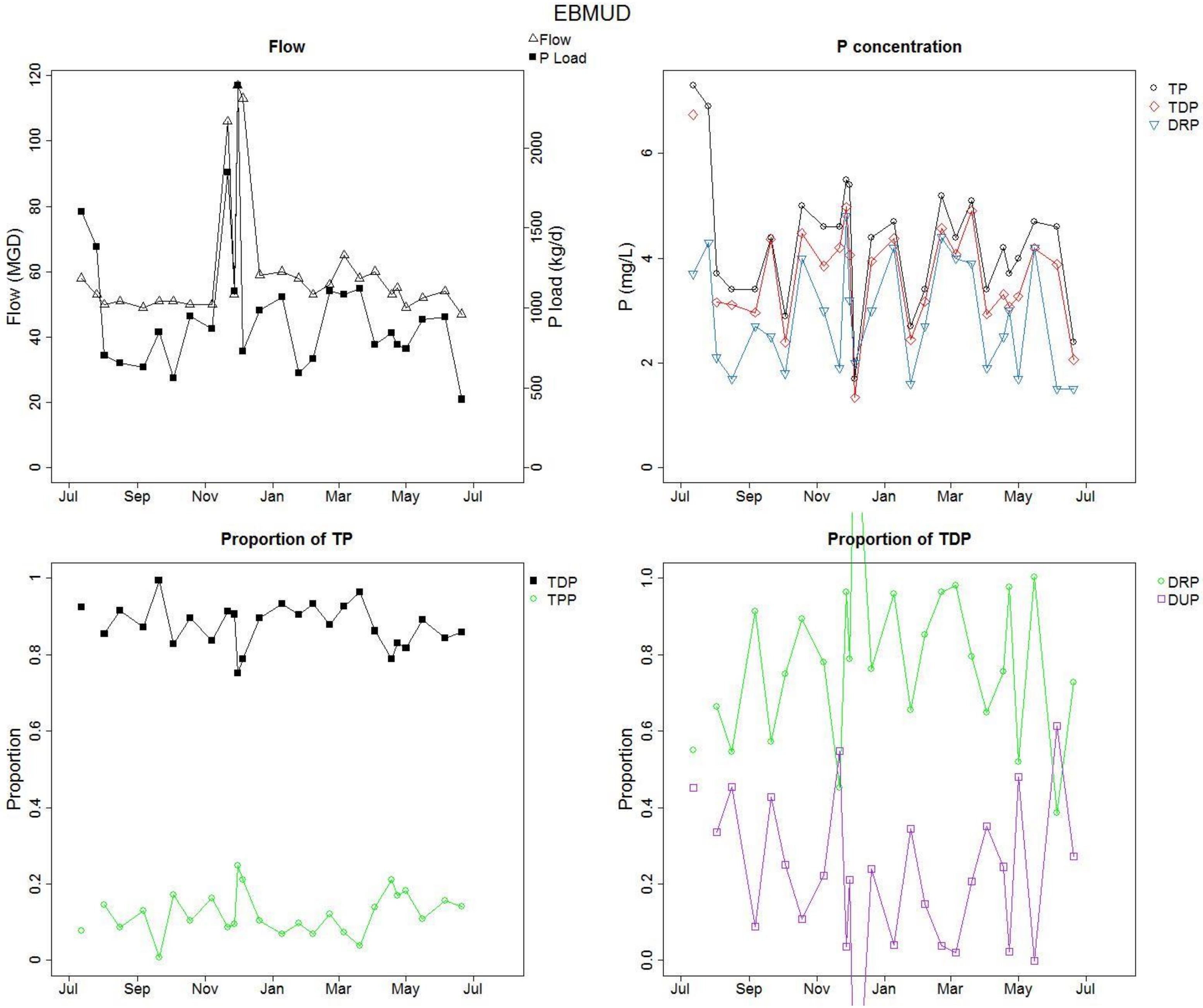
May
Jul

Figure 12

P



EBMUD
Flow
△Flow
■P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
Sep
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