Multidisciplinary
SCIENTIFIC JOURNAL
OF MARITIME RESEARCH

University of Rijeka
FACULTY OF MARITIME STUDIES

Multidisciplinarni
znanstveni časopis
POMORSTVO

https://doi.org/10.31217/p.36.1.19

Ship production processes air emissions analysis

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ABSTRACT

Compliance with modern environmental norms and regulations is an increasingly important requirement in the shipbuilding process of ship design and construction. Related to the ship production process, volatile organic compounds (VOCs), nitric oxides and particulate matter are the main emissions of harmful gases in the shipyard. This paper analyzes air emissions from the ship production process in a shipyard. Air emissions are quantified from either in-situ measurements from emission sources, or by materials that are used in the shipbuilding process, and the acquired data from those measurements is calculated as yearly emissions. Emission quantities of VOCs, nitric oxides, carbon dioxide, carbon monoxide and particulates are analyzed regarding possible reduction techniques considering efficiency and investment costs for using these methods. In conclusion, the best available and feasible emission reduction methods are suggested, and a suggestion for achieving the goal of a net zero emission shipyard.

ARTICLE INFO

Original scientific paper
Received 2 May 2022
Accepted 29 June 2022

Key words:
Air emission
Ship production process
Ecology
Volatile organic compounds (VOCs)
Emission reduction methods

1 Introduction

Ship building industry is known to be one of the oldest productive facilities of mankind. The shipbuilding industry is predominantly a metal processing industry. Shipbuilding and ship repair industry has characteristics of a manufacturing industry also and construction industry. In order to obtain the finished product, i.e., the ship, it is necessary to invest energy, resources, labor and rationally manage these investments. The hull is predominately made of steel sheets and to a lesser extent profiles. Sheets can be composed of different thicknesses, qualities and dimensions. Once the sheets and profiles are delivered to the shipyard, they are stored in a ferrous metallurgy warehouse where they can spend a significant amount of time before being used. Under these conditions, they are exposed to atmospheric conditions, a certain layer of corrosion, dust and other impurities is created, and deformation can occur. It is quite common that the sheet steel has to be straightened before use. In order to know the order of the sheets entering the process, it is necessary to mark them and arrange them in the correct order. Prepared sheets can now be joined by welding into assemblies, flat sections and large sections. It is desirable to equip the sections before the assembly itself.

The main reason for processing sheets and profiles is their protection against corrosion. Corrosion is defined as the destruction or erosion of surface metal caused by various physio-chemical processes. During its working life, the ship is in unfavorable conditions from the point of view of the corrosion-marine environment. Absence of adequate corrosion protection of the hull can result in its damage, which is a highly undesirable phenomenon. Therefore, in order to prevent or slow down this unwanted process, the hull and all materials subject to corrosion need to be protected with anti-corrosion coatings.

Shipyards can be divided into two basic categories: shipbuilding and ship repairing. Some shipyards build exclusively large ships including repair and dry dock facilities. Other shipyards have facilities for building small to medium sized vessels.

The shipbuilding industry is a known major source of pollutants. These include various types of pollutants including harmful gases and particles, harmful chemical substances discharged in wastewater, industrial and harmful waste and other types of pollution like noise pollution. Shipbuilding industry operation is normally large scale, complex, and these activities generate a significant amount of emissions of volatile organic compounds, nitric oxides, carbon oxides (CO and CO_2) and particulate matter.

In recent years researches often focused on pollutants from the shipbuilding and ship repairing industry resulting from shipyard processes and materials. Investigations on volatile organic compounds emissions and hazardous air pollutants (HAPs) especially from painting process [1] have been caried out. Sets of dimensionless correlations for VOC emissions from dry building materials [2] have been developed. VOCs generated in outside operations in shipyards involving the use of paint and solvents and its effects on health risks for people living in the site surroundings [3] have also been studied. Various pollution prevention technologies have been investigated [4] and have provided a comprehensive knowledge of the available control technology and applicability to the shipbuilding and ship repair industry. Best available techniques or BAT for reduction of VOC emission from coating processes in painting have been investigated and suggested [5], as well as innovative proceses based on absorption of emissions from surface coating operations (VOCs) [6]. Emissions from other sources in production such as welding and other processes have been studied, but not to a great extent and comprehensively.

Many of shipbuilding industry processes include surface preparation, painting and coating, metal plating and finishing, solvent and grease removal, machining and metal working, welding, cleaning, and fiberglass application, etc.

