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The Use of C/N Ratio in Assessing the Influence of Land-Based Material in Coastal Water of South Sulawesi and Spermonde Archipelago, Indonesia

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Measurement of C-N magnitude and C/N ratio from particulate matter is used to explain the source of terrestrial and sea particulates. Therefore, this study aimed at using C/N ratio in assessing land-based material in the west coast of Spermonde area, Indonesia on suspended matter. Samples of SPM were collected in two seasons (transition and dry seasons), in coastal waters of Tallo, Maros, and Pangkep estuaries. The results of research showed that C_{tot} was more abundant than was N_{tot} in particulates from river rather than from sea region, reflecting most of the terrestrial organic matter stored before meeting with sea. C/N ratio on the west coast of South Sulawesi was in the range of 7–19.7, showing that organic matter in Tallo estuary in transition season was dominantly autochthonous, while in dry season it was found to be dominantly terrigenous organic matter that gave an indication that land factor was significant in waste supply. The same thing was found in Maros estuary and Pangkep estuary in transition season and dry season; at all points of observation there were findings of particulates coming from terrigenous organic matter. Percentage of nutrient absorbed in particulate was low and could become a eutrophication stressor, where SPM found only ranged from 9.60 to 55.1 mgL^{-1} with maximum average in dry season and minimum in transition season. On the contrary, POM was maximum in transition season and minimum in dry season with dominant particulate organic matter source from the sea itself.

Keywords: C/N, SPM, POM, coast, spermonde, indonesia

INTRODUCTION

Spatial variation of carbon and nitrogen signals that organic matter input from antropogenic (Seitzinger et al., 2010; Kennish and Elliott, 2011; Gao et al., 2012; Strokal and Kroeze, 2013) has a more significant effect on distribution than does natural process (Kauppila et al., 2005; Tewfik et al., 2005; Vizzini and Mazzola, 2006). Through autochthonous and allochthonous, this matter is given to the sediment that supports sediment biogeochemical process, and nutrient flux is produced (Jensen et al., 1990).

Ratio of total element of carbon (C_{tot}) and total nitrogen (N_{tot}), usually stated as C/N or C_{tot}/N_{tot}, has been largely used as proxy to explain the source and fate of organic matter in the environment of waters (e.g., Gordon and Goni, 2003; Wu et al., 2007; Zhang et al., 2007; Ramaswamy et al., 2008), and it enables to discriminate pollutant origins related with sediment organic matter. Degradation of organic matter will probably modify C/N ratio, for example C/N ratio will increase during the sinking of algae organic matter particulate into pond water (Twichell et al., 2002); on the contrary, the process of humification and mineralization in land environment will significantly lower C/N ratio (e.g., Sorensen, 1981; Schmidt et al., 2000). This process produces terrigenous organic matter component, generally the value of C/N ratio for organic matter of sea is 7, organic matter of soil 8–20, and the ratio bigger than 20 is for organic matter of terrigenous (Emerson and Hedges, 1988; Meyers, 1994).

Nutrient absorbance in sediment suspension is the fraction of anorganic particulate matter as an important contributor for nutrient (Qu and Kroeze, 2012; Testa et al., 2013). Fine sediments in suspension probably absorb nutrients and, therefore can obstruct eutrophication (Middelburg and Levin, 2009; Testa and Kemp, 2012; Xu et al., 2013). The strong evidence for this is if SPM∼10 mg/l usually 20% of nutrition is in the form of particulate in estuary waters, and this fraction increases to 60% at SPM∼100 mg/l, and 80% at SPM∼1000 mg/l (Middleburg and Herman, 2007).

With the condition of waters along the west coast of South Sulawesi that is productive, there is a mangrove ecosystem, field of sea grass (*Potamogeton* spp.), and Spermonde coral reef. Ecosystem of Spermonde coral reef is part of Coral Triangle Initiative that plays a crucial role in supporting the economy life of coastal society and food sustainability. It is not impossible, highly potential to undergo a threat of waters quality decrease due to organic and anorganic waste from terrestrial, carried by big rivers. This factor has been indicated to cause variability of chlorophyll-a spatially and temporarily (Nasir et al., 2015). A different composition of organic matter in waste is relative to original organic matter of sea, so it will probably help to trace waste extension in coastal area. In this study, carbon and nitrogen in particulate are used to trace organic source in coastal area. Therefore, the main objective of this research is to analyze matter transport in the west coast of South Sulawesi based on C/N ratio. Study of that thing is highly needed to give fundamental and comprehensive understanding about the impact of water quality change on coastal environment and sea.