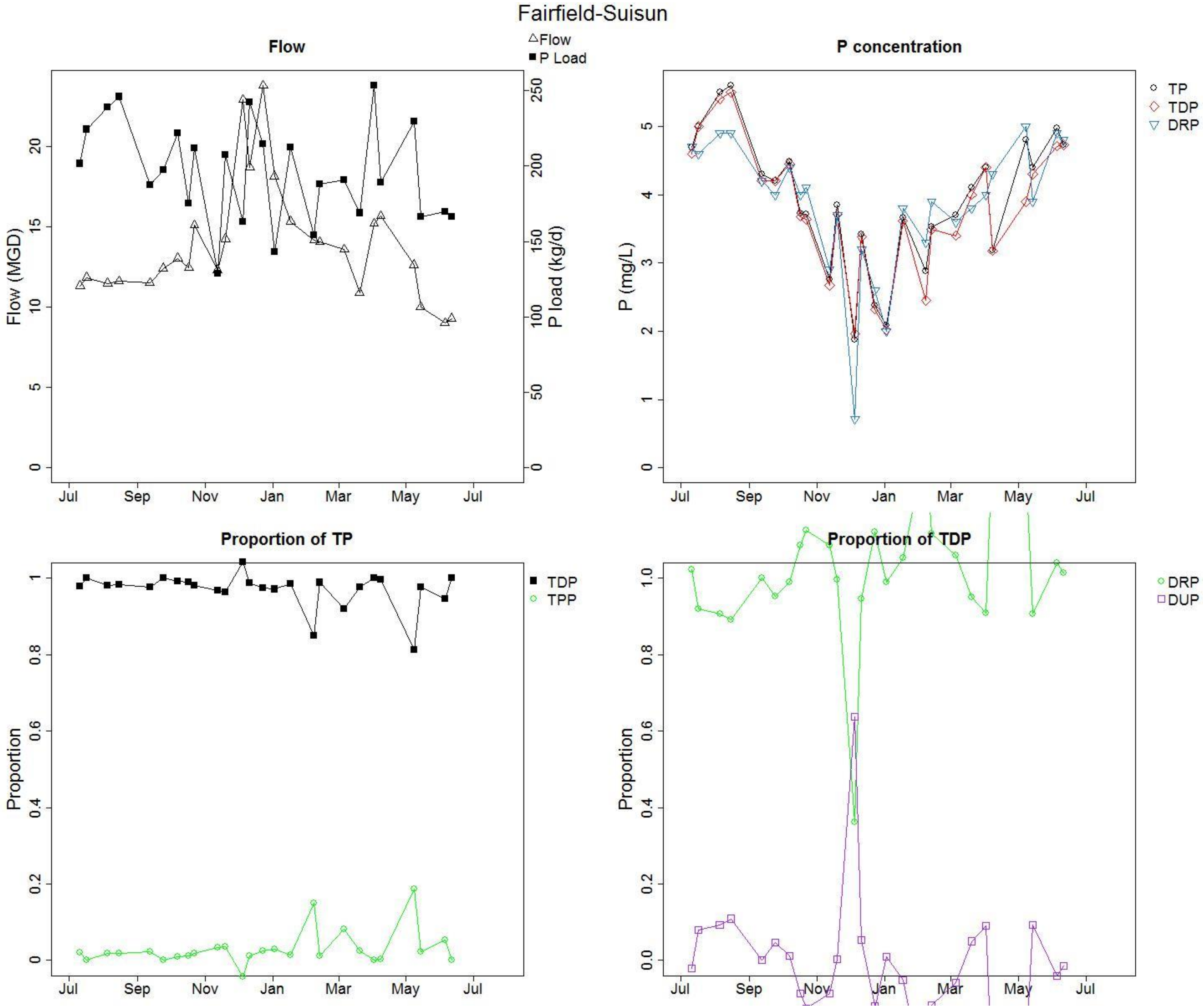
May
Jul

Figure 13

P



Fairfield-Suisun
Flow
Flow
P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
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Figure 14

