

Quantifying the Effect of Chemical Transformation on Pollutant Ground Level Concentrations in Ghana Using the CALPUFF Modelling System

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Abstract: This paper discusses the effect of chemical transformation of dispersed pollutants from the Tema Oil Refinery in Ghana within a 60 km² study area. The MESOPUFF II module within the California Puff (CALPUFF) modeling system was used coupled with Weather Research and Forecasting (WRF) model data driving the dispersion model. The chemical transformation of SO_x and NO_x to sulphates and nitrates respectively was modelled using refinery emission rates of 2009, 2010, 2011 and 2013 together with terrain and land use data of the study area and refinery emission stack characteristics. Daily average concentrations of SO_x and NO_x were predicted at fourteen (14) receptor locations within the study area. Receptors located north and north east of the refinery saw higher levels of SO_x and NO_x due to the south western prevalent wind direction in the study area. Receptors farther from the refinery also recorded relatively lower concentrations. GLCs of SO_x and NO_x predicted at 14 receptors within the study area were compared with GLCs of the same pollutants predicted without the consideration of chemical transformation. It was observed that SO_x and NO_x daily average concentrations for modelling with no chemical transformation were higher than with the chemical transformation module activated, the difference accounting for the sulphates and nitrates. The percentage conversion of the pollutants varied from year to year primarily due to meteorological conditions. It was also observed that there was a reduction in ground level concentrations of SO_x and NO_x at receptors in the study area with percentage conversion of SO_x to sulphates ranging from 2 to 19, and 5 to 22 for NO_x to nitrates.

Keywords: air pollution modelling, nitrates, sulphates, CALPUFF, MESOPUFF II, chemical transformation

1. Introduction

Air pollution cannot be considered as a static phenomenon as it constantly changes with human activities and meteorological conditions. Primary pollutants of the atmosphere include the NO_x and the SO_x whose major sources are the combustion of fossil fuels by refineries and thermal power plants as well as vehicular emissions. These primary pollutants are transformed into secondary pollutants facilitated by the physical and chemical characteristics of the air mass which determine the specific route of a pollutant after release into the atmosphere [4, 5]. The order of changes a pollutant undergoes depends on the pollutants' initial concentrations and a number of physical factors including wind speed, air turbulence, sunlight intensity, temperature, and rainfall frequency [7, 11]. Chemical reactions or photochemical reactions transforming SO_x and NO_x into H₂SO₄ and HNO₃ respectively, are triggered by energy from sunlight. These aerosols lead to the formation of acid rain which affects the terrestrial and aquatic ecosystems and consequently the quality of human life [6, 12]. The evaluation of the impact of air pollutants on air quality is usually done using simplified, stationary dispersion models that do not take into account chemical transformations of pollutants taking place in the atmospheric air [8, 13]. It is very necessary to take chemical transformations of primary pollutants into account as results will better reflect real conditions and hence pollutant control strategies [7]. Many studies on atmospheric pollution have concentrated on

measuring primary pollutants from sources or simulated the dispersion of the same [1, 18]. However, research on the chemical transformation of the emitted pollutant species is limited. The objective of this study therefore is to model and quantify the chemical transformation of SO_x and NO_x from an oil refinery to sulphates and nitrates respectively employing the CALPUFF modelling system.

2. Materials and Methods

2.1 Characteristics of the study area

The source of emission for this study is the Tema Oil Refinery situated within the study area which spans a domain size of 60 km x 60 km and located in the Greater Accra Region of Ghana (Fig 1). The Universal Transverse Mercator (UTM) coordinate of the southwestern corner of the domain in zone 30 are 810 km easting and 610 km northing. The refinery processes crude oil into liquefied petroleum gas, petrol, jet fuel, kerosene, diesel, low - sulphur Fuel oil (LSFO) and fuel oils. The location of the refinery is on an area of 440, 000 square meters positioned in the industrial hub of the Greater Accra Region. The refinery has an installed total capacity of 65 000 barrels per stream day (BPSD) equivalent to 3, 000, 000 tonnes per annum (tpa) with contributions from the Crude Distillation Unit (CDU) - 2, 000, 000 tpa, Residue Fluid Catalytic Cracker (RFCC) - 685, 000 tpa and the Premium Reforming unit (PRF) - 315, 000 tpa [9].