MATERIALS AND METHODS

Study Area

The location of research is in the southern part of Makassar Strait or in the southwest side of South Sulawesi Peninsula (*Spermonde Shelf*), especially the waters around the estuaries of big rivers, i.e., Tallo estuary 05°57 S, 119°26 E–05°11 S, 119°25 E, 04°59 S (11 stations), Maros estuary 119°28 E (7 stations), and Pangkep estuary 04°52 S, 119°30 E–04°49 S, 119°29 E with 15 stations (**Figure 1**). Water sampling was done in transition season (April 2013) and dry season (June 2013). Based on the climate on the west coast of South Sulawesi in its normal condition, the rainy season is from November to April with its peak in the month of January, and dry season is from May to October. Tallo estuary is the estuary of a river that divides Makassar, the capital city of South Sulawesi, and the river leads up to Makassar Strait. Tallo river is a river whose estuary area is highly affected by sea water tide and the bottom of the river lies lower than the sea surface level, so it causes salt water to be available for as long as 10 km. Tallo River has a length of 66 km and an area of 417 sq.km DAS. Around its river mouth there are a very dense residential area and some large industries. Meanwhile, Maros, and Pangkep estuaries largely get the flux from agriculture and fishery activities that also lead up to Makassar Strait.

Sampling and Sample Preparation

Water sampling for SPM is done by using a vacuum pump and 5-liter niskin bottle at the depth of 1–2 m below the river mouth surface and 5 m below sea surface ($n = 6$). Preparation of water samples for SPM analysis is done by using gravimetri method, that is by filtering water sample on GF/F filter (0.7 μm) using a vacuum pump (pressure 200 mm Hg). GF/F filter paper is first heated in an oven at the temperature 105°C for 2 h, and is then weighed (a mg). Sample filter, is dried in the oven at the temperature of 105°C for 2 h, and is then cooled in desicator. After that, the filter paper is weighed (b mg) (Strickland and Parson, 1965). Value of SPM (mgL^{-1}) is then calculated based on the difference between b mg and a mg divided by the filtered sample volume (L).

Sample Analysis

Carbon and Nitrogen Analysis

Total concentration analysis of carbon, organic carbon, and nitrogen in SPM is done by using Eurovector EA 3000 in the Laboratory of Chemical Analysis ZMT Bremen, Germany. After deleting anorganic carbon by acidation with 1 N HCl, filter is dried at the temperature of 40°C and then the total of carbon and nitrogen is analyzed with Elemental Analyzer Eurovector EA 3000. In the analysis, the sample is oxidized at the temperature 1060°C and product oxidation is transported by gas (He) carrier through a reducing tube where NO_x is reduced to be N_2. After removing water and halogen from the development of CO_2 and N_2, gas is separated and measured by thermal conductivity detector (Baum et al., 2007). The relative deviation standard for this method is ±4.5%.

Water Discharge

Water discharges from Tallo, Maros, and Pangkep rivers are based on the measurement of water discharge shown by the observation from flow direction and water tide range. The water discharges on sampling locations are obtained through an equation given by Gordon et al. (1992) that is by multiplying the speed of average flow (V) measured by using current meter with the area of river cross-section (A) to calculate the river total discharge (Qi) (**Table 1**).

