Influence of volatile organic compounds emissions from road marking paints on ground-level ozone formation: case study of Kraków, Poland

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Abstract

Ground-level ozone, worldwide recognised amongst key pollutants responsible for smog and a significant pulmonary irritant is formed in troposphere via a photolytic process from nitrogen oxides (NOx). Volatile Organic Compounds (VOC) during their decomposition in the atmosphere interact with NOx and thus affect ozone formation. Their interactions are not equal and have been quantified in Maximum Incremental Reactivities (MIR). Using MIR, calculated was ozone formation potential of VOCs emitted from an aromatic solvent-containing paint that is used for marking of roads in Kraków, Poland. To simulate possible environmental benefits of using alternative materials, analysis was then extended to model paint without aromatic solvent and a waterborne paint. Ozone formation potential of the road marking paint currently used as standard in Kraków was calculated to be more than twice the amount of VOCs it emits: 240 kg of solvents evaporating from one tonne of paint might cause formation of over 550 kg of ozone – in Kraków that means up to 42 tonnes of tropospheric ozone annually. Elimination of the aromatic solvent would not lead to lesser VOC emissions, but decrease ozone production capability by about 50%. Further reductions could be realised with waterborne paint – VOC emissions lowered by 79% and potentially formed ozone reduced by up to 93%.

A cradle-to-grave Life Cycle Assessment (LCA) performed on the three analysed paints demonstrated that durability is the main environmental impact factor. Assuming service life achieved at our test field, where modern waterborne paints applied at 600 µm wet film and reflectorised with properly selected high-performance glass beads complied with the specification for two years, they definitely are more sustainable choices as compared to solventborne materials.

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Quantification of the effect of produced ozone on health was beyond the scope of this work, but based on literature reports a measureable effect is anticipated due to a well-documented correlation between increased tropospheric ozone level and increased mortality and morbidity.

Keywords: Road marking; waterborne paint; solventborne paint; glass beads; tropospheric ozone; VOC; Life Cycle Assessment; Kraków; road safety; MIR; environmental protection

1. Introduction

Since white line was first painted on a road in 1911 in Michigan, U. S. A., horizontal road markings became ubiquitous, essential safety feature of modern roads. It was observed that in the city of Kraków, Poland almost all road marking is done with thin-layer application of a solventborne toluene-containing paint. Toluene, an aromatic solvent, is generally recognised as harmful to people and environment; on the other hand, its relatively low price, convenient solubility parameters, and evaporation rate make it a preferred choice for solventborne road marking paints, unless banned by a legislation.

The topic of troposphere ozone formation caused by road marking paints have been introduced only very recently, with the first brief note done by Scorgie (2011) and recently by Burghardt (2016).

Knowing of extreme air pollution in Kraków, we postulated that an improvement could be achieved by limiting the VOCs emitted from road marking paints and consequently the formed tropospheric ozone. The currently used road marking system and readily-available alternative paints are analysed herein.

2. Background

2.1. Horizontal Road Marking Materials

Solventborne paints were historically the first road marking materials and still remain in use as they are rather inexpensive and easy to apply, albeit not very durable. Their base resins have changed over time from chlorinated rubber, through alkyds, to acrylics. Film formation is achieved by simple evaporation of organic solvents.

Thermoplastic materials, which are in use since the 1940s, are based on rosin or petroleum derivatives – they are easy to apply and quite durable at the high applied thicknesses. Because they are solvent-free, emissions at the time of application are considered negligible, so they shall not be discussed herein.

A plethora of plural-component materials, comprising epoxy- or urethane-based paints, rely on film forming by chemical reaction taking place on the road surface. Drawback of these highly durable systems that can be prepared in solventborne, water-reducible, or solvent-free versions is relative toxicity of raw materials. These paints are seldom used in Europe and are not specifically included in this analysis. For their solventborne versions, the same composition of emissions as for solventborne paints may be presumed.

Coldplastics are widely used modern materials – they are applied to road surface in the form of acrylic monomers, which polymerize in situ to form durable films of thicknesses ranging from 300 µm (coldspray plastic) to 4 mm (structured marking coldplastic). This solvent-free technology is not included in this work.