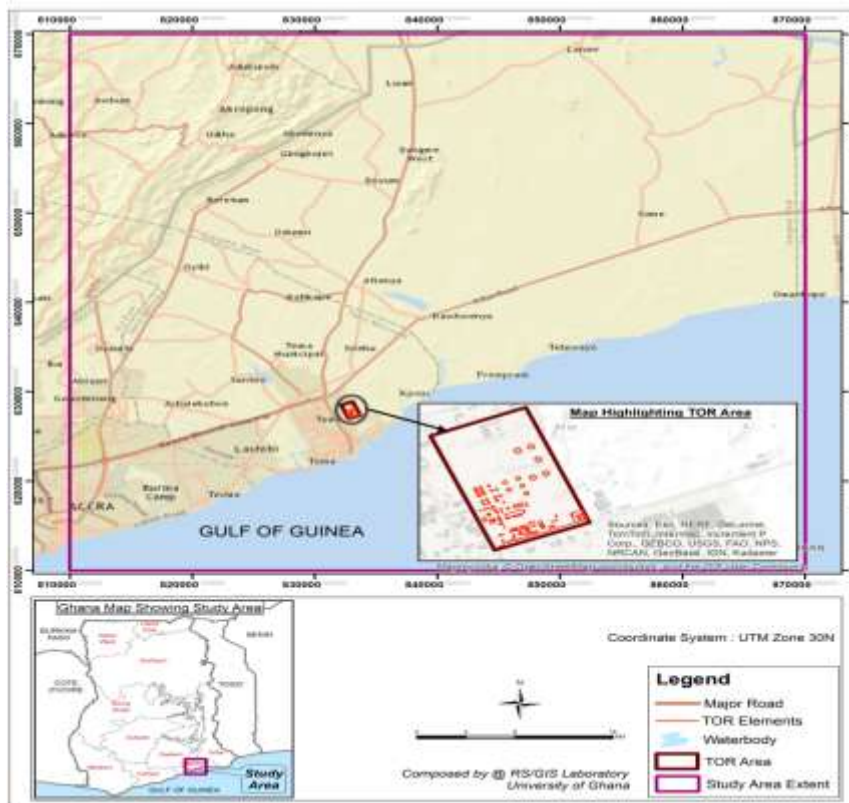


Figure 1: Map of Study Area showing the Tema Oil Refinery

The emissions rates of SO_x and NO_x from the Tema Oil Refinery for 2009 – 2013 which were used for the simulation are presented in Table 1.

Table 1: Pollutants Emission rates

Year	SO _x (kg/hr)	NO _x (kg/hr)
2009	767	354
2010	847	394
2011	782	360
2013	707	366

Source: [2]

2.2 CALMET Model Setup

The CALMET model, the meteorological model in the CALPUFF modelling system, was initialized with Weather Research and Forecasting (WRF) data to generate the meteorological field for the CALPUFF dispersion model via interpolation of the gridded prognostic data to develop a 3 - D fine scale field of wind speeds, directions and other parameters [16].

A geophysical file containing information about the land use type, elevation and surface parameters about the study area was created and integrated with the CALMET data. Data on land use land cover (LULC) and land terrain elevation was obtained from the United States Geological Survey (USGS) web site [USGS]. Comprehensive land terrain features were integrated using the USGS Shuttle Radar Topography Mission (USGS global 3 arc - sec SRTM3 data) [~90m resolution]. Important land features in the study area were adequately resolved with this terrain data³⁸. Land use data was processed to produce a 1 - km resolution gridded field of fractional land use categories. The terrain and land use data were then processed through the TERREL and

CTGPRO CALMET pre - processors respectively. The MAKEGEO pre - processor module of the CALMET model puts together data from TERREL and CTGPROG to create the CALMET GEO file. CALMET was configured with the default wind field options and parameters and executed to createa CALMET. dat file which were then used as input for the CALPUFF dispersion model [16].