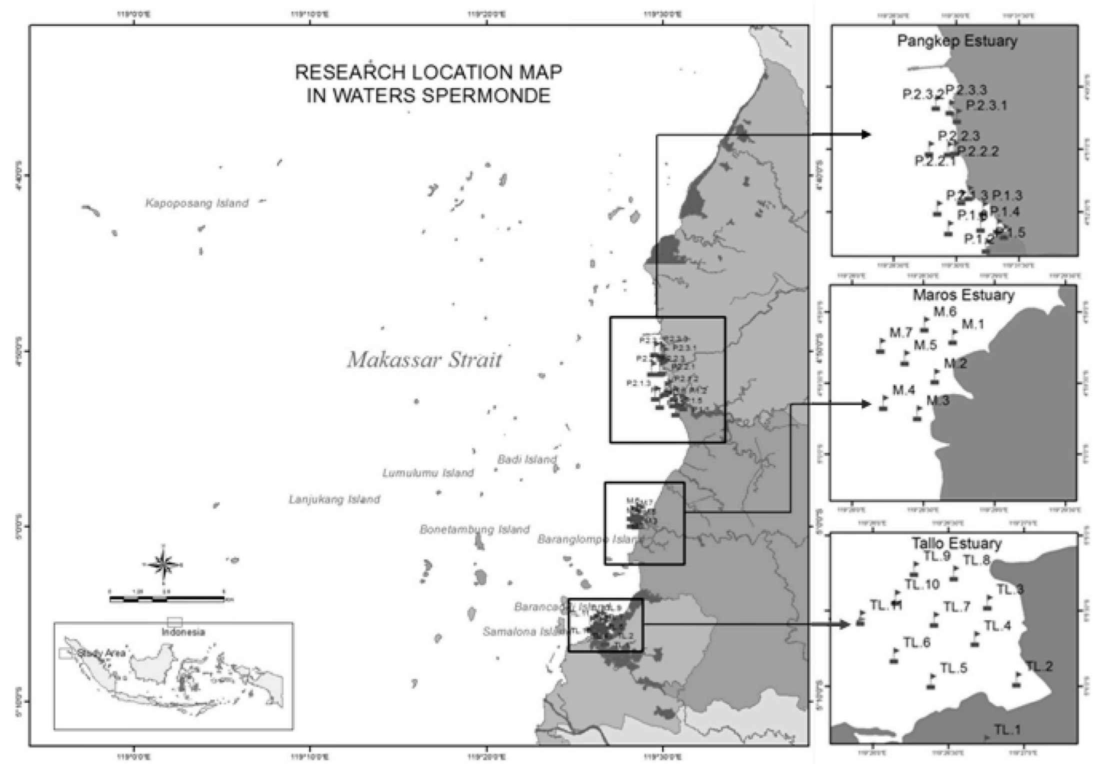

FIGURE 1 | Map of research locations in the waters on the west coast of South Sulawesi, sampling location is marked with a box. TL, Tallo estuary; M, Maros estuary; P, Pangkep estuary. 1, 2, 3,...,11, sampling location points.

TABLE 1 | Comparison of river water discharges, SPM (*Suspended Particulate Matter*), POM (*Particulate Organic Matter*) and chlorophyll-a in transition season and dry season on the west coast of South Sulawesi, Indonesia.

Season	Locations	Waters Discharge ($\times$ 10 ^{4}m^{3}s^{-1})	SPM (mgL^{-1})	POM (μgCL^{-1})	Chl-a (mgm^{-3})
Transition	Tallo estuary	159	16.0–50.1	1622–5615	2.10–11.9
(April 2013)	Maros estuary	31	28.3–39.2	2723–3772	0.53–1.58
	Pangkep estuary				
	P1	60	19.0–37.2	458–738	3.95–6.12
	P2	48	9.60–37.3	341–650	0.51–1.97
Dry	Tallo estuary	94	20.7–44.1	1880–3785	0.38–7.68
(June 2013)	Maros estuary	18	20.0–34.8	1806–3646	0.87–4.08
	Pangkep estuary				
	P1	36	35.2–53.1	3215–5178	2.03–4.28
	P2	28	23.0–55.1	2892–4234	1.30–2.07

RESULTS

Water Discharge and SPM

Water discharge of Tallo estuary is very high in two seasons of observation on the west coast of South Sulawesi, namely around 94–187 $\times$ 10^4 m^3s^{-1} and minimum water discharge in Maros estuary is around 18–33 $\times$ 10^4 m^3s^{-1} with its maximum discharge in transition season and minimum in dry season (**Table 1**). Next, **Table 1** shows that water discharge has an implication on particulate weight increase in transition season, where the average weights of SPM in Tallo, Maros and Pangkep estuaries are 33.5 $\pm$ 15.8 mgL^{-1}; 33.0 $\pm$ 5.59 mgL^{-1}; 27.1 $\pm$ 8.93 mgL^{-1} (P1); 21.3 $\pm$ 7.71 mgL^{-1} (P2); on the contrary, in dry season the water discharge does not have an implication on particulate weight, where the average weights of SPM are 29.1 $\pm$ 9.22 mgL^{-1}; 29.6 $\pm$ 8.32 mgL^{-1}; 41.3 $\pm$ 8.04 mgL^{-1} (P1); 37.1 $\pm$ 11.3 mgL^{-1} (P2).