This paper focuses on the process of shipbuilding, which, like any other production process, has visible effects on the earth's resources. Since the ship is exposed to unfavorable conditions from the point of view of corrosion during its working life or operation, it needs to be protected. Research proves that the process of protecting sheets and profiles from corrosion produces the most emissions, which is why more attention is focused on this issue. Locations where pollutants originate are pinpointed. For this study emission data available from a Croatian shipyard is considered. Available data of measurements taken, as well as calculated annual quantities of pollutants are analyzed. The aim of this study is to identify and quantify main air pollutants that originate from the shipbuilding processes and to offer possible solutions for reducing those emissions.

2 Air emissions sources – case study

The main source of air pollutants are volatile organic compounds released from paints and solvents. Other sources include air heating devices – "thermogens" that use fossil fuels as energy resulting in NO_x and CO emissions, and particulate matter (PM) emission that is vented to the ambient air (usually from the blasting chamber).

The construction process itself begins with the entry of sheets and profiles into the production process. Before they enter the process, they are in the warehouse exposed to the atmosphere for a certain period of time. In that period, in case the ferrous metallurgy warehouse is located near the sea, a slight corrosion process will already begin on the sheet metal. Therefore, the preparation of the surface of the sheets from which the ship is built is a very important and primary step. This phase consists of heating, cleaning the surface and then applying a protective workshop primer.

After entering the process, impurities that can cause peeling of the paint are blown off the sheets and profiles with warm air, thus drying off any moisture. It also improves the quality of painting and shortens the drying time after painting. Hot air is obtained from hot air generators (termogens) that use natural gas as an energy source and provide the necessary hot air. Since they use fossil fuel for combustion (natural gas), they are considered to be a stationary source of CO and NO_x emissions into the air. No devices have been built in the shipyard area to neutralize them at the moment.

In the case study shipyard area, there are 24 fixed emission sources and 6 diffuse emission sources or open sources. Most of them have available VOC emissions data, but there is also a significant amount of data on nitric oxides emission. It was further established that the total VOC emissions during the normal operation of the shipyard exceed the target emission according to the regulation on emission limit values for pollutants.

The process that creates the most air pollution in the shipbuilding industry are operations for corrosion protection or treatment of sheets and profiles.

VOCs that are generated from the painting process are mostly composed of aromatic hydrocarbons like benzenes and ethylene derivates. These compounds, when inhaled by humans, can potentially cause cancer depending on the exposure time and concentrations. For many of these compounds the carcinogenicity has been proven. For the human exposure to these compounds a generally accepted safe concentration limit has not been established. Limit values guidelines recommended by the World Health Organization is are used for some of those compounds. According to [7] neurotoxic effects on humans of the VOCs can include (depending on the compound in question) central nervous system depresion, vertigo, convulsions, spasm, vision loss, tremors, ataxia, etc. Not all VOCs have all these health effects, though many of them have several of the mentioned effects. VOC emissions are important for the formation of tropospheric ozone combined with NO_x emission. It this way VOC emissions contribute significantly to the formation of ozone which is an important greenhouse gas [8].

3 Estimation of VOC and pollutant emissions

There are several methods for calculating emissions from surface painting (coating). The most accurate methods, upon the availability of data and resources, and the degree of accuracy required is:

- direct measurements,
- material balance,
- sampling data and source testing,
- continuous emission monitoring system data and
- predictive emission monitoring (PEM) emission factors.

In this study data acquired from the direct measurements was available for most of the fixed emission sources and a material balance was also possible to calculate.

3.1 Comparison of available emission estimation methodologies

Emission estimation that is preferred and that gives a better estimation on effective emissions is greatly dependent on the origin and source type of those emissions. Point source emissions are easier to calculate based on measurements conducted on air venting ducts and chimneys. In this case emission factors are a preferred choice. Open coating operations include those operations that are open to the atmosphere or non-vented areas. In these cases, there is a choice of methods and material balance is generally preferred over an emission factor unless the assumptions needed to perform a material balance includes a high degree of uncertainty. Source testing shows an instantaneous “picture“ of emissions during the test. Test methods can provide real-time results. Predictive emission monitoring (PEM) is based on a correlation between pollutant emission rates and a process parameter that can be measured.

Emission factor is a pollutant emission rate in comparison to a source activity. In this manner VOCs emitted can be corelated to a liter of surface coating applied, or an air heater generates NO_x gases in a correlation to gas used in the heater. Emission factors are available for surface coating operations, as well as for various types of heating and process equipment, and are based on the results of source tests or material balances performed for one or more facilities within an industry. A continuous emission monitoring system records a continuous stream of date on emissions over a period of time, usually by reporting pollutant concentration. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that effluent stream.