2.3 CALPUFF Model Set up

The CALPUFF model predicts concentrations at specific receptors, which are specified by the user within the modelling domain [17]. Fourteen (14) receptors, whose locations are presented in Table 3.2 and constitute schools, populated areas and a hospital, were identified within the study area and are shown in Fig.2. For this study, the rates of emission from the refinery were assumed constant and that the refinery processed crude throughout the whole year. The MESOPUFF module in the CALPUFF system was activated for the transformation of the pollutant species. The MESOPUFF module (MCHEM = 1) is based on the MESOPUFF II model that utilizes a pseudo first order chemical reactions mechanism describing the conversion of SO₂ into SO₄²⁻, and NO_x (NO+NO₂) into NO₃⁻ in ambient air [17]. It accounts for the space - time variability of environmental factors which include the concentration of ozone atmospheric stability class, relative humidity, total solar radiation intensity and the plume NO_x concentrations [17]. A second simulation was run with the chemical transformation module turned off. Predicted ground level concentrations of SO_x and NO_x at receptors in the study area were then compared with concentrations obtained when the simulation was carried out considering chemical transformation. CALPUFF was also executed for all the years under consideration. The CALPOST post processor

was used to process the files from CALPUFF, producing a concentration contour form. summary of simulation results in tabulated as well as in

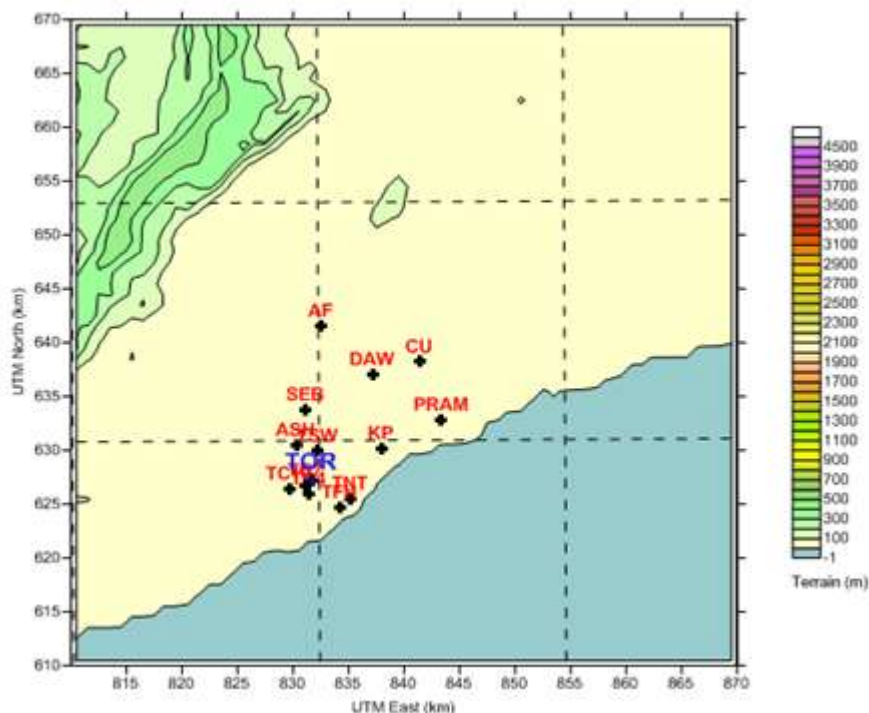


Figure 2: Receptor Locations in study area

Table 2: Receptor Locations in the Study Area

Receptor	Code	Easting (km)	Northing (km)
Afienva	AFN	832.542	641.534
Ashaiman	ASH	830.287	630.477
Central University	CU	841.41	638.219
Dawenya	DWN	837.148	637.054
Kpone	KPN	837.97	630.162
Prampram	PRP	843.381	632.814
Sebrepur	SBP	831.172	633.778
Tema Community 4	TC4	831.463	625.952
Tema Community 7	TC7	831.175	626.749
Tema Community 10	TC10	829.664	626.435
Tema Fishing Harbour	TFH	834.227	624.685
Tema General Hospital	TGH	829.622	628.685
Tema Newtown	TNT	835.168	625.508
Tema Steel Works	TSW	832.215	629.955

explained by the emission rates of the pollutants from the refinery which were highest for 2010, 2011, 2009 and 2013. High GLCs of both SO_x and NO_x were predicted at receptors close to the refinery and in its windward region. These include the TSW, ASH and SBP located north and north east of the refinery with TSW being the closest to the refinery. The prevalent south south - western winds, as seen in the wind rose in Fig.5, in the study area, transport the pollutants to these receptors resulting in their high GLCs. It is for this same reason that receptors located south of the refinery recorded low GLCs of the pollutants. Similar results were obtained by [1, 18]. The varying GLCs predicted at the receptors also reflect the changing emission rates for the years under consideration which were hugely influenced by the availability of crude oil for processing and the yearly meteorological conditions.