The magnitude and speed of flux from terrestrial is largely affected by the season implicating on C_{tot} and $\%N_{tot}$, where the water discharges in Tallo and Pangkep estuaries are larger than the discharge in Maros estuary (**Table 1**); therefore, C_{tot} and $\%N_{tot}$ are significantly different at $p < 0.05$ and in Maros estuary it is not significantly different.

Percentage of C_{tot}, N_{tot}, Ratio of C/N and C_{org}

This comparison of C_{tot} and N_{tot} values is spatially and temporarily different, $\%C_{tot}$ is maximum in particulates on all locations (Tallo, Maros and Pangkep estuaries) and observation seasons (transition and dry seasons) compared to $\%N_{tot}$ (**Figure 2**) especially in transition season. Percentage of C_{tot} and N_{tot} from maximum to minimum in Tallo, Pangkep and Maros estuaries is in the ranges of 1.30–6.42%; 0.13–0.97%, 1.05–4.52%; 0.13–0.42%, 0.83–2.32%; 0.04–0.17% in transition season, while in dry season it is in the ranges of 1.15–2.05%; 0.15–0.29%, 0.75–2.15%; 0.10–0.25%, 0.77–1.32%; 0.09–0.15%. The change of this percentage decreases toward sea especially at distance >875.9 m in Tallo estuary, >488.2 m in Maros estuary and >419.5 m in Pangkep estuary (**Figure 2**).

By carefully examining **Figure 2**, C/N ratio at the distance of 0–1652.7 m in Tallo estuary in transition season is 7, and at the distance of 2240.5 it is 10, while in dry season at the distance of 0–875.9 m it is 7, and at the distance of 1297.9–2240.5 m it is 8. C/N ratio in Maros estuary at the distance of 0–869.4 m is in the range of 14–20 in transition season and in dry season at the distance of 0–488.2 m it is 9–10, and at the distance of 869.4 m it is 9. Meanwhile, in Pangkep estuary (P1) in transition season, C/N ratio at the distance of 0–624.4 m is 9, at the distance of 1271.7–2403 m it is 10, and in Pangkep estuary (P2) at the distance of 0–419.5 m it is 10, and at the distance of 916.4 m it is 9.

In dry season, C/N ratio in Pangkep estuary (P1) at the distance of 0–1271.7 m is 7–8, at the distance of 2403 m it is 9, and in Pangkep estuary (P2) at the distance of 0–916.4 m it is 9. In transition season, C/N ratio tends to increase from sea to land on the west coast of South Sulawesi, except in Pangkep estuary (P2). Meanwhile, in dry season C/N ratio increase at some points of sampling varies: in Tallo, Maros and Pangkep estuaries C/N ratio values in estuaries or near terrestrial are lower than C/N ratio values at location points across from them (between estuaries and sea); and then those ratio values undergo a decrease at sea location points; on the contrary, in Pangkep estuary (P1) occurs C/N ratio increase at sea location point. C/N ratio value in Pangkep estuary (P2) undergoes a decrease from terrestrial to sea.

Value of organic carbon (C_{org}) percentage at the maximum spatial and temporary in the part near terrestrial and lower toward sea (**Figure 2**) is in the range of 2.24–6.08% in transition season with maximum percentage value on the location of Tallo estuary and minimum on the location of Maros estuary. In dry season it is in the range of 1.19–1.88% with maximum percentage value on the location of Pangkep estuary and minimum in Maros estuary.

This C/N ratio change is highly affected by the magnitude of flux indicated in particulate (SPM) with very strong correlation (r^2) in Maros estuary, i.e., 1; in Tallo estuary 0.515, and in Pangkep estuary (P1) 0.338 in transition season, while r^2 in dry season in Pangkep estuary (P1), Tallo estuary, and Maros estuary are 0.909, 0.165, and 0.039 (**Table 1**; **Figure 3**). This condition shows a tendency for SPM weight increase to be linear with C/N ratio increase. On the contrary, in Pangkep estuary (P2) SPM weight increase is not linear with C/N ratio in transition and dry seasons, with $r^2 = 0.869$ and 0.613.