P

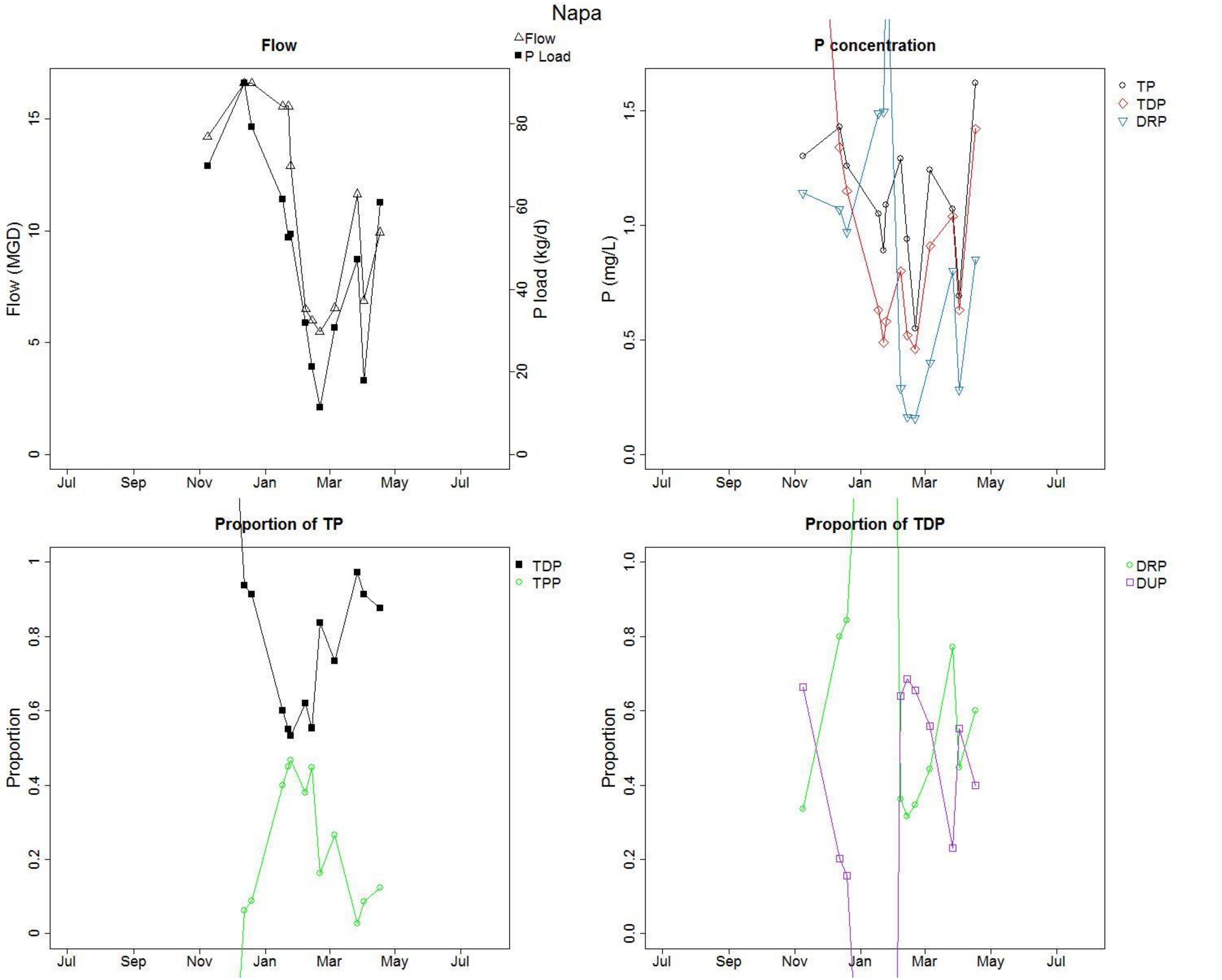
Napa
Flow
Flow
P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