3. Results and Discussion

3.1 Ground level concentrations of SO_x and NO_x

Results of the daily average GLCs from the dispersion modelling of SO_x and NO_x with and without chemical transformation (CT) module (MESOPUFF) activated are presented in Figures 3a - d and 4a - d respectively. It can be observed that the highest GLCs of both SO_x and NO_x in the study area were predicted in the year 2010, followed by 2011, 2009 and 2013. This can be

3.2 Chemical Transformation of SO_x and NO_x

From Fig.3a - d, it can be observed that generally, there was a decrease in the predicted SO_x and NO_x concentrations when the chemical transformation module was turned on. This means that the fraction of SO_x transformed into sulphates (simulated nitrates) is accounted for in the slight decrease of predicted daily average GLCs of SO_x and NO_x when the chemical transformation module was activated.

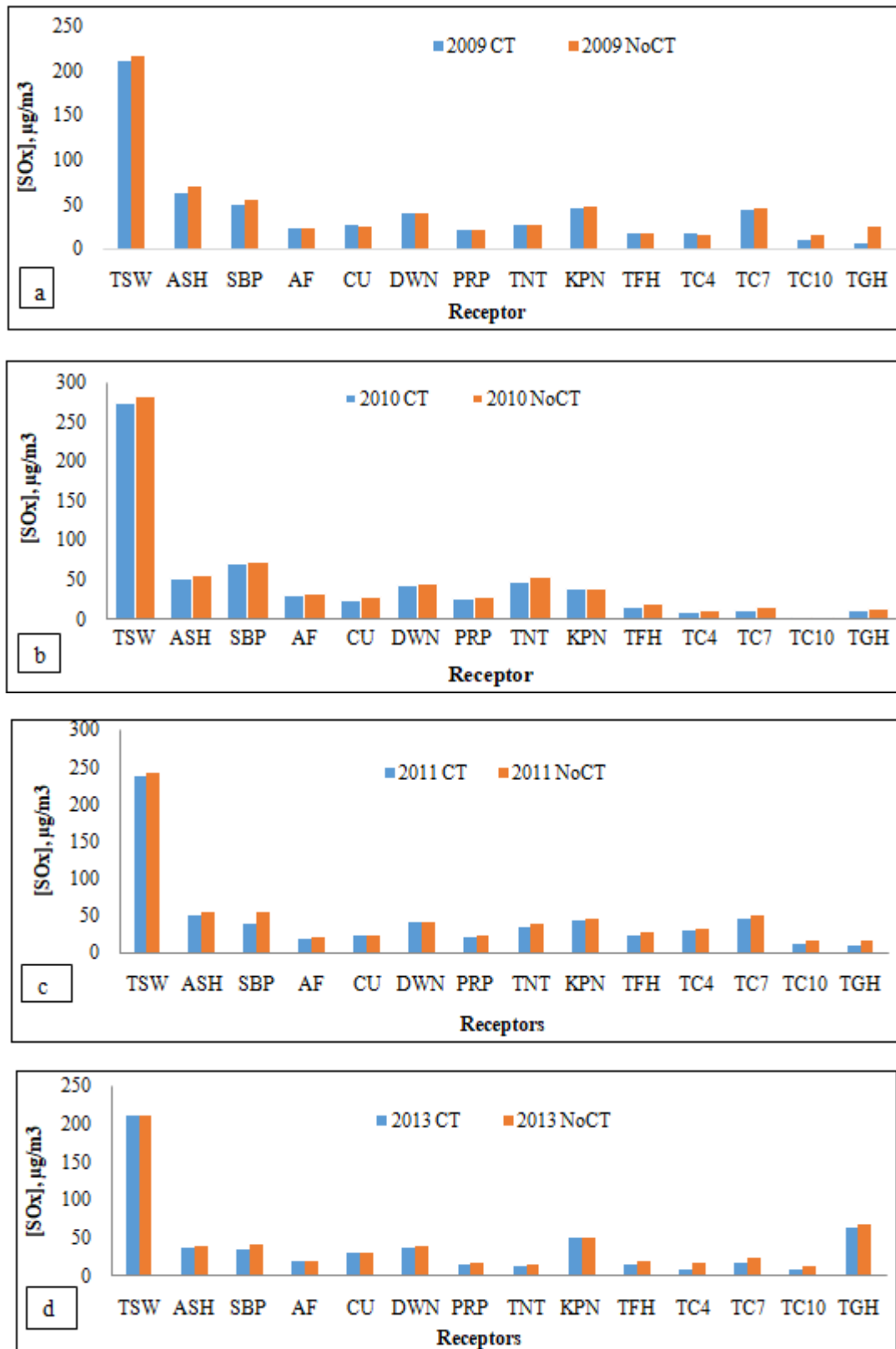


Figure 3 (a- d): Comparison of SO_xdaily average GLCs with and without chemical transformation (NoCT) 2009, 2010, 2011, 2013