Particulate Organic Matter (POM)

Increase of organic particle (POM) on the west coast of South Sulawesi is linear with the increase of (SPM) particulate weight (**Table 1**) and tends to increase on the sea location. Carefully examining **Figure 4**, it is seen that the relationship between POM flux and SPM range in transition season indicates that POM is in the range of 0–15, only originates from Pangkep estuary with the range of 226–344 μgCL^{-1}, and in the range of 15–30 dominant originates from Maros estuary amounting 2723 μgCL^{-1} and minimum from Pangkep estuary is in the range of 425–594 μgCL^{-1}, whereas in the range of 30–60 dominant from Tallo estuary is in the range of 4638–4886 μgCL^{-1} and minimum from Pangkep estuary is 774 μgCL^{-1}, in the range of 60–120 only originates from Tallo estuary with particulate organic amounting 5462 μgCL^{-1}.

In dry season, POM only comes from the range of 15–30 with dominant particulate organic originating from Tallo estuary with the range of 1880–2483 μgCL^{-1} and minimum from Maros estuary, which is 1806 μgCL^{-1} and in the range of 30–60 with dominant originating from Pangkep estuary, which is in the range of 2563–5178 μgCL^{-1}, minimum originating from Maros estuary in the range of 3156–3646 μgCL^{-1}.

DISCUSSION

Water Discharge and SPM

Transfer process of organic matter from terrestrial to sea depends on river water discharge, where the maximum river water discharge is in Tallo estuary in two seasons of observation (transition and dry seasons), except in dry season which is in the range of SPM 30–60, because Tallo river is one of the biggest rivers on the west coast of South Sulawesi having a length of 10 km (Utami, 2013). With this physical condition, it is relevant with the increase of carbon and nitrogen percentage in SPM (**Figure 2**), e.g., Sarà et al. (2006) and Vizzini and Mazzola (2006), that the area and distribution of antropogenic input depends on the quantity and type of waste, local hydrography, hydrodynamic regime and other environmental features of dump area. Besides that, season factor also plays a very important role in accelerating the process of the terrigenous matter transportation, where seasons of observation vary significantly at $p < 0.05$. The magnitude of organic matter concentration in the form of particulate particularly, probably also depends on deposition level, properties of organic source and the amount of flux, matter preservation potential during transportation and preying, mineralization and degradation (e.g., Owen and Lee, 2004; Ogrinc et al., 2005; Gao et al., 2008).

