Overview description of a master thesis project proposal on multivariate statistical data evaluation for the improvement of NOx/NH3 sensors

One of the major concerns regarding urban air-quality over this last decade has been the increasing emissions and aggregation of atmospheric nitrogen oxides (NOx) in densely populated and industrialized areas. Besides the contribution of nitrogen oxides in the formation of acidic rain, affecting all living organisms through the acidification of ground water and the associated increased dissolution of elements (e.g. certain heavy metals) with adverse health effects into sweet-water/ drinking water reservoirs, nitrogen oxides also directly affect the health of humans and animals in increasing the stress level experienced by cells/ tissue in the lungs and lower airways (thereby increasing the risk of contracting infections and other related problems). Moreover, atmospheric nitrogen oxides are also involved in the formation of smog (through the reaction with volatile hydrocarbons when exposed to sunlight) and can act as nucleation centers for the formation of ultrafine particles, another pollutant of recent concern.

As nitrogen oxides mainly emanate from human activity/ man-made processes (other prominent sources including lightning associated with thunder storms and natural fires) and have a significant life-time in both the atmosphere and ground water it is important to reduce the emission of nitrogen oxides, especially from point sources located in close proximity to populated areas (including animal populations). The largest sources of man-made nitrogen oxides are all related to combustion processes or certain chemical processes, in the latter case e.g. from the petrochemical industry, where for the last decade much focus has been directed towards the automotive sector and the internal combustion engine as the major technology currently in use for vehicle propulsion (and projected to still be for at least another 10-15 year period). Stationary sources of atmospheric nitrogen oxides emissions include heat/power plants, lime kilns for cement production, and industrial processes where the necessary process heat is generated from combustion (typically the paper- and pulp-, steel-, and petrochemical industries).

The to date most commonly used measure/ technology for reducing nitrogen oxides emissions from these sources/ processes is termed Selective Catalytic Reduction (SCR) of nitrogen oxides by ammonia (NH3). Ammonia is thereby dosed into the flue gas/ exhaust, usually in the form of urea - (NH2)2CO - or ammonium-sulfate - (NH4)2SO4 - at elevated temperatures in order for the ammonia to react with nitrogen oxides on the surface of a catalyst (an SCR catalyst) to produce nitrogen (N2) and water (H2O). In order for the nitrogen oxides to be completely reduced the ammonia dosage needs to be adjusted such that there is enough ammonia in the gas mixture to react with all of the nitrogen oxide molecules (and usually just a little bit more). Since the ammonia itself also to some extent can contribute to impaired air and water quality, too high a dosage of ammonia should also be avoided. There are a few issues which complicate the control of the ammonia dosage, however.

Firstly, the exhaust/ flue gas concentration of nitrogen oxides is normally varying over quite a wide range over time. Secondly, when dosing more ammonia than required for reduction of the momentary flue gas/ exhaust nitrogen oxides the extra ammonia will adsorb to the surface of and thus be stored in the catalyst, until the catalyst can no longer store more ammonia and the unreacted ammonia thus being emitted to the environment (while at the same time part of the ammonia stored in the catalyst can be consumed by NOx). Thirdly, the amount of ammonia stored/ released is also dependent on the momentary temperature of the catalyst. And last, but not least, the ratio between different nitrogen oxides, mainly NO (nitrogen monoxide) and NO2 (nitrogen dioxide), commonly also vary over time (dependent on e.g. combustion conditions, fuel source, fuel quality), affecting the amount of ammonia which needs to be dosed as NO and NO2 require different amounts of NH3 for complete reduction.

It has therefore been proven difficult to model/ estimate the amount of ammonia which needs to be dosed to completely reduce the nitrogen oxides. In order to improve the situation two sensors measuring the flue gas/ exhaust concentration of nitrogen oxides are usually employed, one located upstream and the other downstream of the SCR catalyst. The idea is that the upstream NOx-sensor will provide a measure of flue gas/ exhaust nitrogen oxides concentration which can be used for adjusting the ammonia dosing to match the NOx concentration, whereas the downstream sensor can provide a diagnostics signal which can be used to "fine-tune" the ammonia dosing.

Two issues still remain, however: For the currently employed sensor technology it is not possible to measure NO and NO2 indvidually, why the upstream sensor can only provide information about the total NOx-concentration, not NO and NO2 separately (i.e. the sensor signal does not always provide a good measure for how much of ammonia dosing is needed). Moreover, the sensor is also sensitive to ammonia and will give a similar signal (response) to ammonia as to NOx, why the downstream sensor can not provide the desired information - whether too much or too little ammonia is dosed and therefore ammonia being released or unreacted nitrogen oxides passing through the catalyst - unless a certain "trick" is used. The trick is to dose some extra ammonia whenever the signal of the downstream sensor increases. If the sensor signal continues to increase it is very likely that ammonia is being emitted from the catalyst, whereas a decrease in sensor signal would indicate that the release of unreacted nitrogen oxides was the cause of the increased sensor signal in the first place. Besides the fact that this assumption does not necessarily have to be correct in 100% of the cases, the method is a bit to coarse for the upcoming legislation, where NOx emission limits over the next five years will decrease to less than half of the emissions permitted today.

It is therefore generally considered that an improvement in the ability to both individually measure the different nitrogen oxides (mainly NO and NO2, but N20 - being a prominent greenhouse gas - may also be of interest) and to clearly separate between nitrogen oxides and ammonia, without the need to play any "tricks", will be necessary for the future. There could of course be a few different pathways to achieve this goal, including to tune the materials (and associated properties) used with the sensor technology to more strongly interact with and thereby measure the nitrogen oxides over ammonia as well as to adjust/ change the sensor technology platform itself. Or to employ both of these options, as has been done in the applied sensor science research unit over the last few years.

There are, however, also strong indications that an improvement in the individual measurement of the different nitrogen oxides as well as ammonia could be achieved by operating the sensor/ sensors in the frequency domain (rather than the common static DC domain). In doing so the amount of data generated increases manifold, however, and both a dimensionality reduction as well as a reduction in each dimension itself will (most probably) be necessary in order to retrieve the relevant information from the sensor signal(s). Furthermore, it would ideally be very useful if the effect of frequency range (or possibly ranges of frequencies) on the quality of information which can be retrieved could be efficiently evaluated, as this has a large impact on the development of the sensor operational mode. As the signal generated by gas sensors in general also to a larger/longer or lesser/shorter extent/time-scale is affected by how the sensor has been operated and what (in terms of ambient gas composition) the sensor has been exposed to just prior to the conditions existing at the very moment when new sensor data is acquired. Therefore time series analysis of sensor data is assumed to play an important role in both evaluation of sensor operation modes and the final implementation of a sensor product (or sensor products).

The combination of the different topics would be too large a scope for one master thesis project, but depending on personal interest and what may fit best with the study profile etc. the master thesis project can be designed such that it will be limited to study one well-defined subject/ question. This subject would then be specified together with the student and the main supervisor and further detailed in a project plan.

As for the timing, the project could start from January 2021 (from the 11th of January or when the student so wishes, depending on e.g. exam periods or other activities). Some preparatory studies on the specific topic (e.g. scientific papers and background sensor theory can be provided) can of course start also before January 2021.