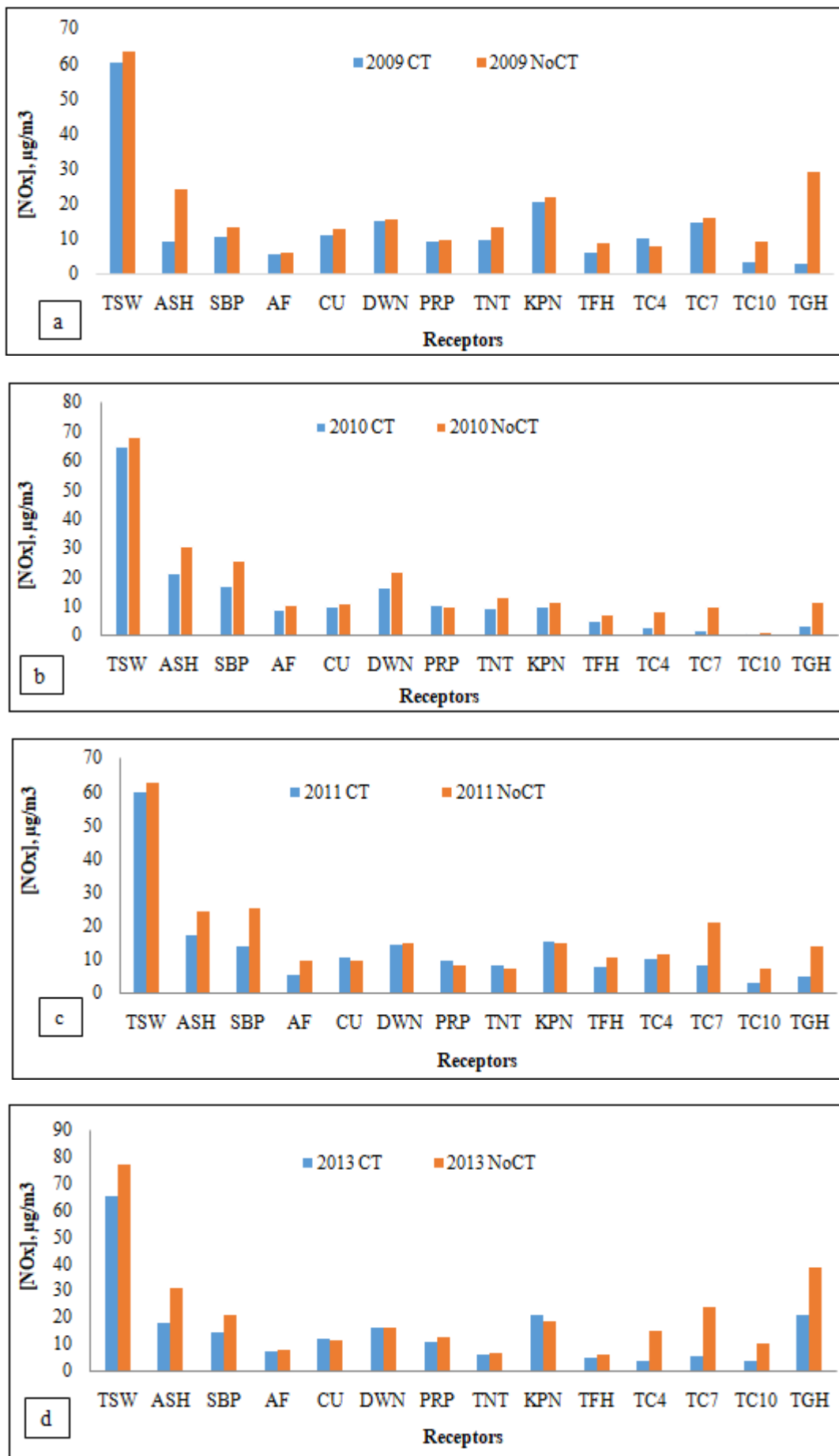


Figure 4 (a- d): Comparison of NO_x daily average GLC with and without chemical transformation (NoCT) 2009, 2010, 2011, 2013