3.2 Material balance

Material balance is most likely to be used where a relatively consistent amount of emissions is generated from the material used and air emissions are mostly uncaptured. This is valid for VOC emissions from fugitive sources and for CO_2 while other air emissions can be calculated via forementioned emission factors and measurement data.

The material balance emission rate is calculated by multiplying the material (paint and solvent) used times the amount of pollutant in the coating, and subtracting the amount of pollutant recycled, disposed, or converted to another form.

Total VOC emissions are determined by compiling an annual balance of organic solvents. Waste consumption is calculated as follows:

$$C = I_1 - O_8, \quad (1)$$

where:

C – solvent consumption [t/year],

I_1 – organic solvent intake [t/year] and

O_8 – organic solvents contained in preparations that are regenerated for reuse [t/year].

The total emission is calculated using the following equation:

$$E = I_1 - O_5 - O_6 - O_7 - O_8, \quad (2)$$

where:

I_1 – total amount of used organic solvents multiplied by the content of VOCs [t/year],

O_5 – organic solvents and / or organic compounds lost due to chemical or physical reactions [t/year],

O_6 – organic solvents in the collected waste [t/year],

O_7 – organic solvents in preparations sold or intended for sale as commercial products [t/year] and

O_8 – organic solvents contained in preparations that are regenerated for reuse but not as raw materials in the process [t/year].

The total fugitive annual emission calculated this way amounts to 57,61 tones of VOCs [9].

3.3 Direct measurement

The direct measurements are calculated using measured data from measurements taken from the air vents (for VOC measurments) or from chimneys and exhaust gases ducts (for NO_x, CO and PM measurments).

The calculation shows that the VOC emission calculated using the forementioned method (material balance) gives a different estimate on VOC emissions that the one obtained by adding emissions calculated by direct measurement from point sources. There is great room to improve performance in reducing emissions using proven technologies that are suitable for VOC emissions capture. The sources are shown here are sorted by type and by their place in the production process.

Table 1 VOC emissions – mass flow, concentration and annual total emission [9]

Process	**Source**	**VOC emissions (total)**		
		kg/h	**mg/m$_N$3**	**t/annum**
Primary sheet metal prep.	EZ2	4.7	361	33,29
	EZ3	0.25	45.4	
	EZ4	0.13	53.6	
Section painting	EZ8	14.85	396.8	35,03
	EZ9	20.11	590.7	
	EZ10	20.9	582.41	
Main painting hall	EZ14	0.24	102.7	1,15
	EZ15	4.58	117.3	
	EZ16	6.53	171.3	35,03
	EZ17	4.58	117.3	
Pipes preparation	EZ23	2.81	141.1	7,81
	EZ24	1.29	101.6	
Fugative sources – open space painting	EZ25			57,61
	EZ26			
	EZ27			
	EZ28			
Pipes painting	EZ20			8,05
Total				177.99

The calculation shows that the VOC emissions calculated using the preferred method (material balance) gives a lower estimate on VOC emissions that the one obtained by adding emissions calculated by direct measurement from point sources. This leads to the conclusion that there is great room to improve performance in reducing emissions using proven technologies that are suitable for VOC emissions capture.

Nitrous oxide (NO$_x$) emission is generated from air heaters are relatively high in comparison with the fuel used and other types of applications. Natural gas during combustion produces thermal NO$_x$ and with the available equipment there is not much room for improvement. There are available NO$_x$ reduction methods shown in the next chapter. For reducing NO$_x$ emission, a better option is to use other equipment without harmful gaseous emissions for heating and drying.

Carbon monoxide (CO) emission data has shown that there is a significantly lesser amount of these emissions than those of the legal limits and can be considered negligible. The main reason is that the fossil fuel used is natural gas, and the process equipment that generates emissions is air heaters that operate in an elevated excess air combustion environment, thus generating low CO emissions.