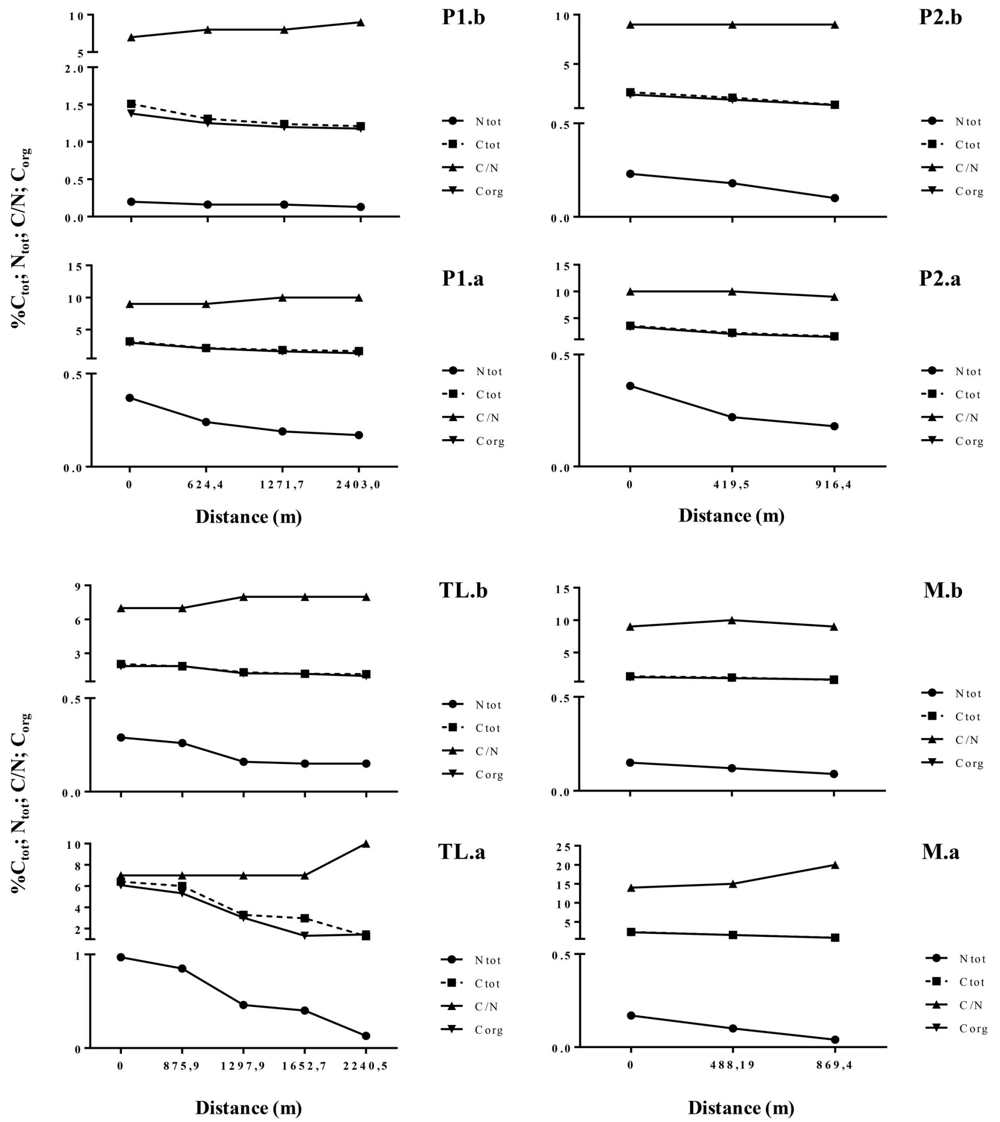

FIGURE 2 | Change of C_{tot}; N_{tot} percentage; C/N and C_{org} ratio from terrestrial to sea. TL, Tallo estuary; M, Maros estuary; P1 and P2, Pangkep estuary. a, Transition Season (April 2013); b, Dry Season (June 2013).

Contribution of terrigenous to the waters on the west coast of South Sulawesi has indicated the magnitude of antropogenic flux to the coastal waters and can become eutrophication stressor. A strong evidence of this is the fact that the SPM found only ranges from 9.60 to 55.1 mgL^{-1} (**Table 1**) with a maximum average in dry season and minimum in transition season, e.g., Middleburg and Herman (2007), if SPM $\sim$10 mgL^{-1} usually 20% of nutrient in the form of particulate in estuarial waters, and this fraction increases to 60% in SPM$\sim$100 mgL^{-1}. So, the percentage of nutrient absorbed in particulate on the west coast of South Sulawesi is categorized as low, where fine sediments in suspension probably absorbs nutrient, and therefore, can obstruct eutrophication (Middelburg and Levin, 2009; Testa and Kemp, 2012; Xu et al., 2013).

Percentage of C_{tot}, N_{tot}, Ratio of C/N and C_{org}

The magnitude of organic matter in the form of particulate from terrestrial flux has also helped to trace the waste extension on the west coast of South Sulawesi. **Figure 2** shows that the percentage of C_{tot} is more abundant compared to that of N_{tot} from river rather than from sea region. This reflects the situation of the majority of terrestrial organic matter stored before meeting with sea. Spatial variation has signaled that the input of organic matter from antropogenic activities has a more significant effect on distribution than does natural process (e.g., Pradhan et al., 2014).

C/N ratio value that varies toward the distance of flux from terrestrial to coast transition season (April) and dry season (June) with a range of 7–19.7 (**Figure 2**) has given an indication that