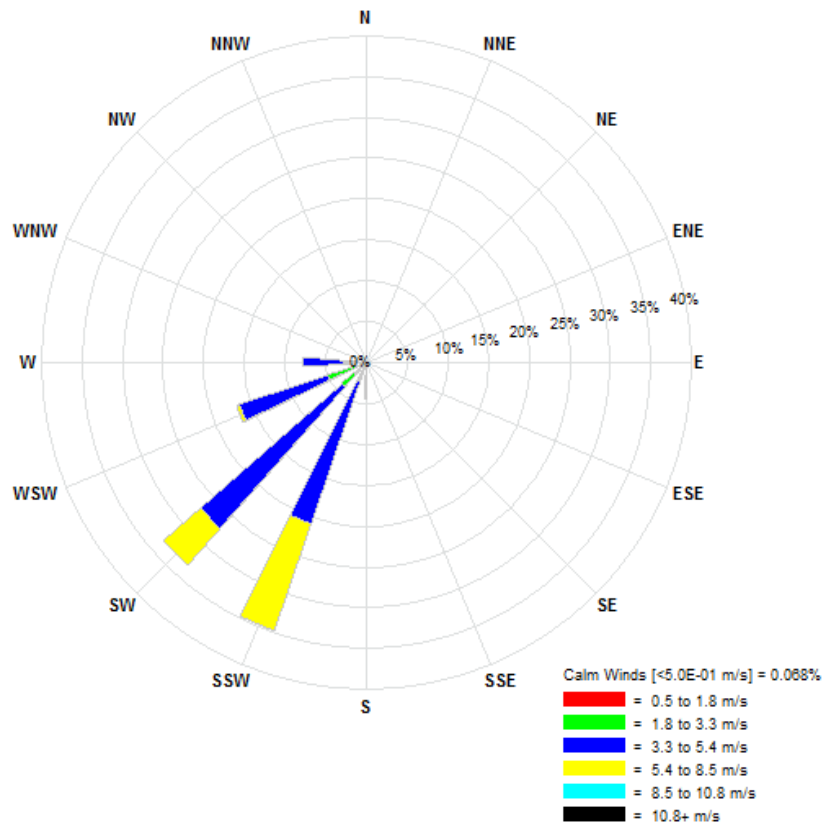


Figure 5: Prevalent surface winds in the study area

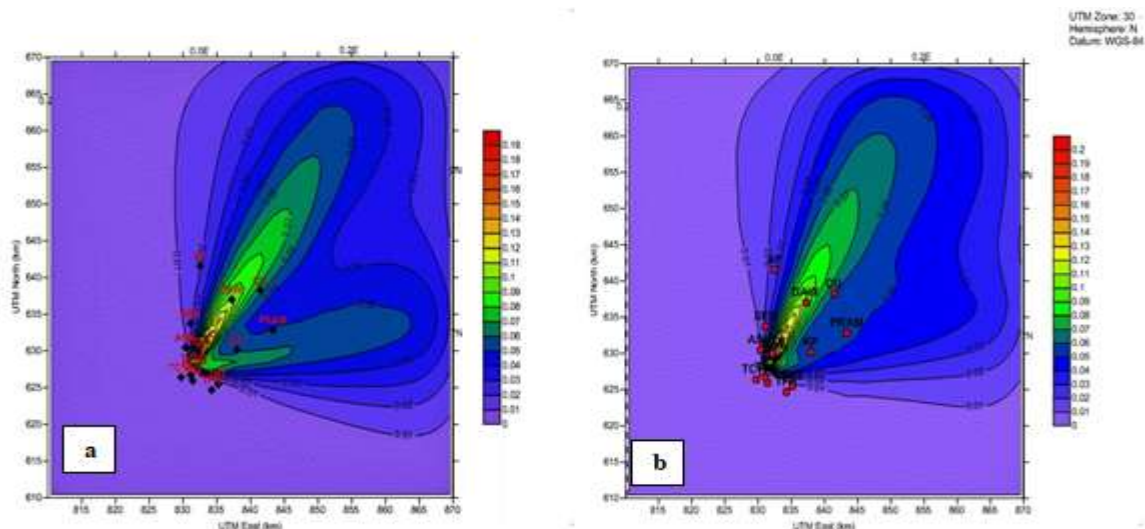
An average decrease in concentrations between 2% and 10% was calculated for the year 2009 for SO_x. In 2010, the percentage reduction increased slightly to 3% and 12%. Table 3 presents the percentage reduction for SO_x and NO_x for the years under study. For GLCs of NO_x, however, the percentage reduction was higher than for SO_x for all the years under study. These findings are corroborated by [15]. Yet the NO_x percent transformation variability at the receptors and among the years was higher than for SO_x. This is because nitrate aerosol formation is also influenced by other factors, including humidity, the availability of base precursors (e. g., ammonia, ozone), and the concentrations of other acids. As a result, the potential responses of the nitrate aerosol concentration to a changing climate are complex and thus require further studies to increase our understanding [14].