First waterborne paints were developed in the 1980s, but because they dried very sluggishly, particularly in unfavourable weather conditions, they were not a big commercial success; nevertheless, the early technology is still in use today as it furnishes quite durable, stable, and rather inexpensive paints that work excellent in hot and dry climates. A conceptual break-through occurred with the development of quick-set technology for waterborne binders, patented by Clinnin et al. (1991). The technology employs polymeric materials that can be kept intermixed and suspended in aqueous media only at high pH – upon drop of pH, irreversible chemical reaction and curing occurs. Numerous modifications to the binders resulted in significant increases in durability and stability, meaningful shortening of drying, and other desired properties. Waterborne paints are essentially devoid of toxic materials and their VOC emissions are marginal.
All of these road marking materials require reflective elements, which most frequently are glass beads. Beads of various refractive indices and sizes ranging in diameter from 100 µm to 2 mm are commonly used. Incorporation of anti-skid particles in glass beads packages assures proper skid resistance, necessary for safety. The selection of glass beads is critical to achieve the optimum performance of the applied systems as they not only provide retroreflectivity, but also protect the paints from abrasion caused by the vehicular traffic.

2.2. Ozone

Ozone, a tri-molecular allotrope of oxygen, is naturally occurring and forms in the atmosphere during lightning. Majority of ozone is found in lower stratosphere, where it plays critical role in absorption of ultraviolet rays and thus protection of life on Earth. Depletion of stratospheric ozone leads to increased ultraviolet irradiation at the ground level, which was linked to increase in occurrence of skin cancer (vide Diaz, 2014). However, ozone is also present in the troposphere, where most of it is created under photolytic conditions from nitrogen oxide (NO₂), according to the overall reactions (1)-(3) shown in eq. 1, as elucidated by Chameides and Walker (1973).

\[
\begin{align*}
\text{(1)} & \quad \text{NO}_2 \xrightarrow{h} \text{NO} + \text{O}^\bullet \\
\text{(2)} & \quad \text{O}^\bullet + \text{O}_2 \xrightarrow{} \text{O}_3 \\
\text{(3)} & \quad \text{NO} + \text{O}_3 \xrightarrow{} \text{NO}_2 + \text{O}_2
\end{align*}
\]

In eq. 1, steps (1) and (2) depict ozone generation, while step (3) – depletion. Since reaction rate \(k_2\) for step (2) is very fast, rate limiting are steps (1) and (3), leading to an equilibrium equation shown in eq. 2, known commonly as Leighton relationship. Since the reaction rate \(k_1\) depends on solar irradiation, diurnal cycles of ozone concentrations are natural. Leighton (1961) reported that VOCs under insolation conditions decompose via hydroxyl radicals, which are capable of reacting with NO, thus affecting the equilibrium shown in eq. 2.

\[
[O_3] = \frac{[NO_2]k_1}{[NO]k_3}
\]  

(2)

Ozone is quite toxic and causes irritation to respiratory system; upon repeated or prolonged exposure, loss of lung function and aggregate effects are well-documented: In a report by Amman (2009), published by the World Health Organisation, in 2008, the loss of 22 thousand lives in 25 countries subjected to the evaluation could be linked to tropospheric ozone. Similarly high mortality caused by ozone pollution was recently confirmed by Madronich et al. (2015). A statistical study done in selected European countries by Hänninen and co-workers (2014) has shown that tropospheric ozone was responsible for 30-140 Disability Adjusted Life Years per million inhabitants, with the larger values expectedly measured in the South, where insolation is high. An OECD report (2012) indicated annual worldwide premature mortality caused by ground-level ozone pollution (after separation from the effects of other air contaminants) to be between 50 and 350 thousands, with outlook for more than doubling in the next 35 years if the current trends continue. A comprehensive risk factors evaluation done by Lim and el. (2010) attributed to tropospheric ozone pollution 152434 deaths worldwide in 2010. A 15-year study lead by Bell (2004) has correlated an increase in ozone concentration of 10 ppb to increase in mortality by 0.52%. Touloumi and co-workers (1997) attributed increases in deaths in six European cities of up to 2.9% to ozone concentrations rising by 50 µg/m³.