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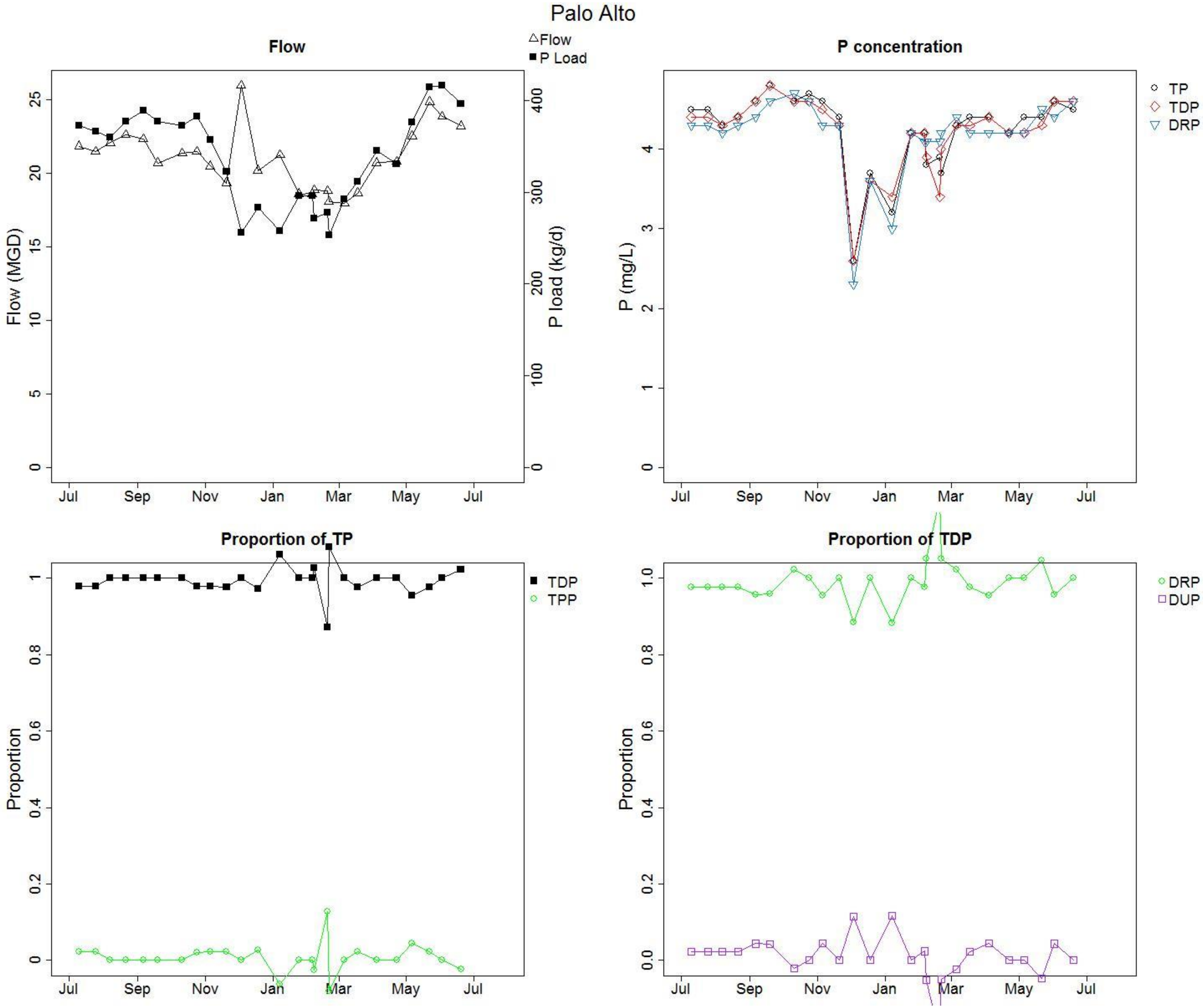
Figure 15