Table 3: Percentage conversion ranges for SO_x and NO_x

Year	SO _x	NO _x
2009	2% - 10%	5% - 14%
2010	3% - 12%	5% - 18%
2011	2% - 10%	2% - 22%
2013	4% - 19%	7% - 16%

3.3 Spatial Distribution of Sulphates and Nitrates in the study area

Annual average concentration contour maps of the sulphates and nitrates converted from the SO_x and NO_x from the refinery are presented in Figs 6a - d and 7a - d. The spatial distribution of the sulphates and nitrates within the study area confirms the strong presence of the SO_x and NO_x at receptors close to the refinery and in the direction of the wind.



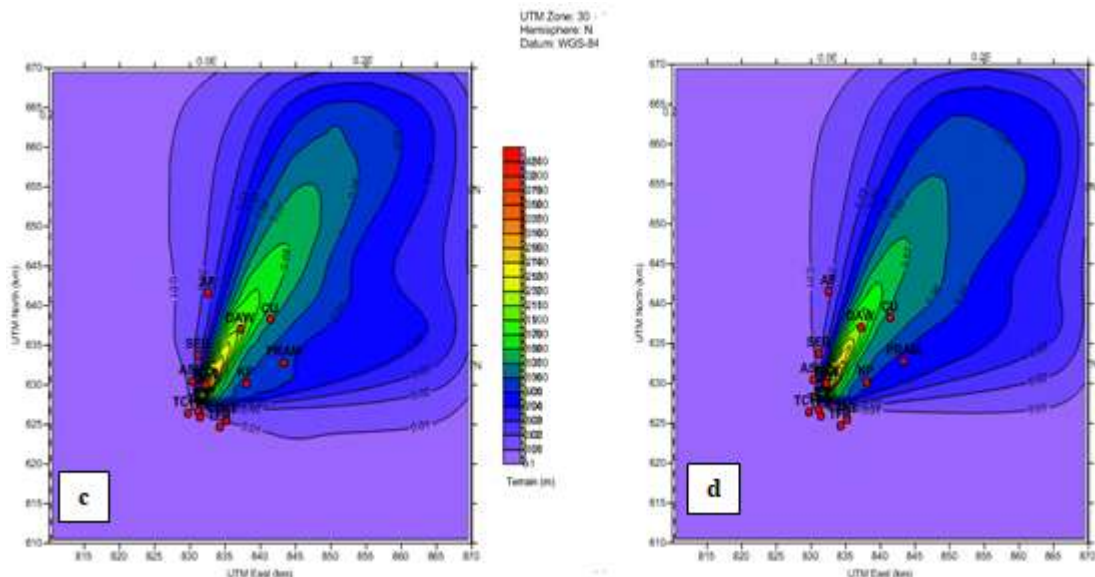


Figure 6 (a- d): Annual average concentration contour maps for SO₄²⁻ for a) 2009 b) 2010 c) 2011 and d) 2013