Annually-averaged background ozone concentration was reported to rise from 10-15 ppb to 25-35 ppb over the past century with prediction for further increases, per analysis prepared by Vingarzan (2004).
2.3. **Maximum Incremental Reactivity (MIR)**

Measurements have shown that individual VOCs during their photolytic decomposition pathways affect ozone production to a different extent (vide Carter and Atkinson, 1987). Hence, Carter (1994) devised a practical and quite straightforward protocol and a measurement scale, using VOCs’ incremental reactivity defined as „the amount of additional ozone formation resulting from the addition of a small amount of the compound to the system in which ozone is formed, divided by the amount of compound added”. This model depends on many factors, but generally the reactivity is governed by the atmospheric conditions, under which VOC and NOx react to form ozone, their concentrations, irradiation, temperature, and the presence of other chemicals. VOCs were measured to have highest incremental reactivities under high NOx concentrations, when the rate limiting step is the speed of hydroxyl radical formation. For some chemicals and under certain NOx concentrations, ozone scavenging could occur, which is another confirmation that not all VOCs are equal. In comparison with other scenarios used to measure ozone formation, MIR was demonstrated to provide very consistent predictions, as was verified by Martien and co-workers (2003).

In this paper, we have used MIR values published in California Code of Regulations, Title 17, §94700, thus assuming a scenario of unlimited NOx availability. These values were revised by Carter (2009), based on information and analytical technology that became available since the original publications.

2.4. **Air pollution in Kraków, Poland**

Kraków is an extremely polluted city, particularly in terms of air-suspended particulate matter (exceeding the norm on about 150 days every year) and absorbed on it carcinogenic benzo[a]pyrene that is exceeding the norm on 8 months every year; for example, in February 2015 – by an average of 2013% (sic!), per air quality monitoring data (WIOŚ, 2015). As explained by Bokwa (2008) in her comprehensive assessment spanning 40 years, unbelievably high pollution in Kraków has a few key anthropogenic sources: firstly – the local residents using low quality coal to warm their homes, secondly – severely polluting heavy industry that was constructed in the city by the communist governments for purely political reasons, and thirdly – exhausts of motor vehicles. These are exacerbated by geographic location of the city in a valley, which severely limits air movement: The mean wind speed in Kraków was reported to be only 2 m/s, atmospheric calm present about 100 days every year, and daytime low-level temperature inversions quite frequent. Furthermore, even those mild winds bring pollution to Kraków from the neighbouring Upper Silesian industrial region.

Bokwa (2008) reported that annually-averaged concentration of NO2 stayed quite steady over 15 years, at 30 to 70 µg/m3, depending on location within the city. However, per WIOŚ database, in 2014, NO2 concentrations in Kraków city centre averaged 111 µg/m3 and NOx – 230 µg/m3, while the maximum permissible concentration is set at 30 µg/m3.

Typical annual average ozone concentration of 50-60 µg/m3 reported by Bokwa (2008) agrees with an earlier work done by Godzik (1997), who confirmed the measurements by evaluating damage to ozone-sensitive plants. However, Bokwa in the same work noted that in 2003, maximum permissible 8-hour average concentration of 120 µg/m3 was exceeded on 47 hottest days. Moreover, quite curiously, Piotrowicz and Cieranek (2014) demonstrated that high ozone levels were also occurring during cloudy and rainy days. Per WIOŚ monitoring data, in extremely hot July and August 2015, 8-hour ozone concentration was averaging 107 µg/m3, with a peak on 10.08.2015 – 8-hour average of 164 µg/m3 and hourly maximum of 188 µg/m3.