P



Palo Alto
Flow
△Flow
■P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
Sep
Nov
Jan
Mar
May
Jul

Figure 16

P

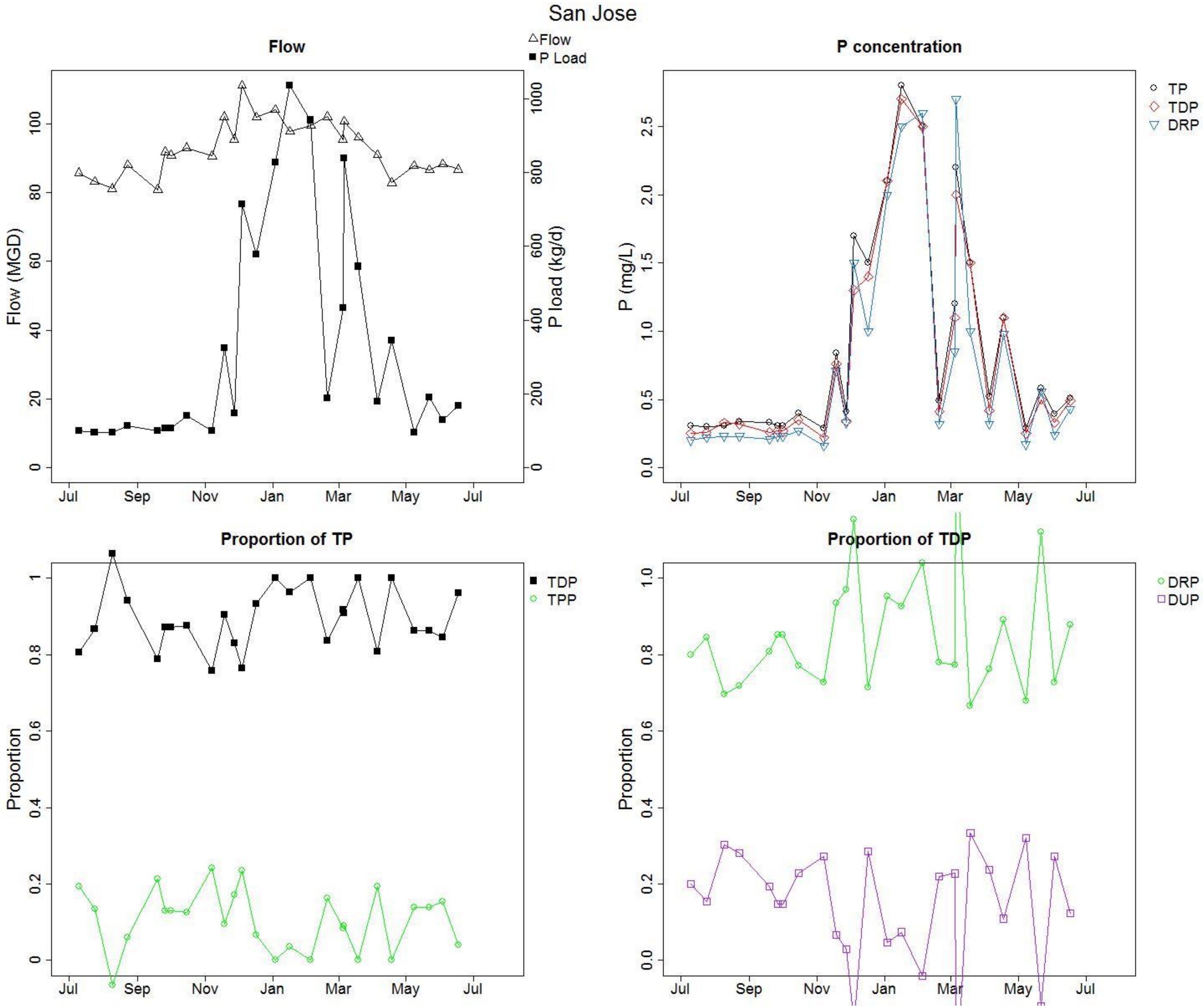
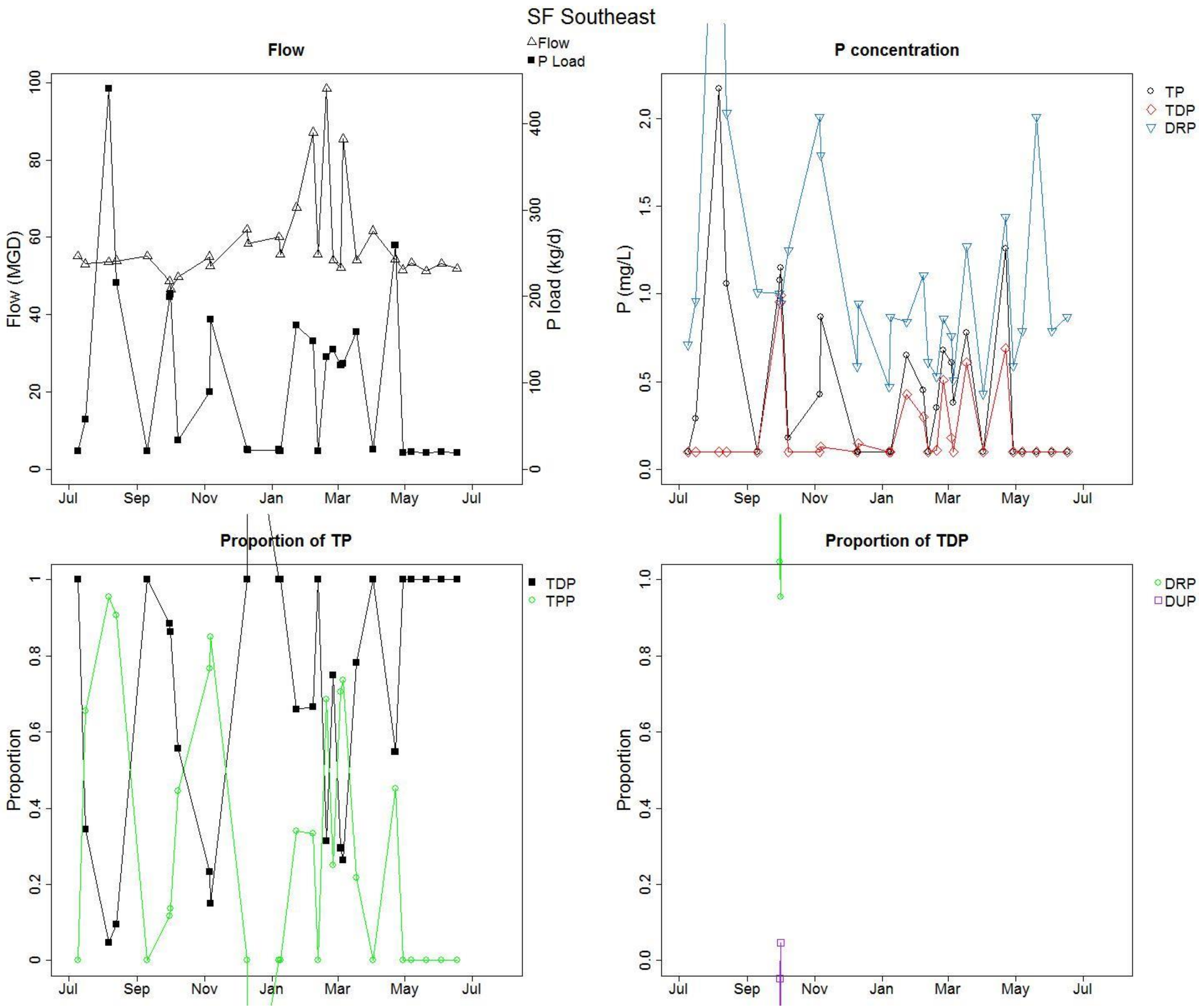