Table 2 NO$_x$ and CO emissions – mass flow, concentration and annual total emission [9]

Process	**Source**	**NOx**			**CO**		
		kg/h	**mg/m$_N$3**	**t/annum**	**kg/h**	**mg/m$_N$3**	**t/annum**
Primary sheet metal preparation	EZ1	0.77	143.1	N.A.	0.0454	83.5	N.A.
Preparation for painting	EZ5	N.A.	107.8	0.022	0.00005	1.5	0
Painting hall 1	EZ11	0.037	102.8	0.015	1.5	0.0005	0
	EZ12	0.036	98.7	0.014	1.5	0.0005	0
	EZ13	0.033	89.6	0.013	0.0032	8.8	0
Painting hall 2	EZ18	0.045	125.3	0.018	0.0005	1.3	0
	EZ19	0.046	128.5	0.019	0.0005	1.3	0
	EZ20	0.046	128	0.019	0.0005	1.3	0
Total				0.12			0

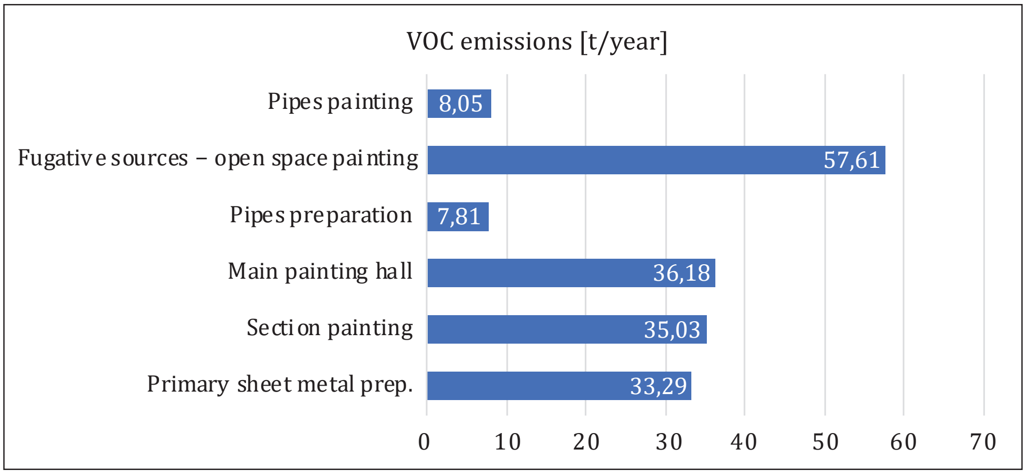

Figure 1 Annual VOC emissions from processes [9]

Table 3 Particulate matter (PM) emissions – mass flow, concentration and annual total emission [9]

Process	Source	PM		
		kg/h	mg/mn3	t/annum
Metal sheets blasting	EZ6	0.091	3.1	0.27
	EZ7	0.342	11.3	1
Pipes and equipment blasting	EZ21	0.31	16.4	0.3
	EZ22	0.53	14.6	N.A.
Total				1.57

Particulates or particulate matter (PM) emission is significant, and it originates from the blasting procedures that are carried out in the metal preparation process.

Regarding carbon dioxide (CO_2) emissions, since fossil fuel is used, they cannot be avoided using conventional means and equipment. The CO_2 formation can be calculated via material balance knowing the fuel or energy consumption and natural gas composition.

4 Methods for VOC emissions control

In regard with VOC emissions control, only methods that are suitable for relatively low concentrations of VOCs in exhaust air can be used, so only those are stated in this paragraph.

4.1 VOCs capture using adsorption via activated carbon

Adsorption is a process in which organic molecules remain on the surface of a porous solid, in this case activated carbon. Activated carbon is a compound known as a substance with a very large internal surface area compared to mass. Gas molecules pass through its pores and are absorbed into the material in contact with activated carbon. The amount of adsorbed gas depends not only on the characteristics of coal but also on the characteristics and concentration of VOCs. In principle, the adsorption capacity increases with increasing VOCs molecular weight and concentration.

The system is ready to accept very large amounts of VOCs in the stream of polluted gas, and thus over time it becomes saturated. Exhaust gases come through ventilation channels to the unit, i.e., the filter, and pass through it through activated carbon cartridges. Activated carbon is absorbed by the diluent contained in the waste gases and the amount of thinner, i.e., volatile organic compounds released into the environment is reduced. It is important that the operating temperature of the process must be below 40 °C because the absorption capacity decreases with increasing temperature. Efficiency above 95% can be achieved when the gas concentration is higher than 1000 ppm, thus limiting the efficiency of this method applied in the case studied.

This technique is used in the shipyard to neutralize volatile organic compounds, but it has been shown that activated carbon cartridges become saturated very quickly and need to be replaced frequently [10].