2.5. **Life Cycle Assessment (LCA)**

Life Cycle Assessment is a recognised tool for making decisions based on sustainable development. It is a compilation and evaluation of inputs, outputs, and potential environmental impacts of a product throughout its life cycle, taking into account extraction and treatment of raw materials, product manufacturing, transport and distribution, use, and end of life disposal. Composition of the analysed materials, environmental cost of their preparation and usage, and their durability are the key inputs. To permit for comparison of dissimilar technologies rendering identical service, a functional unit and a service life are specified.
As summarized by Carlson (2011), LCAs pertaining to roadways are plentiful. However, we have failed to find any environmental evaluations from academic sources pertaining to the relatively lesser impacts of road marking materials.

Typical factors used for LCA include the following: (1) Depletion of abiotic resources, (2) Greenhouse Gas Effects, a key factor for global warming, (3) Acidification potential, which impacts soil, water, and ecosystems, expressed relative to acidifying effect of SO₂, (4) Human toxicity or effects of toxic substances on human environment, but – importantly – excluding effects of health risks in the work environment, (5) Eutrophication potential, aquatic ecosystem’s response to natural fertilizers expressed in relation to effects caused by phosphates, (6) Primary non-renewable energy consumption used for the life cycle of analysed product, (7) Chemical Oxygen Demand, generally interpreted as measure of overall water pollution, (8) Solid waste production and disposal, (9) Total water consumption, and (10) Non-methanic VOC emissions – directly tied to production of tropospheric ozone.

3. Measurements of durability

To assess durability, a critical parameter for LCA, two waterborne paints from Swarco Limburger Lackfabrik GmbH (Diez, Germany) were applied perpendicularly to the traffic flow and tested against a standard high-solids aromatic-free solventborne paint on a road in France with Average Daily Traffic (ADT) of about 5000 vehicles (including ~15% articulated lorries). Since aromatic-containing solventborne paint is not allowed in France, it could not be included in the evaluation and its usable service life was assumed to be the same as measured aromatic-free material. The paints were reflectorised with high-performance glass beads produced by M. Swarovski GmbH (Amstetten, Austria), designed to furnish optimum results in the tested systems. The dropped-on glass beads included beads prepared in SolidPlus technology for enhanced retroreflection, Swarcolux material for high performance, and large size Megalux-beads capable of maintaining retroreflectivity even in wet conditions. The beads were pre-mixed with anti-skid particles to fulfil skid resistance requirements. Airless application technique commonly used in the industry was employed. Retroreflectivity of the systems was measured periodically and its drop below 150 mcd/m²/lx indicated the limit of paints’ usable lives.

<table>
<thead>
<tr>
<th>System (paint with actual applied film build + glass beads with actual applied loading)</th>
<th>Initial</th>
<th>3 months</th>
<th>6 months</th>
<th>11 months</th>
<th>18 months</th>
<th>Durability (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard aromatic-free solventborne (570 g/m²) + SolidPlus10 200-800 T14 M30 (340 g/m²)</td>
<td>391</td>
<td>241</td>
<td>139</td>
<td>119</td>
<td>86</td>
<td>6</td>
</tr>
<tr>
<td>Waterborne W13 (650 g/m²) + SolidPlus10 200-800 T14 M30 (370 g/m²)</td>
<td>243</td>
<td>226</td>
<td>202</td>
<td>180</td>
<td>119</td>
<td>12</td>
</tr>
<tr>
<td>Waterborne W15 (650 g/m²) + SolidPlus10 200-800 T14 M30 (370 g/m²)</td>
<td>240</td>
<td>285</td>
<td>240</td>
<td>243</td>
<td>193</td>
<td>18</td>
</tr>
<tr>
<td>Waterborne W13 (960 g/m²) + SolidPlus10 300-1000 T14 M30 (380 g/m²)</td>
<td>235</td>
<td>247</td>
<td>214</td>
<td>213</td>
<td>159</td>
<td>18</td>
</tr>
<tr>
<td>Waterborne W13 (930 g/m²) + Swarcolux50 212-1400 T14-T15 M30 (400 g/m²)</td>
<td>297</td>
<td>316</td>
<td>279</td>
<td>261</td>
<td>168</td>
<td>18</td>
</tr>
<tr>
<td>Waterborne W15 (930 g/m²) + SolidPlus10 300-1000 T14 M30 (360 g/m²)</td>
<td>293</td>
<td>302</td>
<td>267</td>
<td>258</td>
<td>206</td>
<td>24</td>
</tr>
<tr>
<td>Waterborne W15 (940 g/m²) + Swarcolux50 212-1400 T14 M30 (350 g/m²)</td>
<td>336</td>
<td>312</td>
<td>280</td>
<td>264</td>
<td>211</td>
<td>24</td>
</tr>
<tr>
<td>Waterborne W15 (950 g/m²) + Megalux 600-1400 T14 (370 g/m²)</td>
<td>432</td>
<td>388</td>
<td>361</td>
<td>338</td>
<td>278</td>
<td>&gt;24</td>
</tr>
</tbody>
</table>