San Jose
Flow
△Flow
■P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
Sep
Nov
Jan
Mar
May
Jul

Figure 17

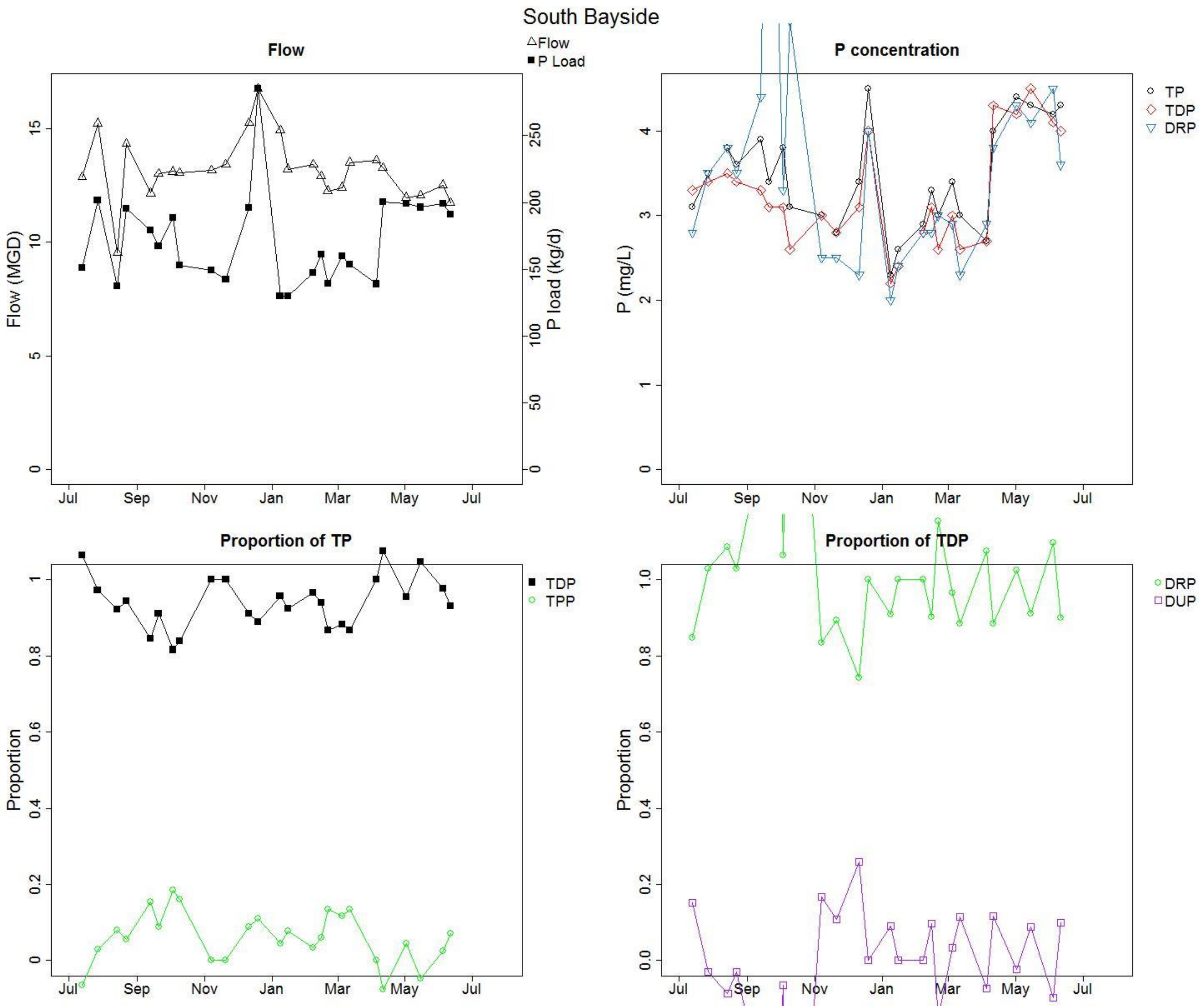
P



SF Southeast
Flow
Flow
P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul Sep Nov Jan Mar May Jul