4.2 Biofiltration

The principle of operation of the biofilter is based on the decomposition of VOCs from contaminated gases by microorganisms or bacteria. Since bacteria survive in a humid environment, in order for the gas to be treated, it must first be moistened and only then pass through a filter with the bacteria planted. The concentration of VOCs in the gases before and after humidification is the same. The final by-product of the process can be biomass, CO_2 and water. In order for decomposition to be possible, optimal conditions must be maintained, enough moisture, oxygen and nutrients for bacteria. The pH value varies around the neutral range, i.e., between 6 and 8, but the value can change during filter operation. Thus, an acidic environment can sometimes be created, and therefore peat as a material may be a good choice for systems that have to operate at a narrow pH range due to their buffering capacity. Solutions that are resistant to changes in pH should be added to other materials to regulate the pH value inside the reactor. Most biofilters are inhabited by bacteria that live in mesophilic conditions or at temperatures of 20-45 °C. It is recommended that the water content be at the level of 50% of the material capacity. Various studies have shown the ability of certain species of bacteria to best neutralize the desired compound, such as aromatic compounds, while others can neutralize styrene. The best results are shown by biofilters where fungi and bacteria are combined, with fungi being the dominant species [11]. Compared to other methods of neutralizing volatile organic compounds, biofiltration has proven to be cost-effective even at higher flows (104-105 m^3/h).

4.3 Activated carbon adsorption and combustion

This approach is extremely cost-effective for systems where gases contain lower VOCs concentrations and high flows, for example in varnishing and coating processes. The system combines activated carbon adsorption technology and incineration. Since the process is intended for gases of lower concentrations, activated carbon participates in the concentration of VOCs compounds to a certain value, followed by final processing or combustion. This process has many advantages: higher efficiency, little or no wastewater or solid waste, low fuel consumption [11].

4.4 Incinerators

Incinerators are relatively simple devices for neutralizing VOCs, and they convert or destroy volatile organic compounds to CO_2 and water vapor using high temperature flames. There are two types of thermal incinerators, regenerative and recuperative.

Thermal incinerator consists of chambers resistant to high temperatures, most often made of ceramic materials. In the first chamber there is a preheating of gases from 40 °C to 780 °C, and in the next there is oxidation or combustion of gases at a temperature of 820 °C which produces CO_2 and water vapor and thus the process is complete. For the process to be satisfactorily efficient, the contaminated gas must be kept for a certain time in the chamber at the prescribed temperature, of about one second. A very high efficiency of 95% can be achieved, which is supported by operational reliability and relatively low initial costs. The disadvantage is the high costs due to fuel consumption, which leads to CO_2 emissions. Since it is necessary to develop very high temperatures, there is a problem with the formation of thermal nitrogen oxides. Regenerative thermal incinerators consist of a combustion chamber and ceramic blocks that absorb waste heat and then serve as preheaters of the input polluted gas. This reduces the need for additional fuel. They are characterized by high heat recovery or utilization of 90% of the system energy. Recuperative design is less efficient, but installation costs are lower. This system is more economical for use in small systems with concentrated VOCs in gases that have a high thermal value. The device has been developed like a heat exchanger so that the waste heat generated by combustion is further used to preheat the incoming polluted air. Because of the added CO_2 emissions, it is our opinion that this method is not suitable if the aim is to obtain a net zero emission shipyard.

4.5 Catalytic incinerators

The technology is very similar to thermal incinerators where the end products of the process are CO_2 and water. The presence of catalysts reduces the need for high oxidation temperatures so that this process takes place at about 300 °C which is significantly lower than thermal incinerators. Before entering, the polluted gas is cleaned of dust and various impurities, then preheated and passes through the catalytic layer where the catalyst promotes the oxidation of organic compounds.

The catalyst can be in the form of grains, ceramic and metal monoliths. They are most often made of platinum, copper, chrome, nickel. Also, waste heat is used to preheat the polluted gas at the inlet. In order for the catalyst to be effective, no accumulations must form on it, otherwise they will slow down or stop the contact between the catalyst and the gas, i.e., the oxidation process. The catalyst can be reactivated by blowing air or by increasing the temperature by 40 °C. The advantages are high efficiency, even higher than 95%. Fuel consumption due to lower temperatures is reduced by 60-100%. At the end of the process there is no residue or sediment. Due to the presence of the catalyst, the reaction rate is high and yet at significantly lower temperatures. With this in mind, the problem of the formation of harmful NO_x compounds that are otherwise formed at high temperatures is avoided, but CO_2 emissions result from using this method. It requires a significant amount of space, and due to the existence of a catalyst [12].