Source: Authors. (a) Average from 13 measurements of retroreflectivity per line 15-cm wide and 300 cm long applied perpendicularly to traffic flow. (b) Durability is extrapolated when needed, in six-month increments. Failure is defined as retroreflectivity drop below 150 mcd/m²/lx. (c) Initial measurements were taken in 2-4 weeks after application, as is customary in the road marking industry.
As is evident from Table 1, durability depended on the applied film build and the selected road marking material. While the solventborne paint applied at 400 µm wet film (~600 g/m²) failed quickly, waterborne paint W13 was performing satisfactorily and paint W15 was even better. The waterborne paints outperformed solventborne despite the latter one providing higher initial retroreflectivity. The increased durability of paint W15 was expected, because it is based on a binder capable of some self-crosslinking, patented by Schall and co-workers (1997).

Application of the waterborne paints at wet film build of 600 µm (~900 g/m²) lead to improvement in performance, with W15 showing capability for two-year service life. It must be mentioned that due to excessive drying times, application of solventborne paints at high film builds is not practical; this deficiency is alleviated in modern waterborne paints by their physicochemical drying mechanism.

While introducing new technologies, teaching the users about advantages, disadvantages, and shortcomings of the newly devised systems is very important. To train the application crew, evaluate application characteristics, and measure performance under normal usage conditions (not perpendicular to traffic), waterborne paint W13 was recently applied at two sites in Kraków. At the selected roads, we had measured very high ADT, over 15000 vehicles (including 4-12% articulated lorries). Three types of glass beads were tested, including high-index material designed to provide retroreflectivity significantly beyond the requirements. The application crew, who had never before worked with waterborne road marking paints, was satisfied with the paint and was impressed by its quick drying. Different visual appearance of the high-index glass beads and their exquisite retroreflection were also observed. The used paint has been certified in Austria and Germany, with pending homologation in Poland; all of the glass beads pre-mixed with anti-skid particles had CE-mark approval. Markings were done with the standard application machine and technique the same as for solventborne paints.

The initial retroreflectivity expectedly depended on the used glass beads, with the highest measured values – over 630 mcd/m²/lx – achieved with high-index beads SolidPlus100. Enhanced-quality SolidPlus30 and Swarcolux50 beads provided retroreflectivities in the range of 300-400 mcd/m²/lx. These results are in line with those obtained during similar test described by Babić and co-workers (2015), done in 2014 near Zagreb, Croatia.

High retroreflectivity and durability achieved with these glass beads ought to directly translate to increased road safety by making the markings more visible and clear, thus easier to follow. Improved perception of safety on roadways with horizontal markings, likely attributed to their better legibility, was reported by Żakowska (1997). In addition, two-year usable life may be achieved even at high ADT conditions due to very high initial retroreflectivity. From a perspective of road administration authorities, the advantages include increased safety and economic benefits. The test areas are being monitored.

4. Results and discussion

4.1. VOC emissions and potential ground-level ozone formation

To perform the analysis and calculations that were the main objective of this work, compositions of the volatile materials presented in Table 2 were used.

For solventborne paints, it was obvious that all of the solvents evaporate and are thus VOC. Since the use of alternate solvents would not have influenced the VOC emissions and had rather small impact on ozone production potential in relation to the presented alternatives, the assumed composition of solvent blends was simplified; the amount of toluene was the maximum permitted in Poland, per specification published by IBDiM (2007).