Figure 18

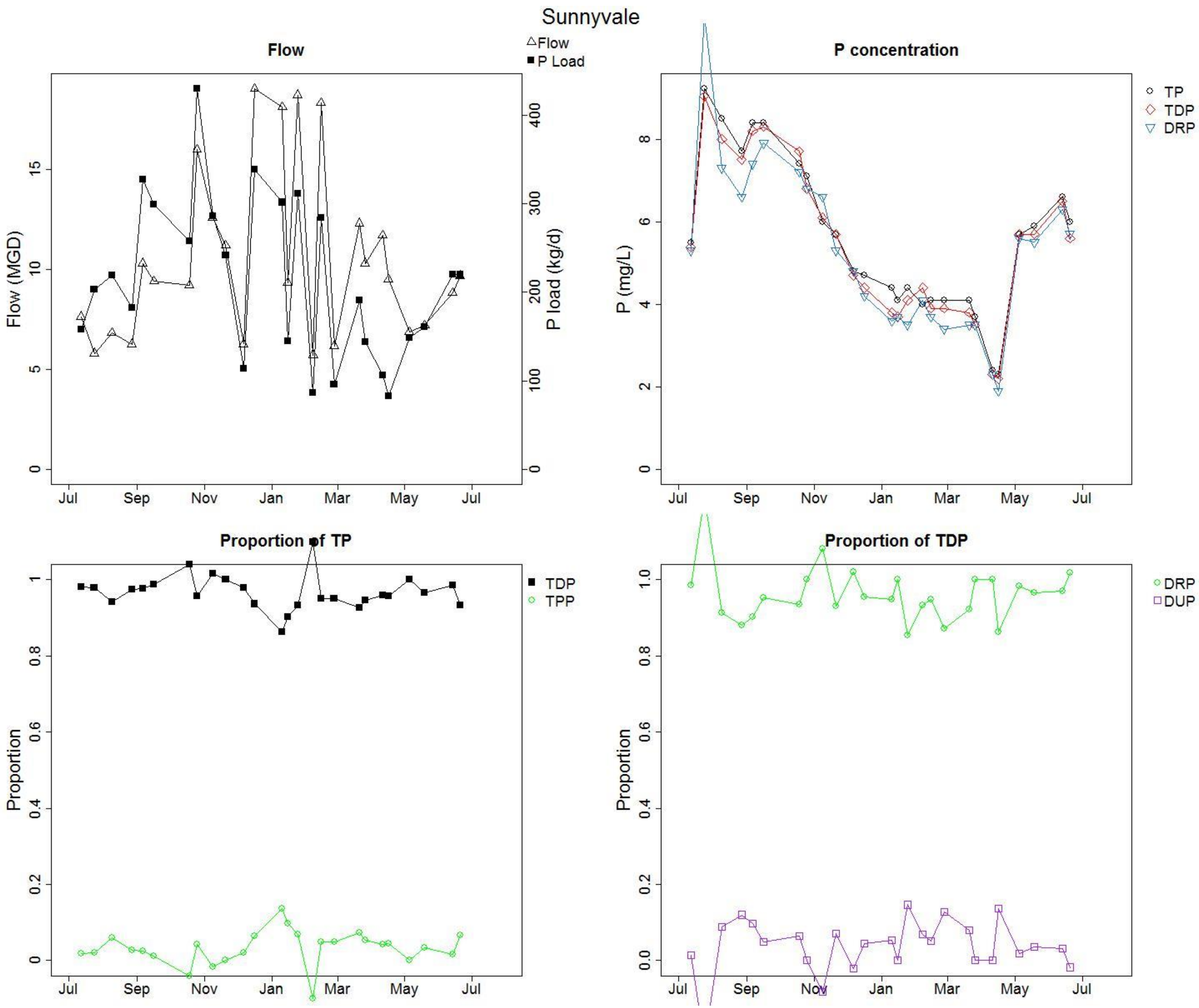
P



South Bayside
Flow
Flow
P Load
Flow (MGD)
P load (kg/d)
P concentration
TP
TDP
DRP
P (mg/L)
Proportion of TP
TDP
TPP
Proportion
Proportion of TDP
DRP
DUP
Proportion
Jul
Sep
Nov
Jan
Mar
May
Jul

Figure 19

P



Sunnyvale
Flow
△Flow
■P Load
Flow (MGD)
P load (kg/d)
0
5
10
15
0
100
200
300
400
Jul
Sep
Nov
Jan
Mar
May
Jul
P concentration
TP
TDP
DRP
P (mg/L)
0
2
4
6
8
Proportion of TP
TDP
TPP
Proportion
0
0.2
0.4
0.6
0.8
1
Proportion of TDP
DRP
DUP
0.0
1.0

Figure 20