5 NO_x emissions reduction methods

Some of the simpler ways to neutralize or prevent the formation of NO_x compounds include the use of fuels with a lower nitrogen content. This is only relevant if fuels containing nitrogen are used. Since it is not the case here, other methods have to be considered.

Reduction of combustion air excess can also be resorted to, which is a good measure to save energy without any investment costs. On the other hand, air heaters that are a prime source of this pollutant, have limited possibilities for reducing excess air.

5.1 Combustion air staging

This method can reduce NO_x emissions by up to 60%, but changes to the combustion chamber are required. Due to the gradual addition of air, incomplete combustion and soot products may be emitted. It is a specially designed firebox with air supply ducts. Fuel and primary air are brought together, then secondary air comes through the first secondary channel and mixing occurs and combustion begins. The mixture is now rich, but the combustion is worse and therefore tertiary air must be added through the duct, where there are much fewer NO_x compounds but there is a significant amount of carbon monoxide.

5.2 Flue gas recirculation

A method in which exhaust gases are used to mix with the combustion inlet air which results in less fresh air with oxygen. This prevents the formation of high temperatures associated with the formation of NO_X compounds. This method is effective for fuels with low nitrogen content, and the emission of incomplete combustion products is lower than for graduated air supply. Due to the change of the firebox or air duct, the costs increase and there is an additional energy consumption due to the fan for the transmission of flue gases.

5.3 Treatment of flue gases by selective catalytic reaction

By adding ammonia to flue gases, their reaction produces harmless N_2 and H_2O. Due to the presence of catalysts - vanadium and titanium, platinum and zeolite materials, these are relatively low temperatures of 340-380 °C. This method is limited mostly to large units with large amounts of flue gases to be treated, and in this case, it is not a valuable option.

6 Conclusion and discussion

In this article a comprehensive analysis of the air emissions from a shipyard has been conducted. The analysis shows and identifies main air pollutant emission originating from the shipbuilding, i.e., ship production process. Other emissions from other processes originating from other sources in the shipyard like energy production, transportation, etc. have not been considered since those are not strictly corelated with the shipbuilding process itself.

Main pollutants that are of interest are: volatile organic compounds originating mainly for the painting process, nitrous oxides (NO_x) originating from mainly heat generation or hot air generation, and particulate matter (PM) originating from blasting processes. All identified emissions are very important for air quality especially in areas that are in the vicinity of the shipyards. These emissions cause formation of photochemical smog and some of them cause other harmful effects like acid rain. For this reason, it is of vital importance to control and reduce those emissions that in this example appear all in the same area, potentially causing harmful effects to human health.

While the forementioned gases and pollutants aren't directly of any significant effect on greenhouse gas (GHG), they can indirectly contribute to photochemical smog and tropospheric ozone formation. The energy consumed in the shipyard indicates that GHG emissions originating from fossil fuel combustion are significant.

The previous chapter describes relevant and applicable methods that can be used to control and minimize pollutant emissions. Some of those methods are applied in the treatment of waste gases from the painting and drying shops, but there is still great room for improvement.

In the process of analysis of the emissions from the shipyard production process a novel approach could be formulated that would have a goal of making these processes net zero emission. This approach would include a comprehensive analysis of all air GHG and pollutants emission. Energy generation required for the process of heating and drying should be generated using renewable energy that produces zero GHG emission. A valid assumption is that due to the location of the shipyard in question, that is located in the proximity of the city center, there are options to consider that can include the use of renewable energy combined with cogeneration and district heating that can result in a carbon neutral or net zero emission shipyard [15].

Emissions from welding, metal cutting processes have been studied by other authors, and for achieving net zero emission shipyard these emissions have to be taken into account.

VOC emissions still remain a challenge, particularly for those diffused emission sources that cannot be eliminated entirely.

In the process of analysis of available data on air emissions it has been found that the most accurate VOC emissions data will result from using source sampling results.

These data can be correlated with surface coating operation parameters, such as coating usage rates, pieces of equipment coated, or time. These correlations can be a leading value for reducing VOC emissions either by using paint with low VOC emissions and/or other measures.

Funding: The research presented in the manuscript did not receive any external funding.

Author Contributions: Research, Viktor Dragičević; Verification, Viktor Dragičević; Writing, Viktor Dragičević, Ivan Lorencin, Marina Levak; Data collection, Marina Levak, Ivan Lorencin; Validation Ivan Lorencin; Review and editing, Anton Turk.

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