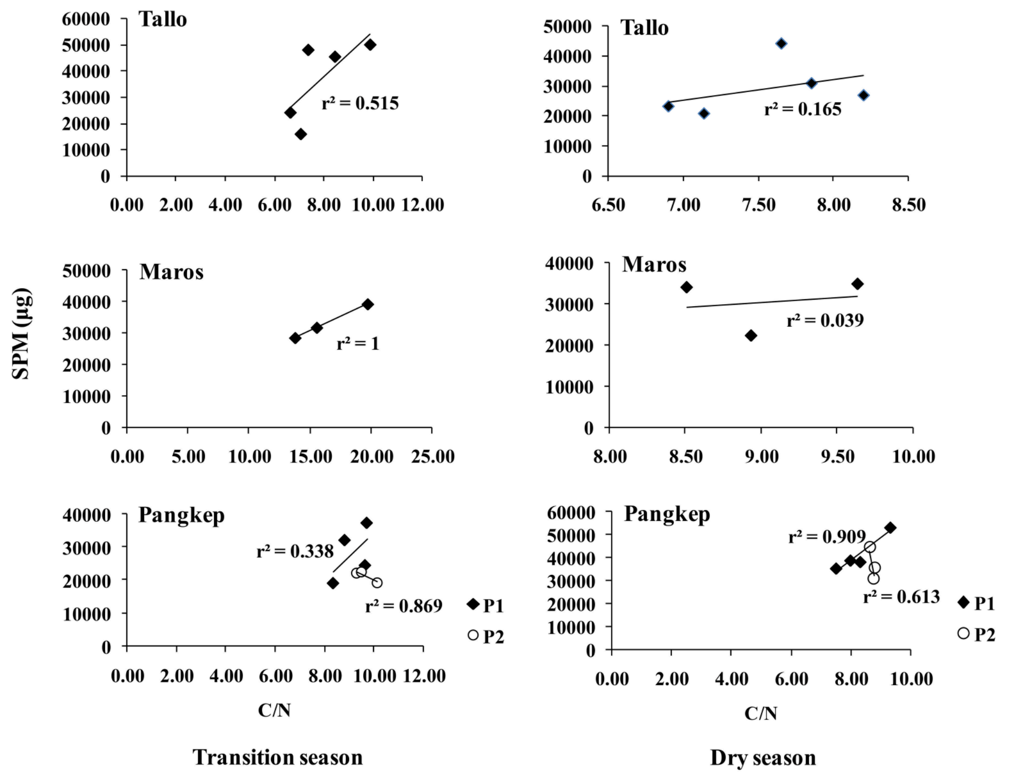

FIGURE 3 | Correlation of SPM with C/N ratio on the west coast of South Sulawesi. Transition Season (April 2013); Dry Season (June 2013).

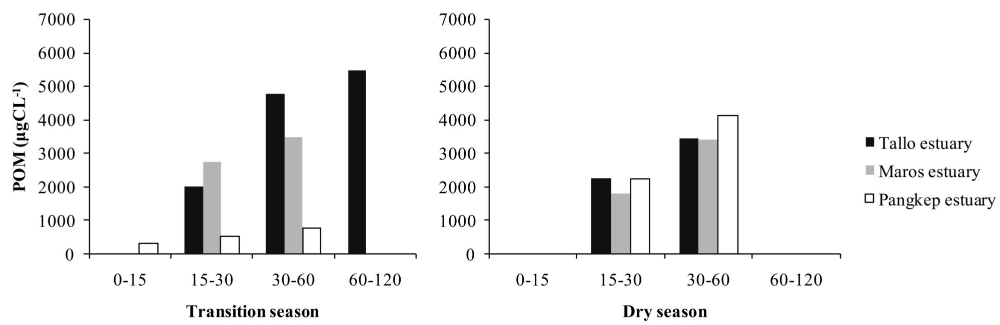

FIGURE 4 | Increased particulate organic matter (POM, μgCL^{-1}) in the concentration range of suspended particulate (SPM) on the west coast of South Sulawesi. Transition Season (April 2013); Dry Season (June 2013).

organic matter originates from sea and terrigenous (*soil organic matter*) (Emerson and Hedges, 1988; Meyers, 1994). Tallo Estuary for example, in transition season gives an indication of dominant organic matter from sea. This is also related with the physical condition of Tallo river, where the river bottom is lower than sea surface, so it causes salt water to be available along ~10 km (Utami, 2013), so at some points of sampling it is possible to find organic matter originating from sea (*autochthonous*). In dry season, organic matter from soil is dominantly found, the matter that is a terrigenous component as a result of the process of humification and mineralization in terrestrial or land environment (Holtvoeth, 2004) giving an indication that terrestrial factor is significant in waste supply. The same thing is also found in Maros estuary and Pangkep estuary in transition season and dry season; at all points of observation there are findings of particulates from terrigenous organic matter. This condition is also proven with the percentage of maximum organic matter (C_{org}) in terrestrial area on all locations and seasons of observation, and tends to decrease toward sea (**Figure 2**).