For waterborne paints, VOCs are limited to ammonia, which has no reported effect on ozone formation, ethanol that is used to improve stability and processing, and possibly also the coalescent. Possibly, because the most common coalescent, Texanol® (a product of Eastman Chemical Company, of Kingsport, Tennessee, U. S. A.) – a mixture of C12 hydroxyesters with boiling point of 254 °C and miniscule evaporation rate – is considered a VOC according to the United States regulations (per U. S. Code of Federal Regulations, Chapter 40, §59.406) and its MIR has been reported; however, Texanol® is not a VOC according to European methodology (European Parliament Directive 2004/42/EC defined VOC as „any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa”). In our calculations, we consider Texanol® as VOC and contributing to ozone formation.
Table 2. Assumed composition of volatile contents of the analysed paints and their Maximum Incremental Reactivities.

<table>
<thead>
<tr>
<th>Paint Type</th>
<th>Solventborne paint (aromatic-containing)</th>
<th>Solventborne paint (aromatic-free)</th>
<th>Waterborne paint(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>4.00</td>
<td>8.0%</td>
<td>–</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>1.48</td>
<td>16.0%</td>
<td>12.0%</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>0.83</td>
<td>–</td>
<td>12.0%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.53</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ammonia (25% aq. NH₄OH)</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Texanol®</td>
<td>0.81</td>
<td>–</td>
<td>0.5%</td>
</tr>
<tr>
<td>Water</td>
<td>0.00</td>
<td>–</td>
<td>19.0%</td>
</tr>
</tbody>
</table>

(a) Paint currently used in Kraków. (b) Alternative readily-available paint.

One of the advantages of using MIR is that it permits for using direct mathematical calculation to find the maximum amount of ozone that may be produced due to the emitted VOCs (grams of potentially formed ozone per gram of VOC). With emissions shown in Table 2, calculations of the emitted relative and total amounts of VOC, the potentially formed ozone, and the potential increase of ozone concentration over Kraków that could be attributed to these road marking paints were done. The results are provided in Table 3.

Per road authority ZIKiT (2015), 126,767 m² of Kraków city roads were painted in 2014 with thin-layer solventborne paint, which at a typical applied weight of 600 g/m² gives usage of 76,060 kg. To calculate approximate ozone concentration over Kraków, the altitude of lower troposphere where ozone would concentrate was assumed to be 400 m, a mid-point for typical summertime inversion zone over Kraków as reported by Bokwa (2008). At city area of 327 km², disregarding the local topography, that gives air volume of about 130 km³. The assumed lower troposphere boundary is likely an overestimate, because Godzik reported (1997) that ozone concentration in the city was lower as compared to neighbouring villages, located only slightly higher – 258 m above sea level as compared to the city centre of Kraków laying at 220 m.

Table 3. Emissions and potentially formed ozone.

<table>
<thead>
<tr>
<th>Paint Type</th>
<th>Solventborne paint (aromatic-containing)</th>
<th>Solventborne paint (aromatic-free)</th>
<th>Waterborne paint(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC emitted from 1000 kg of paint (kg)</td>
<td>240</td>
<td>240</td>
<td>50</td>
</tr>
<tr>
<td>Maximum ozone formed from 1000 kg of paint (kg)</td>
<td>557</td>
<td>277</td>
<td>36</td>
</tr>
<tr>
<td>Maximum ozone formed from annually utilised paint (kg)</td>
<td>42,350</td>
<td>21,084</td>
<td>2,738</td>
</tr>
<tr>
<td>Potential annual contribution of the analysed paints to ozone concentration over Kraków (µg/m³)(c)(d)</td>
<td>324</td>
<td>161</td>
<td>21</td>
</tr>
</tbody>
</table>

(a) Paint currently utilised in Kraków. (b) Alternative readily-available paint. (c) Assuming the use of 76,060 kg of paint. (d) Maximum potential increase in ozone concentration over Kraków due to emitted VOCs, assuming 400 m troposphere thickness.