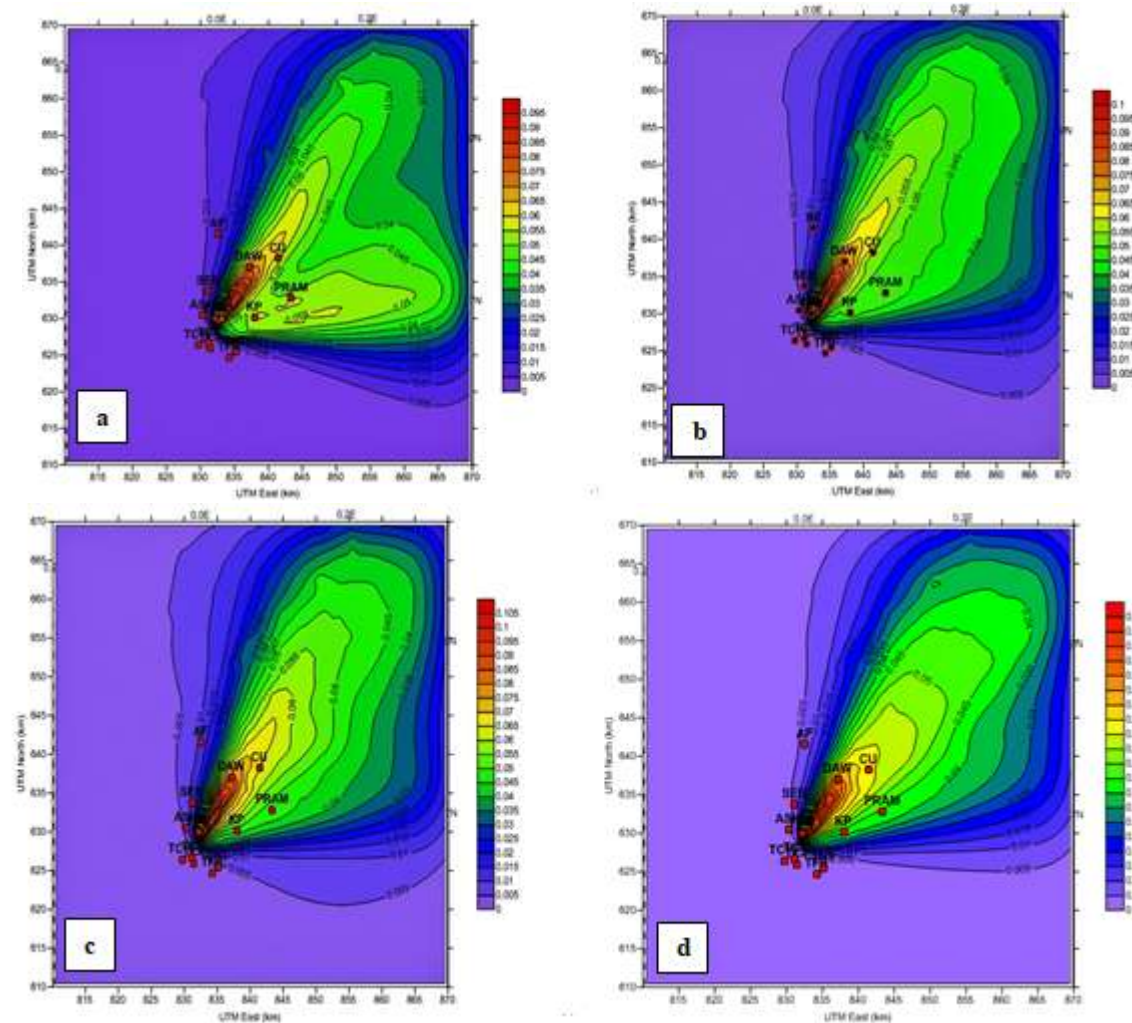


Figure 7 (a- d): Annual average concentration contour maps for NO₃⁻ for a) 2009 b) 2010 c) 2011 and d) 2013

4. Conclusion

Based on results from modelling the chemical transformation of emitted and dispersed SO_x and NO_x, it was observed that there was a reduction in ground level concentrations of SO_x and NO_x at receptors within the study area. Percentage conversion of SO_x to sulphates ranged from

2 to 19, and 5 to 22 for NO_x to nitrates. Therefore, the omission of chemical transformation of primary pollutants in the atmosphere will significantly affect modelling results. Moreover, receptors found on the north and north - eastern areas of the refinery showed comparatively higher concentrations of pollutant than other parts of the study area as a result of the predominant south - westerly winds in the

study area. On the other hand, receptors located at the southwestern parts of the refinery were the least impacted by refinery emissions.

5. Acknowledgement

The authors are grateful to the Tema Oil refinery for access to the plant and providing all relevant data used for the simulation.

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