If connected with the farthest distance of observation from the coast in **Figure 2**, i.e., 2403 m, the effect of flux originating from terrigenous (*allochthonous*) still gives an impact. This is probably because the particulate organic matter from terrestrial surviving the transportation to that distance extends pre-oxidized and is more resistant to microbe degradation, especially if it is physically protected by clay mineral (e.g., Holtvoeth, 2004), so it will give a further possibility to detect the organic matter terrigenous contribution. Besides that, the tendency of C/N ratio value from sea to terrestrial to be higher can be caused by the addition of organic matter originating from sea itself, for example from organism-plankton decomposition process.

The increase of C/N ratio value also highly correlates with SPM (**Figure 3**), where the increase of SPM weight tends to be linear toward C/N ratio, except in Pangkep estuary (P2) where the increase of SPM weight is not linear toward C/N ratio. This condition is because N_{tot} concentration in particulate in Pangkep estuary (P2) tends to be higher than the minimum amount for a good result between the comparison of C and N, i.e., 25 μg and 2.5 μg. This thing is related with the domain around the estuary (P2), i.e., the fishery aquaculture and agriculture that largely make use of fertilizers containing N, so it will give an impact on the type of waste to the coast.

Particulate Organic Matter

Organic particulate (POM) in ponds of water from estuary consists of living organisms (especially fitoplankton, bacteria and animal) and non-living particulate (detritus, i.e., all kinds of biogenic matter in various steps of decomposition, that represent potential energy source for consumer species). With the tendency of POM increase on the west coast of South Sulawesi from sea to terrestrial, it gives an indication that particulate organic matter source (potential energy source) on sea location mostly originates from sea itself (*autochthonous*) and is dominantly found in the particulate range of 30–60.

This pattern of POM increase is in line with the tendency of C/N ratio increase from terrestrial to sea. Therefore, to differentiate the source of POM, the C/N ratio approach is used because ratio is different in algae and soil matter (Lobbes et al., 2000), for example by calculating the contribution of soil 21–96% based on C/N ratio of soil 13.5 (Guggenberger et al., 1994; Hedges and Oades, 1997) and C/N ratio of algae/bacteria 6 (e.g., Meybeck, 1982). This thing is also in line with the concentration of chlorophyll-a on the west coast of South Sulawesi that is categorized as low (**Table 1**), dominated by diatoms (Nasir et al., 2015). For example Cauwet and Sidorov (1996), fitoplankton biomass only contributes 2% carbon organic matter for river. So, the high POM from sea can explain that probably particulate organic matter from land survives the transportation to that distance, extend pre-oxidized and is more resistant to microbe degradation, it is also affected by tide factor at the time of sampling that adds the particulate organic matter concentration originating from sea.

The observation season factor also affects POM concentration; by carefully examining **Figure 2**, it is seen that concentration of POM from SPM in dry season is lower than that in transition season. This thing can also be related with the effect of temperature on each location of observation, where in dry season the temperature range tends to be higher than the temperature range in transition season (Nasir, unpublished results). This means that most of organic carbon in terrestrial region has rotten because of the relatively high temperature (e.g., Ittekkot and Laane, 1991).

CONCLUSION

C/N ratio on the west coast of South Sulawesi dominantly lies in the range of 7–19.7 and gives a description about the condition of the waters that in transition season and dry season has gotten pressure from the flux of anthropogenic (*terrigenous*). The runoff discharge have implicated on $\%C_{tot}$, $\%N_{tot}$, and $\%C_{org}$, where the water discharges in Tallo estuary and Pangkep estuary are larger than the discharge in Maros estuary, so $\%C_{tot}$, $\%N_{tot}$, and $\%C_{org}$ are very significantly different at $p < 0.05$ and in Maros estuary the discharge is not very significantly different.

Percentage of inorganic nitrogen absorbed in particulate is also low, so it can become a eutrophication stressor, where SPM found only ranges from 9.60 to 55.1 mgL^{-1}, with a maximum average in dry season and a minimum average in transition season. On the contrary, POM that is a potential energy source for consumer species, is maximum in transition season and minimum in dry season with a dominant particulate organic matter source originating from sea itself (*autochthonous*).

AUTHOR CONTRIBUTIONS

AN, ML, and AT designed the study; AN, ML, RT, and N carried out the experimental and analytical measurements; AN and MH conducted the statistical analysis; and AN and ML wrote the manuscript.

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