Our calculations show that the amount of potentially produced ozone very significantly exceeds the emitted VOCs in case of aromatic-containing solventborne paint – the main culprit is toluene, with its very high MIR. A possible production of 557 kg of ozone from a tonne of paint at an annual usage of 76,060 kg could mean formation of up to 42,350 kg of ozone. A switch to an aromatic-free paint would limit the potentially formed ozone by 50% without changing the VOC emissions. From environmental perspective, much better would be the use of waterborne paint, with possible 79% reduction in VOC emissions and potential tropospheric ozone formation lowered by 93%.

Expansion of our work to cover other paints compositions and entire Poland is under way (2016).

At present, there is no readily available method to measure the actual ozone formed under direct influence of the emitted VOC in the field conditions; therefore, it was not possible to validate our simulation. Environmental chamber
Even though level of NO\textsubscript{x} in Kraków is high and ozone formation can proceed under its unlimited availability conditions, it is unlikely that the maxima for ozone production provided in Table 3 can be reached daily. Among abating factors, one must list the insolation, which at 50°N was measured to be only about 3,800 MJ/m\textsuperscript{2} annually, per multi-year trend study by Matuszko (2010), and temperature usually not exceeding 30 °C (however, in 2015 there were 31 days with higher temperature). In addition, since some of the road marking activities are done after sundown, ozone formation is inhibited.

We are aware that in comparison with vehicular emissions, mostly NO\textsubscript{x}, the contribution of road marking materials to air pollution appears quite insignificant. However, while the paints emit VOCs that interact with NO\textsubscript{x}, the vehicles supply the nitrogen oxides that make tropospheric ozone production possible.

Estimating influence of the emitted ozone on human health and quantification of potential benefits that could be achieved by using more sustainable road marking paints was beyond the scope of our effort. With high probability, based on the aforementioned literature pertaining to detrimental effect of ozone on human life, emissions from the toluene-containing solventborne road marking paints do have their measureable contribution, particularly in highly polluted cities. Literature search failed to discover such analyses concentrating on the population of Kraków.

4.2. Life Cycle Assessment

LCA was performed based on the existing available inventories and best-practice methods, using TEAM software (from PriceWaterhouseCooper) according to ISO 14040 requirements described by Hauschild et al. (2013). Presumed composition of all of the paints was the same in terms of solids composition (acrylic binder, pigments and fillers, and processing additives), with the only variations in the volatile portion. Glass beads were included in the analysis, as they are an integral part of all road marking systems. Calculations were done on a functional unit of 1 m\textsuperscript{2} with a service life of 10 years (renewal of markings was assumed to be done with the same paints as the original applications, at frequencies dictated by their durability measured at our test field).

Amongst life stages of the analysed road marking materials, essentially all of the environmental impact can be attributed to preparation of the raw materials. Major effects were measured for synthesis of the binders, very significant contributions were attributed to glass beads and solvents, and quite harmful was preparation of titanium dioxide; the effects of fillers and processing additives were marginal. The analysis was limited to white paint, but based on composition of coloured markings, similar trends would apply.

Since the analysis is proprietary to industry and confidential, absolute values cannot be disclosed. Relative comparisons are, however, a standard amongst LCAs as they permit for quick identification of major impactors.

Consumption of Earth’s resources relative to the aromatic solvent-containing paint is provided in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Durability (years)</th>
<th>Non-methanic VOC</th>
<th>Primary energy</th>
<th>Acidification</th>
<th>Eutrophication</th>
<th>Greenhouse gas effects</th>
<th>Human toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solventborne (aromatic)\textsuperscript{(a)}</td>
<td>0.5</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Solventborne (aromatic-free)\textsuperscript{(b)}</td>
<td>0.5</td>
<td>+10%</td>
<td>+10%</td>
<td>+12%</td>
<td>+18%</td>
<td>+14%</td>
<td>+33%</td>
</tr>
<tr>
<td>Waterborne\textsuperscript{(c)}</td>
<td>1</td>
<td>-50%</td>
<td>-50%</td>
<td>-41%</td>
<td>-47%</td>
<td>-44%</td>
<td>-44%</td>
</tr>
<tr>
<td>Waterborne (900 g/m\textsuperscript{2} film build)</td>
<td>2</td>
<td>-98%</td>
<td>-75%</td>
<td>-71%</td>
<td>-74%</td>
<td>-72%</td>
<td>-72%</td>
</tr>
</tbody>
</table>

\textsuperscript{(a)} As provided by the industry. The effects include all stages of life cycle, including processing of raw materials. \textsuperscript{(b)} At 400-µm applied wet field build.
Amongst data presented in Table 4, surprising might appear marginally stronger impact of aromatic-free paints as compared to the toluene-containing standard. That is caused by including in the assessment all of the steps in synthesis of the solvents.

Since we have measured service life of only 6 months for solventborne paint and one-year for waterborne (Cf. Table 1), the advantage of the more durable systems is clear. Superior results could be achieved with a waterborne paint system applied at 600 µm wet film that provided two-year durability – even with accounting for 50% higher applied film build. It must be reminded here that the test field application was perpendicular to the traffic flow, so the stress on paint would not be so high under normal usage conditions and longer service lives could be measured.

It is clear from Table 4 that durability of a road marking system is the key parameter for its environmental impact; therefore, its increase ought to be the main goal for sustainable development. This can be achieved by the use of high-end glass beads or/and by enhancement of the binders.

Generally accepted in LCA is basing the analysis of raw materials at their source; however, an interesting consideration would be adding as an additional parameter the location of the emissions. In our work, the fact that VOC emissions take place in a city with already high atmospheric pollution, potential negative health effects are likely to be aggravated, because a meaningful correlation between the length of exposure and pulmonary response was measured (vide Lippmann, 1991).

5. Conclusions

It has been demonstrated that the choice of road marking paint has profound influence on the environment in terms of emissions of Volatile Organic Compounds and possibility of tropospheric ozone formation. Calculations based on Maximum Incremental Reactivities indicate that up to 43,050 kg of tropospheric ozone could be produced annually from VOCs emitted by the aromatic solvent-containing road marking paint that is currently used in Kraków, Poland. Change to an aromatic-free solventborne paint would lead to reduction of up to 50% of the potentially produced ozone, and to a waterborne paint – up to 93%. If durability of road markings were to double or even triple, which possibility was demonstrated in our road test, annual ozone forming potential and emissions of VOCs could be lowered further.

Annual elimination of 14,500 kg of VOCs and consequent reduction of up to 39,600 kg of potentially produced ozone without meaningful expenses can be easily achieved in Kraków by the use of modern waterborne road marking paints in lieu of the current aromatic solvent-containing standard.

Utilization of properly selected high-performance glass beads is one of the critical parameters in designing road marking systems. Glass beads not only furnish retroreflectivity that directly leads to better visibility and thus increased safety for all road users, but also affect overall durability of road markings by protecting the binder from direct abrasion by passing vehicles. Hence, their selection also meaningfully affects sustainability.

Influence of tropospheric ozone on human life was reported to be significant, with annual premature mortality of up to 0.35 million worldwide, forecasted to increase to up to 0.75 million in 2050 if current trends continue. Based on our calculations presented herein, a decrease in tropospheric ozone concentration could be expected if aromatic solvents were to be abandoned, which ought to translate into improved health and quality of life.

Application of Life Cycle Analysis tools to evaluate the road marking systems indicated durability as primary factor for their environmental impact. The use of modern waterborne paints, which have longer service life than solventborne materials was found to be advantageous from the overall cradle-to-grave perspective.

Even though our work was based on surrogate compositions and environmental analysis narrowed to one city, the findings are fully applicable to road marking paints used worldwide, providing for regional differences and formulation requirements.

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References


ZIKiT (Zarząd Infrastruktury Komunalnej i Transportu w Krakowie / Kraków Community Infrastructure and Transport Authority), 2015. Response to authors’ query.